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Couplage d’une décharge à barrière diélectrique avec un aérosol pour le dépôt de couches minces (multi)fonctionnelles : rôle de l’injection pulsée de précurseurs

Par

Laura CACOT

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Couplage d’une décharge à barrière diélectrique avec un aérosol pour le dépôt de couches minces (multi)fonctionnelles : rôle de l’injection pulsée de précurseurs

Présenté par :

Laura Cacot

A été évaluée par un jury composé des personnes suivantes

Joëlle Margot et **Françoise Massines**
Présidentes du jury

Nicolas Naudé et **Luc Stafford**
Directeurs de recherche

Richard Clergereaux
Codirecteur de recherche

Ahmad Hamdan et **Mireille Richard-Plouet**
Membres du jury

Fiorenza Fanelli et **Pierre-Luc Girard-Lauriault**
Examinatrice/eur externes

Résumé

L'objectif de cette thèse est de réaliser une étude fondamentale de pointe du couplage d'injections pulsées d'aérosols avec une décharge à barrière diélectrique (DBD) à la pression atmosphérique pour le dépôt de films minces (multi)fonctionnels. Dans ce contexte, à partir de mesures électriques et spectroscopiques de la DBD, couplées à la simulation de l'écoulement gazeux, nous avons d'abord étudié la perturbation d'une injection pulsée de gaz sur la stabilité de la décharge. Nous avons observé que le fonctionnement pulsé introduit des changements significatifs dans la composition du gaz dû à des phénomènes de recirculation et de dégazage en amont de la cellule de décharge. Nous avons également examiné les effets d'une injection pulsée de liquide d'un précurseur organosilicié (HMDSO) sur la décharge et les couches minces déposées. Il s'avère que la décharge devient filamentaire et que la vitesse de dépôt est limitée par la quantité d'énergie fournie aux gouttelettes de précurseur, et non par la quantité de précurseur. Dans ces conditions, le dépôt repose sur le chargement des gouttelettes micrométriques par le plasma et leur transport vers le substrat par les forces de Coulomb et de traînée par les neutres. De plus, la morphologie de la couche mince et la fragmentation du précurseur sont fortement liés à la quantité d'énergie fournie par la décharge filamentaire aux gouttelettes d'HMDSO. Alors que des revêtements réticulés et lisses sont obtenus à de faibles énergies comme pour les plasma-polymères standards, des films minces visqueux sont déposés à des énergies plus élevées. Ce dernier matériau est attribué à une polymérisation douce des gouttelettes d'HMDSO. Selon un contrôle judicieux des interactions plasma-gouttelettes, par exemple en variant les paramètres de la décharge comme la fréquence d'excitation, il est possible d'ajuster l'efficacité du dépôt, le degré de polymérisation et la cinétique de formation de poudres. Enfin, nous avons intégré l'ensemble de ces connaissances afin d'explorer le potentiel d'un réacteur-injecteur (permettant l'injection pulsée de précurseurs et de nanoparticules) pour la synthèse de films minces nanocomposites dans les décharges à barrière diélectrique à la pression atmosphérique.

Mots-clés : Décharge à barrière diélectrique, Dépôt à la pression atmosphérique, Injection pulsée de gaz et de précurseurs, Aérosol, Couche mince organosiliciée, Nanocomposite.

Abstract

The objective of this thesis is to perform a fundamental state-of-the-art study of the coupling of pulsed aerosol injections with a dielectric barrier discharge (DBD) at atmospheric pressure for the deposition of (multi)functional thin films. In this context, from electrical and spectroscopic measurements of the DBD, coupled with gas flow simulation, we first studied the perturbation of a pulsed gas injection on the stability of the discharge. We observed that pulsed operation introduces significant changes in the gas composition due to recirculation and outgassing phenomena upstream of the discharge cell. We also examined the effects of pulsed liquid injection of an organosilicon precursor (HMDSO) on the discharge and the deposited thin films. It is found that the discharge becomes filamentary and the deposition rate is limited by the amount of energy supplied to the precursor droplets, not the amount of precursor. Under these conditions, the deposition relies on the charging of the micrometer droplets by the plasma and their transport to the substrate by the Coulomb and neutral drag forces. In addition, the thin film morphology and precursor fragmentation are strongly related to the amount of energy supplied by the filamentary discharge to the HMDSO droplets. While smooth cross-linked coatings are obtained at low energies as for standard plasma-polymers, viscous thin films are deposited at higher energies. The latter material is attributed to a soft polymerization of HMDSO droplets. Depending on a judicious control of the plasma-droplet interactions, for example by varying the discharge parameters such as the excitation frequency, it is possible to adjust the deposition efficiency, the degree of polymerization and the kinetics of powder formation. Finally, we have integrated all this knowledge to explore the potential of a reactor-injector (allowing pulsed injection of precursors and nanoparticles) for the synthesis of nanocomposite thin films in dielectric barrier discharges at atmospheric pressure.

Keywords: Dielectric Barrier Discharge, Atmospheric Pressure Plasma Deposition, Pulsed Injection of gases and precursors, Aerosol, Organosilicon Thin films, Nanocomposite.

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Introduction générale

Depuis plusieurs années, les revêtements sont au cœur de plusieurs applications dans des domaines d'importance stratégique comme l'aéronautique, l'aérospatial, la microélectronique, l'optique, la photonique, l'environnement, le développement durable, etc. En effet, ces couches apportent de nouvelles fonctionnalités au matériau revêtu. Selon l'application technologique envisagée, différentes propriétés peuvent être visées telles que des propriétés optiques (couche antireflet, couche anti-UV), électriques (oxyde de grille, couche en passivation), mécanique (anti-rayure) ou de surface (hydrophile, hydrophobe, superhydrophobe) [1–5].

Aujourd'hui, de nombreuses applications nécessitent l'utilisation de revêtements dits multifonctionnels offrant plusieurs propriétés en un seul et unique système. Ces propriétés peuvent être obtenues, par exemple, à partir de couches minces nanocomposites, c'est-à-dire composée de nanoparticules dispersées dans une matrice de composition chimique distincte. Les propriétés multifonctionnelles varient en fonction de la concentration, de la taille, de la forme et de la distribution des nanoparticules, ainsi que des caractéristiques de la matrice et de l'interface, notamment dans le cas de nanoparticules de très petite taille.

Les plasmas hors équilibre thermodynamique, couramment appelés plasmas froids, sont fréquemment utilisés pour déposer des couches minces fonctionnelles, voire multifonctionnelles. Grâce à leur faible coût et la possibilité de traiter en continu de grandes surfaces les procédés à la pression atmosphérique ont suscité un grand intérêt au niveau mondial [6]. Par exemple, pour les couches fonctionnelles, des travaux récents issus de l'Université de Montréal ont montré que les plasmas froids permettaient la synthèse de membranes sur des électrodes à base de cellulose pour la fabrication d'une nouvelle génération de batteries vertes [7]. Un autre exemple prometteur est celui de *Fannelli et al.* [8] qui sont parvenus à produire des matériaux superamphiphobes à l'aide de couches hydrocarbonées avec encapsulation de nanoparticules d'oxyde de zinc déposées par plasma. Pour la synthèse de couches minces nanocomposites, l'injection de nanoparticules dans la phase plasmagène permet de réaliser en une étape de tels matériaux [9]. Habituellement, les nanoparticules sont injectées dans le plasma sous la forme

d'un aérosol, c'est-à-dire un ensemble de fines particules solides ou liquides en suspension dans une phase gazeuse. Comprendre la physique des procédés permettant la création de couches minces nanocomposites résulte alors de différents facteurs tels que l'injection de l'aérosol, le transport des nanoparticules et des gouttelettes, ainsi que les interactions plasmas-nanoparticules et plasmas-gouttelettes.

Dans ce travail, nous avons exploré la possibilité de produire des revêtements (multi)fonctionnels en ayant recours à un réacteur-injecteur de nanoparticules [10][11]. Les avantages de cette méthode sont nombreux : l'utilisateur n'est pas directement exposé aux nanoparticules (safer-by-design), la synthèse suivie de l'injection des nanoparticules en simultanée avec le précurseur de la matrice permet de réaliser le dépôt en une seule étape. En dépit de son fort potentiel, cette injection soulève toutefois plusieurs défis scientifiques et technologiques. En effet, contrairement aux aérosols habituels [12], cet injecteur fonctionne en régime pulsé et avec une injection directe de liquide dans le plasma sous forme de gouttelettes. Ce type de fonctionnement transitoire résulte du fait qu'un minimum de temps est nécessaire pour la synthèse de nanoparticules [13] avant leur injection dans le procédé situé en aval. On obtient alors des nanoparticules par pulses de courtes durées (ms) avec des cadences d'injection sont de l'ordre du Hz. Le système de réacteur-injecteur est ici couplé à une décharge à barrière diélectrique à la pression atmosphérique.

Les premiers essais de l'implémentation du réacteur-injecteur à la pression atmosphérique ont soulevé plusieurs nouvelles questions. Ainsi, l'étude réalisée dans cette thèse de doctorat n'a pas pour objectif de déposer des couches minces multifonctionnelles spécifiques, mais plutôt de réaliser une étude fondamentale de pointe au niveau du couplage d'un aérosol avec une décharge à barrière diélectrique pour jeter les bases du procédé. Dans ce contexte, nous désirons d'abord examiner la stabilité de la décharge à barrière diélectrique dans ce nouveau régime d'injection pulsée. Puis, nous étudierons des facteurs gouvernant le dépôt du film mince par injection directe de liquide. Cette étude se concentrera principalement sur l'injection pulsée du précurseur hexamethyldisiloxane (HMDSO) pour lequel la littérature est bien documentée dans les régimes plus habituels, offrant ainsi des comparaisons directes et complètes. Enfin, nous explorerons quelques facettes de l'injection pulsée de nanoparticules issues du réacteur-injecteur pour la

synthèse de couches minces nanocomposites. Ici, nous nous concentrerons sur les nanoparticules de ZnO pour lesquelles la synthèse dans le réacteur-injecteur est bien maitrisée [14].

Ainsi, dans une perspective plus large, cette thèse contribuera à l'essor d'un procédé safe-by design à pression atmosphérique, pour la synthèse de couches minces (multi)fonctionnelles ouvrant une nouvelle voie vers le développement de procédés souples et éco-responsables.

Le travail mené dans cette thèse peut être brièvement résumé par les points suivants :

- l'étude détaillée d'une injection pulsée de gaz sur le régime de fonctionnement d'une décharge à barrière diélectrique ;
- l'étude de la cinétique de dépôt par injection pulsée de liquide de précurseur, ainsi que l'analyse de la polymérisation assistée par plasma dans ces conditions ;
- l'étude paramétrique de l'influence de divers facteurs opératoires tels que le débit de gaz continu, la tension plasma ou la fréquence d'excitation du champ électrique, et la nature du précurseur sur la vitesse de dépôt et le type de couche ;
- l'exploration de la synthèse de couches minces nanocomposites par injection pulsée de nanoparticules et de précurseurs liquides dans les plasmas à pression atmosphérique en comparaison avec les plasmas basse pression

Cette thèse a été réalisée en cotutelle entre l'Université Toulouse III - Paul Sabatier et l'Université de Montréal dans les groupes de recherche Sciences et Ingénierie des Plasmas Réactifs et des Arcs (ScIPRA) du LAPLACE et le groupe de recherche de Physique des Plasmas Hautement Réactif (PPHARE), respectivement.

Le premier chapitre introduit les notions générales du dépôt de couches minces (multi)fonctionnelles en commençant par les différentes méthodes de dépôt assistées par plasma. Par la suite, un accent est mis sur les méthodes développées à pression atmosphérique ainsi que sur l'injection de précurseurs et les différentes interactions dans une phase plasmagène.

Cette section permettra ainsi de dresser un portrait de l'état de l'art des procédés plus habituels afin d'initier l'étude des procédés en régime pulsé.

Le chapitre 2 transcrit l'effet d'une injection pulsée de gaz sur le fonctionnement et la stabilité d'une décharge à barrière diélectrique à la pression atmosphérique. Dans un premier temps, le réacteur ainsi que les différentes méthodes de caractérisations que nous avons mises en place sont présentés. Par la suite, les résultats de cette étude sont déclinés sous forme d'un article publié en 2022 : *« Influence of pulsed gas injections on the stability of Townsend dielectric barrier discharges in nitrogen at atmospheric pressure ».*

Le troisième chapitre porte sur l'étude du procédé de dépôt de couches minces avec injection pulsée de précurseur liquide. Pour cela, ce chapitre décrit dans un premier temps le procédé expérimental avec l'injection de précurseur liquide ainsi que la méthode de caractérisation des couches minces. Les résultats obtenus sont présentés dans deux articles. Le premier, *« Kinetics driving thin-film deposition in dielectric barrier discharges using a direct liquid injector operated in a pulsed regime »*, décrit la cinétique de dépôt d'une couche organosiliciée par injection pulsée d'un aérosol d'hexamethyldisiloxane (HMDSO). Le second, *« Soft polymer thin-film deposition by coupling a pulsed aerosol injection of HMDSO into a dielectric barrier discharge »*, met en évidence les conditions opératoires menant à une polymérisation dite « douce », i.e. avec une faible fragmentation du précurseur et peu de réticulations.

Le chapitre 4 se focalise sur le rôle des paramètres opératoires sur le type de couches minces obtenues et souligne l'importance du contrôle des interactions plasmas-gouttelettes dans nouveau régime d'opération des décharges à barrières diélectriques. Les résultats sont présentés dans l'article « *Control of plasma-droplet interactions during thin-film deposition by pulsed direct-liquid injections into dielectric barrier discharge* ». Ce chapitre présente également l'impact d'un changement de la nature du précurseur.

Capitalisant sur l'ensemble des connaissances obtenues dans les derniers chapitres, le chapitre 5 explore l'injection pulsée de nanoparticules et le dépôt de couches minces dans un plasma à la pression atmosphérique. Ces travaux sont aussi comparés à ceux réalisés à basse pression. Ces données sont déclinées dans l'article « *Direct Liquid Reactor Injector of*

Nanoparticles : an aerosol assisted method for plasma deposition of nanocomposite thin films ».

Enfin nous allons conclure et présenter quelques perspectives s'inscrivant à la suite de ce travail.

Chapitre I. Généralités et revue bibliographique

I.1. Introduction

Les matériaux multifonctionnels combinent diverses propriétés en un seul et unique système. Une des méthodes permettant d'atteindre cette multifonctionnalité est l'utilisation de matériaux composites. Ces derniers sont définis comme la combinaison d'au moins deux phases [15]. De nombreux travaux rapporte l'intérêt et l'apport de ces matériaux. Par exemple, en 1912, des études ont montré que l'introduction de poudre de noir de carbone dans la préparation des pneumatiques permettait d'améliorer fortement leur résistance à l'usure. Cependant, le terme nanocomposite fut peu utilisé jusqu'à ce que Toyota approfondisse ses recherches [16]. Dans ce cadre, en 1992, *Usuki et al.* [17][18] proposent de renforcer du Nylon 6 en le chargeant d'un minéral argileux, la montmorillonite, pour former un nouveau composite (Nylon 6-clay hybrid NHC) avec des propriétés mécaniques améliorées (augmentation du module d'élasticité et de la résistance thermique).

Depuis cette époque, les matériaux nanocomposites ont suscité l'intérêt d'un nombre grandissant de chercheurs au niveau mondial : par exemple, d'après Web of Science, 534 articles contenant le mot « nanocomposite » dans le titre sont publiés en 2000 contre 17 044 articles en 2021. De nos jours, ces matériaux se sont aussi imposés dans une vaste gamme d'applications technologiques, incluant la microélectronique [19], l'optique [20], les télécommunications [21], la production et la conversion de l'énergie [22][23], la synthèse de revêtements protecteurs [24][25], ainsi que dans le domaine médical [26] et la réduction de l'impact environnemental des applications humaines [27][28]. Par exemple, General Motors Corp. remplace certaines pièces automobiles en acier par des nanocomposites à base d'oléfine thermoplastique (TPO). Ces nouvelles pièces plus légères permettent une diminution de la consommation du véhicule réduisant l'impact environnemental [29]. Au-delà des propriétés structurelles, certains nanocomposites possèdent également des propriétés barrières, notamment une perméabilité aux fluides très faible. Ces propriétés sont utilisées dans le monde de l'automobile (traitement anticorrosion [24]), et constituent un réel intérêt pour l'emballage alimentaire [30][3].

La littérature scientifique récente révèle qu'il existe plusieurs types de nanocomposites et qu'ils peuvent être classés suivant différents critères. La matrice désigne la phase en quantité majoritaire. Elle peut être de type céramique, métallique ou polymère [1]. La seconde phase, appelée renfort ou inclusion, définie le type de composite. Si l'un des matériaux est de taille nanométrique, on parlera alors de nanocomposites. Une des classifications les plus courantes se fait suivant leurs dimensions. Comme le montre la Figure 1, *Cammarata et al.* [31] définissent 3 catégories:

(a) les composites nanocouches composées de couches alternées de dimensions nanométriques ;

(b) les composites nanofilamentaires composés d'une matrice chargée en filaments ou en tubes de taille nanométrique ;

(c) les composites nanoparticulaires composés d'une matrice chargée en nanoparticules.

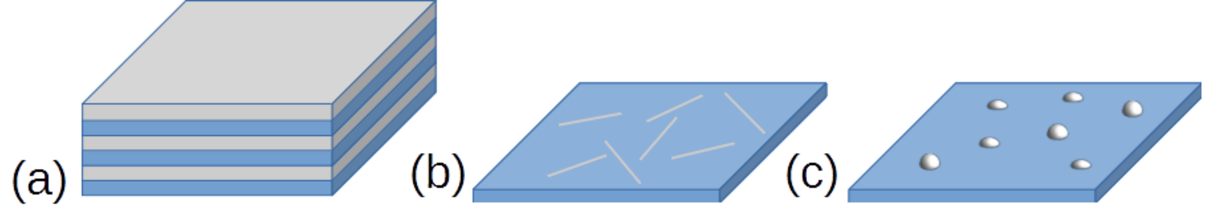


Figure 1: Schéma des différentes organisations microstructurelles des nanocomposites [32]

Les propriétés physiques et chimiques des nanocomposites présentés sur la Figure 1 sont en grande partie définies par la nature des inclusions et de la matrice, de la taille et de la forme des inclusions, de leur fraction volumique dans le matériau ainsi que la distribution des nano-objets, c'est à dire la distance moyenne entre les inclusions [33]. À titre d'exemple, pour des composites nanoparticulaires (cf. Figure 1, (c)), la taille et la forme des nanoparticules réparties dans la matrice jouent un rôle majeur sur l'évolution des propriétés macroscopiques des nanocomposites. Ce phénomène peut être expliqué entre autres par le rapport surface/volume. En effet, si on considère un nano-objet, de forme cubique pour simplifier les calculs, une particule de 1 nm contient près de 1000 atomes de 1 Å, dont 50% sont à la surface. Au contraire, une particule de 10 nm aura seulement 5% de ses atomes à la surface [9]. Par ailleurs, si on considère

des nano-objets cubiques, l'agrégation tendra à diminuer le nombre d'atomes présents en surface de 83 à 72% si on considère un agrégat linéaire ou un empilement autour d'un noyau central. En comparant ces deux cas de figure, on note que l'interaction de la surface de l'inclusion avec la matrice sera différente en fonction de sa taille. En conséquence, les propriétés apportées par les inclusions seront différentes en fonction de leur taille. Le Tableau 1, reprend différentes propriétés en fonction de la taille pour différentes nanoparticules.

Propriétés	Taille des inclusions (nm)
Effet catalytique	< 5
Effet magnétique	< 20
Variation de l'indice de réfraction (visible)	< 50
Modification de la dureté et la plasticité	< 100

Tableau 1: Influence de la taille des inclusions sur les propriétés des nanocomposites [34]

Pour les propriétés et les applications mentionnées précédemment, le composite ou le nanocomposite peut être utilisé sous sa forme massive, mais également sous forme de couches minces. Parmi les différentes méthodes de dépôt de couches minces abordées dans la littérature scientifique [35], celles assistées par plasmas s'avèrent particulièrement intéressantes pour plusieurs applications. L'un des principaux avantages des plasmas est de réaliser une couche mince en une seule étape. En effet, en général, les polymères ou les sol-gel nécessitent une étape de synthèse suivie d'une étape de mise en forme (avec éventuellement une étape de post-traitement de réticulation, de calcination, etc.). La synthèse dans le milieu plasma, souvent hors équilibre thermodynamique (température des électrons largement supérieure à celles des ions et des neutres), représente un outil très attrayant, procurant une solution économique et écologique à divers problèmes difficiles, voire impossibles à résoudre par les approches physiques ou chimiques traditionnelles. De plus, les procédés assistés par plasma se distinguent bien souvent des autres méthodes physiques et chimiques puisqu'ils possèdent l'avantage d'être rapides, souples, se prêtant bien à l'automatisation et respectueux de l'environnement [36].

Ce chapitre se veut une revue critique de la littérature scientifique sur les procédés de dépôt assistés par plasma de couches minces nanocomposites à inclusions particulaires. Dans ce contexte, la première partie discute des différentes méthodes physiques et chimiques basées sur les plasmas pour la synthèse des nanoparticules et de la matrice. La seconde partie présente une synthèse des travaux

sur le dépôt par plasma de couches minces nanocomposites dans le cas particulier des plasmas hors équilibre thermodynamique à la pression atmosphérique.

I.2. Revue des méthodes de synthèse par plasma de couches minces (multi)fonctionnelles

Il existe une grande variété de procédés permettant d'obtenir des couches minces nanocomposites à inclusions particulaires. Ceci comprend plusieurs approches physiques et chimiques pour la synthèse des nanoparticules, mais également pour le dépôt de la matrice. Dans le cas des procédés basés sur les plasmas décrits dans la littérature, ils peuvent reposer sur une combinaison de processus purement physiques, de processus purement chimiques, ou encore de processus hybrides. Cette section vise à présenter un survol des procédés et des mécanismes de dépôt de la matrice, c'est à dire d'une couche mince homogène. Puis, les approches pour l'incorporation de nanoparticules, c'est à dire la formation d'une couche mince nanocomposite seront décrites. En lien avec les objectifs de cette thèse, nous allons nous limiter aux procédés assistés par plasmas hors équilibre thermodynamique.

I.2.1 Synthèse de couches minces homogènes par plasma

a. Méthodes physiques

L'une des méthodes les plus simples pour déposer des couches minces par un procédé par plasma consiste à éjecter des atomes d'une cible solide par évaporation (apport d'énergie thermique), ablation (apport d'énergie par un laser) ou pulvérisation (apport d'énergie par des ions incidents), les transporter dans la phase gazeuse pour finalement les déposer sur un substrat. Ces méthodes sont dites physiques ou PVD (*Physical Vapor Deposition*) [37]. En plus de ses vitesses de dépôt élevées, de son faible coût d'opération et de sa bonne reproductibilité, la pulvérisation par plasma permet d'obtenir des couches minces formées de plusieurs éléments, ce qui est difficile à obtenir par d'autres méthodes de dépôt physiques et chimiques. De plus, selon un choix judicieux des conditions opératoires, il est possible de contrôler les propriétés fondamentales du plasma et la dynamique de croissance et donc les propriétés physicochimiques de la couche mince.

Les plasmas couramment utilisés pour la pulvérisation peuvent être classés en deux catégories, à savoir, les décharges en courant continu (CC) et les décharges en courant alternatif (CA). La Figure 2 montre un exemple de réacteur à plasma dont le couplage de l'énergie électrique vers le plasma s'effectue de manière capacitive.

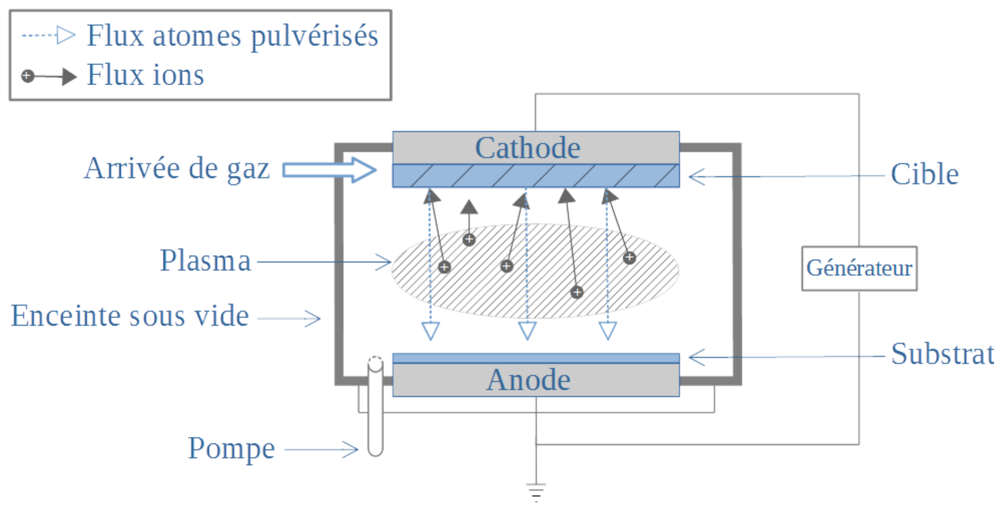


Figure 2 : Schéma de base de la pulvérisation physique dans les plasmas à couplage capacitif

Il s'agit d'une enceinte à pression réduite (1-100 mTorr) contenant le gaz plasmagène, le plus souvent l'argon. Le plasma est créé par l'application d'une tension CC ou CA entre deux électrodes parallèles, les parois du réacteur mises à la terre consistant fréquemment en une des deux électrodes. L'échantillon à pulvériser (cible) est utilisé comme cathode tandis que le substrat sur lequel on désire faire le dépôt est souvent placé sur l'anode [38]. Pour la pulvérisation de matériaux moins conducteurs, semiconducteurs ou isolants, la cathode (cible) est reliée à une alimentation CA, plus souvent dans la gamme des radiofréquences (RF). Dans la plupart des systèmes, la fréquence du générateur est fixée à 13.56 MHz, tandis que les tensions RF sont typiquement de 100 à 1000 V. Ces procédés sont produits dans des plasmas hors équilibre thermodynamique dont la densité de particules chargées est de l'ordre de 10^9 - 10^{10} ions ou électrons par cm^3 [39]. Les ions sont accélérés dans la gaine ionique au voisinage de la cathode conduisant à la pulvérisation de la cible. La tension de polarisation et le flux d'ions incidents sur la cible contrôlent la vitesse de pulvérisation et par conséquent la vitesse de dépôt à la surface du substrat [40]. Cette technique est notamment utilisée par Carcia *et al.* [41] pour la pulvérisation de cibles d'oxyde de zinc destinées au dépôt de couches minces de ZnO.

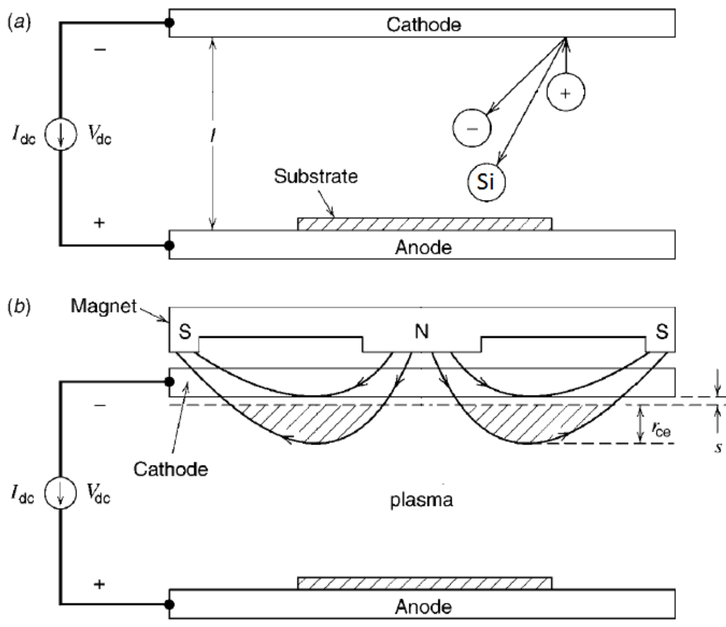


Figure 3: Comparaison entre une décharge CC a) et une décharge magnétron b) pour la pulvérisation [38]

b. Méthodes chimiques

Les couches minces homogènes peuvent également être déposées par voies chimiques, par exemple, par dépôt chimique en phase vapeur couplé avec un plasma. Dans ces conditions, le dépôt de la couche mince résulte des 5 étapes résumées à la Figure 4 [35]. Dans un premier temps (étape 1 à la Figure 4), les précurseurs du dépôt sont soumis à un apport d'énergie qui, dans les plasmas hors équilibre thermodynamique, provient le plus souvent des collisions inélastiques avec les électrons. Ces collisions incluent les processus d'excitation, d'ionisation, de dissociation et d'attachement dissociatif, donnant ainsi lieu à une grande variété d'espèces réactives [19]. Ces dernières sont ensuite transportées dans la phase gazeuse vers le substrat (étape 2 à la Figure 4) où s'effectuent les processus d'adsorption (étape 3 à la Figure 4), mais aussi de diffusion et de recombinaison en surface des espèces réactives pour former un film (étape 4 à la Figure 4). Finalement, les réactions à la surface du substrat peuvent donner lieu à une désorption de produits de réaction volatils (étape 5 à la Figure 4).

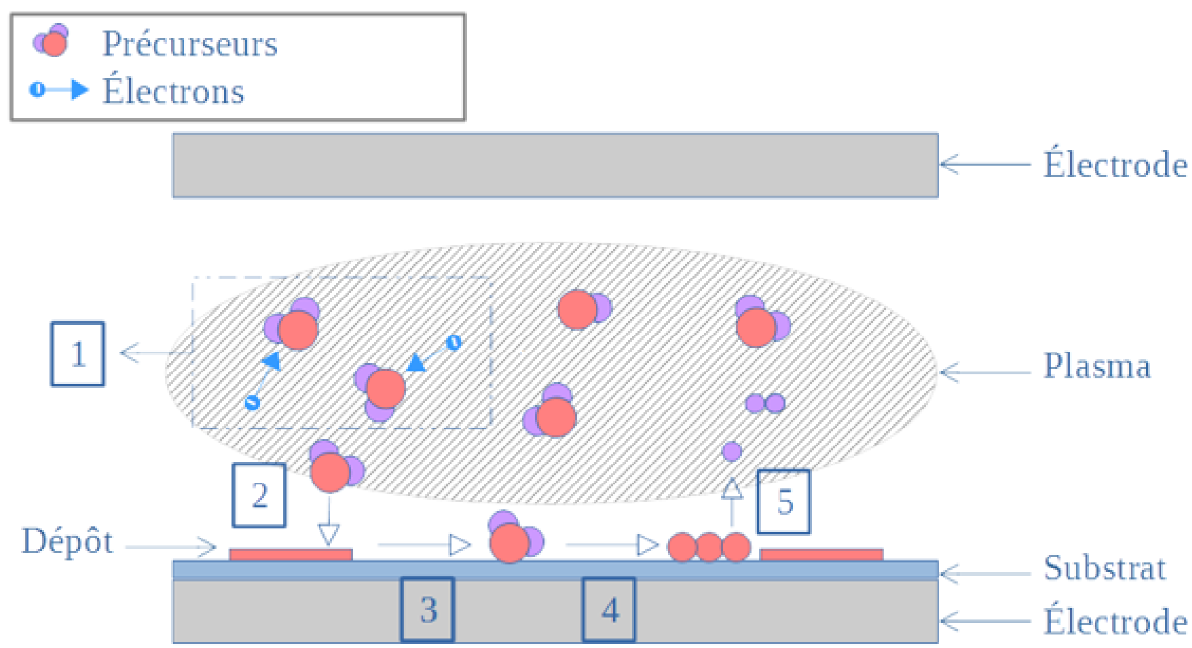


Figure 4: Schéma des étapes d'un procédé de PECVD

Les plasmas utilisés pour la PECVD sont souvent produits en régime capacitif par un champ électrique CC ou CA. Dans la majorité des cas, comme pour la pulvérisation, l'alimentation est de type RF. Un exemple est présenté à la Figure 5 pour le dépôt de couches minces de nitrure de silicium à partir du silane et de l'ammoniac [42].

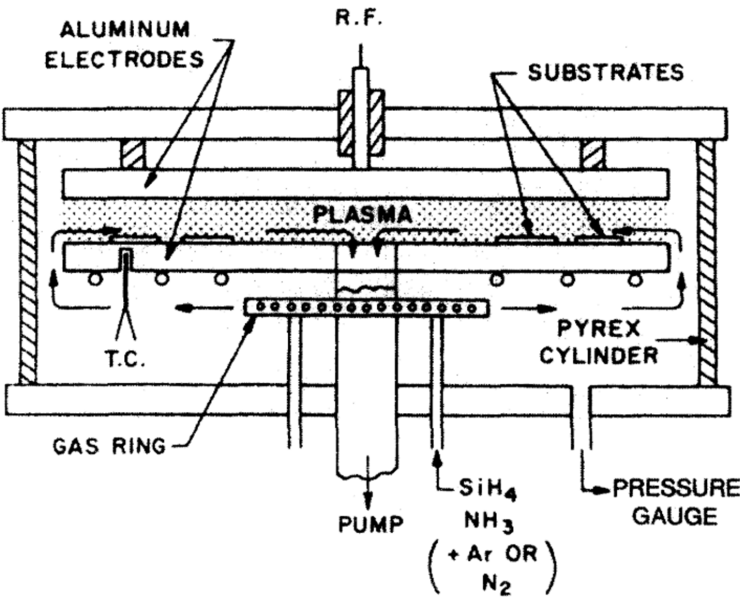


Figure 5: Réacteur à plasma RF pour le dépôt de film de nitrure de silicium[42]

I.2.2 Incorporation des nanoparticules

Pour produire des couches minces nanocomposites à inclusions particulaires, le procédé de dépôt de couche mince homogène par PVD ou par PECVD doit être couplée à un apport de nanoparticules. Ces nanoparticules peuvent être formées *in situ* par PVD ou PECVD ou encore synthétisées *ex situ* par diverses méthodes physico-chimiques puis injectées dans le plasma via différentes méthodes d'injection.

a. Production in situ de nanoparticules par PVD

Dans le cas de la pulvérisation, l'utilisation de différentes cibles dans la même chambre de dépôt permet la production de couches minces nanocomposites à inclusions particulaires. Dans ce cas, les processus physiques de dépôt intervenant lors de la pulvérisation de la cible constituent des paramètres majeurs intervenant dans la formation des nanoparticules, mais aussi de la matrice. De plus, les premiers stades de formation de la couche mince à la surface du substrat jouent des rôles fondamentaux : ils influencent non seulement les propriétés d'adhésion du dépôt avec le substrat, mais aussi l'évolution des propriétés structurelles. En particulier, pour obtenir des nanoparticules en surface, il est nécessaire que les atomes pulvérisés se condensant sur la surface

se déplacent peu de manière à obtenir des germes qui croissent pour former des îlots de taille nanométrique (croissance par îlots dite de Volmer-Weber [43], voir Figure 6 a). Ce mode de croissance est favorisé lorsque les atomes formant les nanoparticules sont plus fortement liés entre eux qu'avec les atomes du substrat ou les autres atomes de la matrice. Au contraire, pour la matrice, les atomes condensés à la surface doivent se déplacer suffisamment rapidement en surface avant l'arrivée d'atomes supplémentaires de manière à obtenir une couche mince homogène (croissance couche par couche dite Franck-van de Merwe [44], voir Figure 6 b). Ce mode de croissance est favorisé lorsque l'énergie de liaison entre les atomes de la matrice est moindre ou égale à celle entre la couche mince et le substrat. À titre d'exemple, Ulrich Schurmann *et al.* ont étudié la synthèse de nanocomposites argent-polytétrafluoroéthylène à travers l'utilisation d'une pulvérisation alternée des deux cibles [45]. D'autres travaux ont également montré la faisabilité de ce procédé de co-pulvérisation pour obtenir des couches minces nanocomposites à inclusions particulaires [46][47].

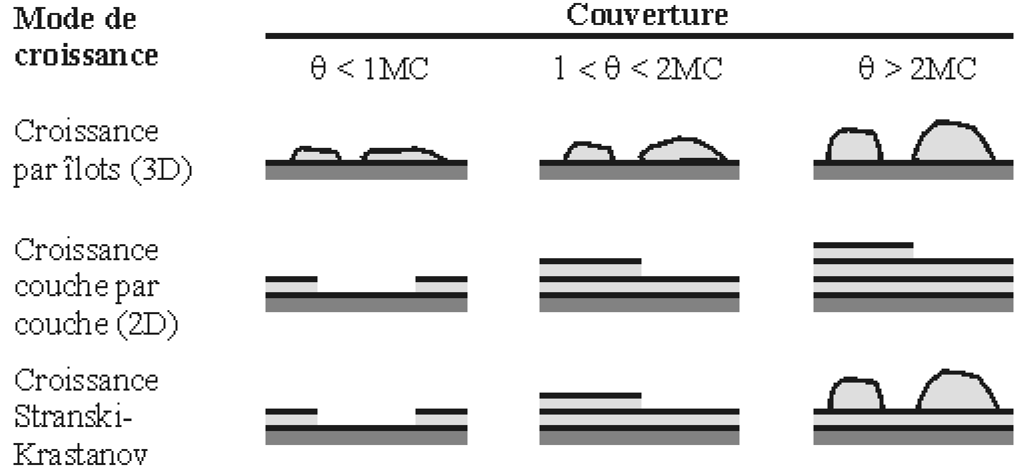


Figure 6: Illustration des modes de croissance par îlots pour les nanoparticules et couche par couche pour la matrice pour différents niveaux de couverture jusqu'à 2 monocouches (MC) [48].

En plus des processus de surface décrits plus haut, la pulvérisation peut aussi être couplée à une chambre d'agrégation pour créer des nanoparticules en phase gazeuse. Un exemple issu des travaux de Kratoschvíl *et al.* [49] est présenté à la Figure 7. Ce procédé consiste à faire passer les atomes issus de la pulvérisation dans une chambre refroidie par un circuit d'eau. En conditions de supersaturation, c.-à-d. lorsque la pression partielle des atomes pulvérisés dans le mélange gazeux dépasse la pression de vapeur saturante, les atomes vont commencer à s'associer pour

former les premiers germes, aussi appelés nuclei (groupe d'atomes présentant une structure ordonnée), et par la suite des nanoparticules. Comme le montre la Figure 7, la taille des nanoparticules peut être contrôlée en fonction des conditions de pression de la chambre d'agrégation ainsi que la durée du procédé. Pour obtenir une couche mince nanocomposite à inclusions particulaires, les nanoparticules issues de la chambre d'agrégation doivent être couplées à une autre source ou pour le dépôt de la matrice.

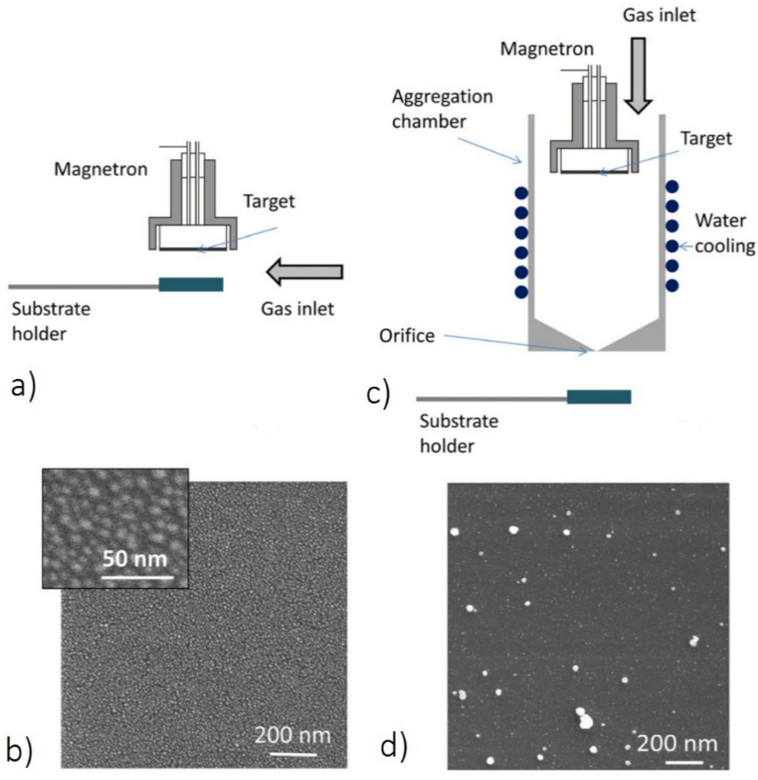


Figure 7: Schéma du réacteur de pulvérisation magnétron a) avec image SEM à 5s b). Schéma du réacteur GAZ c), avec image SEM à 30s d).[49]

Malgré le potentiel des procédés de pulvérisation multicible, les approches hybrides couplant la pulvérisation physique pour l'incorporation des nanoparticules avec l'incorporation de gaz réactifs pour le dépôt de la matrice offrent une plus large gamme de possibilités. Par exemple, on retrouve dans la littérature une vaste gamme de couches hydrocarbonées contenant des inclusions de chrome [50], de nickel [51], de platine [52] et même de carbure de titane [53] réalisées par pulvérisation dans des plasmas réactifs. Une contrainte de cette technique hybride PVD-PECVD est la pollution de la cible liée au dépôt d'une couche sur la cible à pulvériser. Ce

mécanisme affecte la pulvérisation. Néanmoins, des solutions ont été proposées. Une d'elles les plus intuitives est de travailler avec un faible pourcentage de précurseurs, limitant la contamination de la cible et assurant la formation de la couche nanocomposite [54]. Cependant, avec une injection continue, cette solution nécessite un contrôle très fin des propriétés fondamentales du plasma et de ce fait limite la gamme de matériaux atteignables, en particulier en termes de fraction volumique de nanoparticules dans la couche. Despax *et al.* [55] ont proposé d'injecter le précurseur de façon pulsée pour déposer des nanocomposites à base de polysiloxane dans lesquels sont incorporées des nanoparticules d'argent. La fraction volumique d'argent dans la couche ainsi que les propriétés physiques et chimiques des couches nanocomposites peuvent être variées sur une très grande plage avec des pulses de gaz précurseur de l'ordre de la centaine de ms pour des fréquences de l'ordre de 0.2 Hz. Quand le précurseur est injecté, c'est le mode PECVD qui domine et qui conduit à la croissance d'une couche polysiloxane sur le substrat et sur la cible. Lorsque seul le gaz de pulvérisation est injecté (argon dans ce cas), la pulvérisation nettoie la cible et permet la formation des nanoparticules. Ainsi, la gestion du rapport cyclique d'injection du précurseur constitue un paramètre clé contrôlant la quantité de métal finalement déposé dans la couche ainsi que l'évolution des propriétés physiques et chimiques.

b. Synthèse in situ de nanoparticules par PECVD

Comme mentionné précédemment, la PECVD est largement utilisée pour le dépôt de couches minces homogènes. Cependant, l'introduction d'un précurseur dans un plasma peut également conduire, selon les conditions opératoires, à des processus de croissance de nanoparticules en phase gazeuse. Ces nanoparticules peuvent être collectées sur le substrat simultanément avec les espèces réactives du dépôt pour ainsi former un matériau nanocomposite. La présence de particules dans les plasmas RF de silane a été mise en évidence la première fois par Spears *et al.* en 1986 [56] et est resté un sujet d'étude pendant de nombreuses années. Si l'objectif de ces études a pour la plupart du temps été la compréhension des phénomènes gouvernant la formation des particules dans ces plasmas [57][58], la fabrication de films nanocomposites à partir de ces systèmes a également été étudiée par plusieurs auteurs. À titre d'exemple, on peut citer les travaux de P.Roca i Cabarrocas *et al.* [59][60] montrant la fabrication de couches de

silicium amorphe dans lesquelles des nanocristaux de silicium, formés en phase homogène, sont inclus. On trouve également des travaux dans des plasmas hydrocarbonés à basse pression [61,62].

Dans certains plasmas réactifs, l'interaction du précurseur avec les électrons du plasma peut mener à la production d'ions négatifs par attachement électronique. Par exemple, le silane peut former des ions SiH_3- et l'acétylène des ions C_2H- qui sont fréquemment décrits comme les précurseurs des nanoparticules formés dans la phase gazeuse. En effet, les ions négatifs sont efficacement confinés dans le plasma par la chute de potentiel aux parois et possèdent donc un temps de résidence supérieur aux neutres et aux ions positifs [63,64]. La croissance débute par recombinaison dans le plasma, c'est à dire par une étape de nucléation. Dans le cas très étudié d'un plasma de silane, ces premières réactions menant à la formation de protoparticules (agrégats de quelques nanomètres) peuvent s'exprimer comme :

$$\mathrm{Si_nH}_x^- + \mathrm{SiH_4} \rightarrow \left(\mathrm{Si_{n+1}H}_{x'}^-\right)^* + \left(\text{produits de H, H}_2\right)$$

La phase de coagulation débute lorsqu'une densité critique de protoparticules est atteinte. Elle conduit à la formation d'agglomérats de protoparticules [65,66]. Lorsqu'une particule atteint une taille de quelques dizaines de nanomètres, une gaine se forme autour de la particule placée au potentiel flottant toujours négatif par rapport au plasma. Ceci conduit à une charge négative de la particule qui va limiter le processus d'agglomération et conduire à la dernière phase de croissance, l'accrétion. Cette dernière est décrite par l'ajout d'espèces moléculaires à la surface de la nanoparticule, comme montré dans la partie droite de la Figure 8. Lors de l'interaction plasma-nanoparticules, le flux d'électrons et d'ions ainsi que les mécanismes de recombinaisons contribuent à la charge mais aussi au chauffage de la particule [67] qui peut conduire à la cristallisation des nanoparticules, mais aussi à l'évaporation du solide [68].

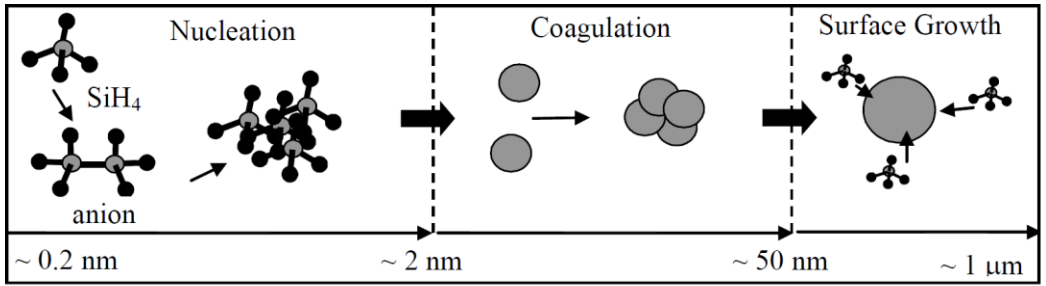


Figure 8 : Les trois phases de croissance distinctive des nanoparticules dans un plasma : nucléation, coagulation et accrétion. Tiré de Merlino [69].

La dynamique de croissance et l'évolution en taille et en structure des nanoparticules obtenues par PECVD sont étroitement liées aux conditions opératoires du plasma qui gouvernent la cinétique de fragmentation du précurseur, la dynamique de chargement des nanoparticules, mais aussi le transport des nanoparticules via le bilan des forces (gravité, force électrostatique, force d'entraînement, thermophorèse, etc.). À titre d'exemple, Shimada *et al.* [70] ont eu recours à la PECVD avec des précurseurs de triméthylgallium et d'ammoniac pour synthétiser des nanoparticules de nitrure de gallium (GaN) dans un plasma micro-ondes. Dans ces conditions, les auteurs notent qu'une augmentation de la puissance entraine une diminution de la taille des nanoparticules (7.3 nm à 800 W, 5.6 nm à 1000 W et 5.2 nm à 1200 W). De plus, comme le montre la Figure 9, ils expliquent ce comportement par une augmentation de la densité de particules chargées dans le plasma avec la puissance. Ceci augmente la fragmentation des précurseurs via les collisions avec les électrons, mais limite également l'agglomération des particules liée à la répulsion électrostatique. De plus, l'augmentation de la puissance favorise le nombre d'impacts électroniques avec les espèces du plasma, ce qui entraîne une diminution de la température des électrons, ce qui engendre une différence dans la croissance des nanoparticules [71].

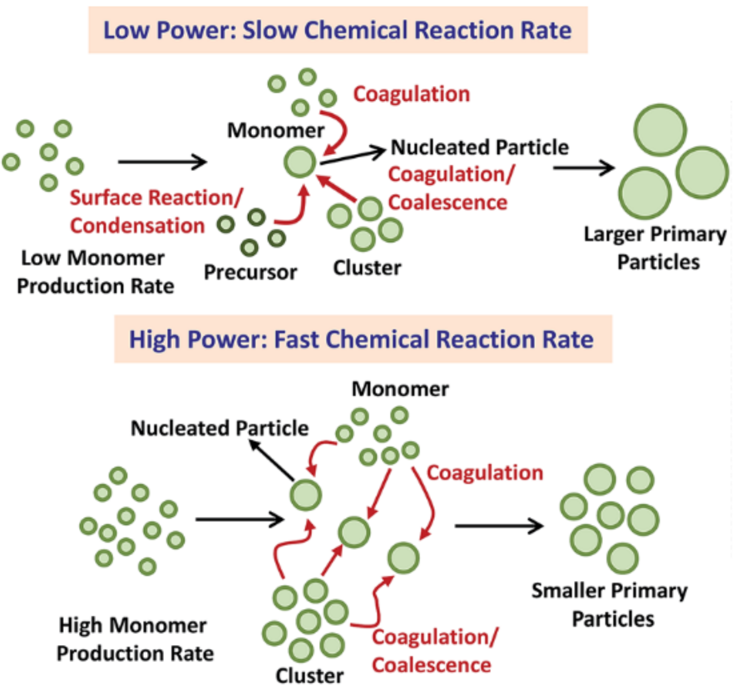


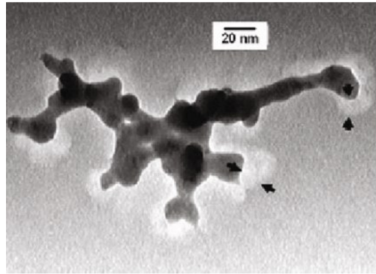
Figure 9: Mécanisme de croissance des nanoparticules par PECVD en fonction de la puissance micro-ondes. [71]

c. Synthèse ex-situ de nanoparticules par voies physico-chimiques et injection dans le plasma

Comme décrit précédemment, l'introduction d'un précurseur dans un plasma peut donner lieu à une couche mince homogène, mais aussi à des couches minces nanocomposites à inclusions particulaires. Cependant, dans ces procédés basés uniquement sur la PECVD, les compositions chimiques des nanoparticules et de la matrice sont généralement similaires ; ce sont principalement les propriétés structurales qui diffèrent. À titre d'exemple, on peut citer les couches de silicium amorphe avec des inclusions de nanocristaux de silicium [59,60], ainsi que les couches de carbone amorphe contenant des nanograins de graphite [62]. Afin d'obtenir une meilleure souplesse au niveau des propriétés physiques et chimiques des nanoparticules et de la matrice, certains auteurs ont proposé de réaliser la synthèse ex-situ des nanoparticules par voie chimique et de coupler cette synthèse à un procédé plasma en injectant le précurseur sous la

forme d'un aérosol, c'est-à-dire un ensemble de fines particules en suspension dans un milieu gazeux.

On retrouve dans la littérature quelques travaux décrivant cette démarche hybride. Ainsi, Tachibana *et al.* [72] montrent la production de particules monodisperses parfaitement sphériques en injectant une poudre de carbone dans un plasma de méthane à basse pression. De façon similaire, Kiatamura *et al.* [73] décrivent la croissance de couches de silice sur des particules pré-synthétisées d'oxyde de zinc à partir d'un plasma argon-oxygène à basse pression en présence d'un précurseur organosilicié. C. Nessin *et al.* [74] utilisent quant à eux différentes géométries de décharges à barrière diélectrique à la pression atmosphérique pour revêtir des nanoparticules d'aluminium ou de silice amorphe (cf.Figure 10).



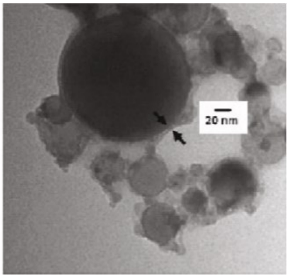


Figure 10: Imagerie de nanoparticules de silice avec revêtement obtenu par PECVD avec un précurseur d'éthylène (gauche) et de nanoparticules d'oxyde d'aluminium avec revêtement organosilicié obtenu avec hexamethyldisiloxane (droite). [74]

Une des méthodes récentes proposées dans la littérature consiste à préparer une suspension colloïdale, c'est-à-dire une suspension de nanoparticules dispersées de façon homogène dans un liquide, puis de l'injecter dans le plasma. Ces colloïdes peuvent être formés de différentes manières, par exemple par sol-gel, par synthèse organométallique ou encore par ablation laser d'une cible solide en milieu liquide [75–78]. Évidemment, la nature, la distribution en taille et la stabilité des nanoparticules dans le milieu liquide sont étroitement liées au mode et aux conditions de synthèse. Par exemple, Behnajady *et al.* [79] ont synthétisé des nanoparticules de TiO_2 par sol-gel et ont étudié l'influence de la nature du précurseur et du solvant sur les propriétés physiques et chimiques des nanoparticules. Des structures de type rutile ou anatase et diverses distributions en taille peuvent être obtenues selon les conditions opératoires.

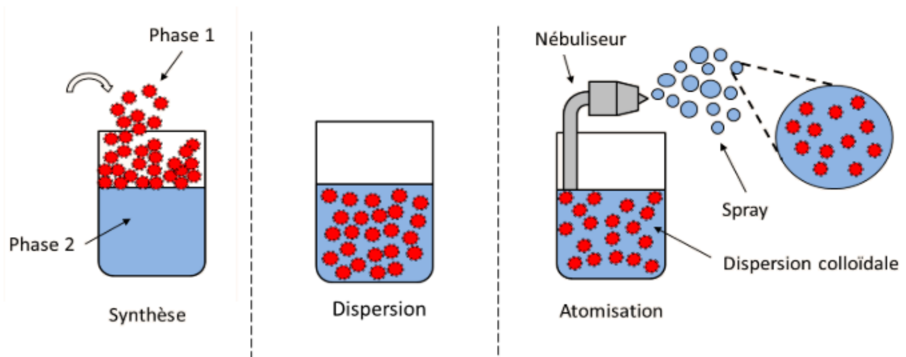


Figure 11: Synthèse, dispersion et atomisation d'une solution colloïdale[80]

Comme le montre la Figure 11, la suspension peut ensuite être insérée dans le plasma en ayant recours, par exemple, à un nébuliseur permettant de la transformer en un aérosol, c'est à dire un nuage de gouttes extrêmement fines chargées en nanoparticules. Les nébuliseurs les plus communs utilisent l'effet Venturi pour aspirer le liquide et l'injecter [81]. Cette méthode a été mise en œuvre dans différents procédés, dont les décharges à barrière diélectrique à la pression atmosphérique et les plasmas RF à basse pression[82]. Par exemple, à partir de cette méthode, *Fanelli et al.* [83] ont déposé des couches minces nanocomposites formées de nanoparticules de ZnO imbriquées dans une matrice organique, Profili *et al.* ont déposé des couches minces nanocomposites $ZnO\text{-}SiO_2$ [84], *Brunet et al.* Ont déposé des nanoparticules de TiO_2 dans une matrice hydrocarbonée [75], *D. del Frari et al.* [85,86] ont synthétisé des couches organosiliciées contenant des inclusions de nanoparticules d'$Al\text{-}CeO_3$. Néanmoins, dans plusieurs cas, la Figure 12 montre que les nanoparticules [87] sont présentes sous la forme d'amas figés dans la matrice. Ceci suggère que des processus d'agglomération en phase liquide, en phase aérosol, en phase plasma ou en phase solide interviennent pendant le procédé de dépôt.

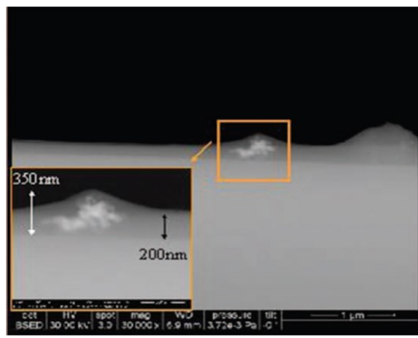


Figure 12: Image obtenue par microscopie électronique d'une couche nanocomposite avec inclusions particulaires [85]

I.3. Procédés assistés par plasma à pression atmosphérique

Le travail de cette thèse consiste à étudier un procédé de dépôt par plasma froid à la pression atmosphérique. Dans ce contexte, des efforts de recherche importants ont été déployés au niveau mondial afin de mettre au point des sources possédant des caractéristiques comparables à celles des plasmas de basse pression (milieu faiblement ionisé et hors équilibre thermodynamique). Par exemple, les décharges à barrière diélectrique (DBD) à la pression atmosphérique sont caractérisées par des températures du gaz voisines de la température ambiante (plasma froid) et possèdent des densités d'espèces actives (atomes, radicaux, photons) élevées, offrant ainsi la possibilité de traitements rapides, en continu, de substrats de grandes dimensions, incluant ceux sensibles à la chaleur [88]. Cependant, dans ces conditions, les procédés de dépôts de couches minces sont davantage chimiques (PECVD) que physiques (PVD). En effet, à la pression atmosphérique, les gaines permettant l'accélération des ions au voisinage des cathodes deviennent collisionnelles de sorte que les ions n'ont généralement pas assez d'énergie pour pulvériser les atomes.

Cette section vise à présenter un état des connaissances dans le domaine du dépôt de couches minces nanocomposites avec inclusions particulaires à partir de plasmas froids à la pression atmosphérique. En lien avec le caractère hautement collisionnel de ce type de plasmas et les conclusions de la dernière section, nous allons nous focaliser sur les méthodes de dépôt couplant le PECVD avec une injection de nanoparticules formées *ex-situ*. Dans ce contexte, cette section est découpée en trois parties décrivant respectivement : les réacteurs et les caractéristiques des décharges à barrières diélectrique, les phénomènes physico-chimiques gouvernant la cinétique de dépôt et la polymérisation de la matrice, ainsi que les facteurs influençant l'injection des nanoparticules et des gouttelettes dans ces systèmes.

I.3.1 Réacteurs et caractéristiques des plasmas froids destinés au dépôt de couches minces

L'une des méthodes les plus simples pour produire un plasma à la pression atmosphérique est de soumettre un gaz contenu entre deux électrodes métalliques à un champ électrique CC ou CA. Pour éviter la formation d'arcs électriques, il est d'usage de ralentir la multiplication

électronique par l'ajout d'un diélectrique sur au moins une des deux électrodes. Dans ces conditions, l'accumulation de charges sur le ou les diélectriques au cours de chaque demi-période du champ électrique oscillant permet d'écranter le potentiel électrique appliqué, ralentissant ainsi la multiplication électronique avant le passage au régime d'arc [6]. Ce type de décharge est appelé décharge à barrière diélectrique (DBD). Brevetée en 1857 par Siemens afin de produire de l'ozone [89], les DBD sont de nos jours grandement utilisées pour les dépôts de couches minces fonctionnelles et multifonctionnelles sur divers substrats, en particulier ceux sensibles à la chaleur comme les polymères. La Figure 13 présente quelques configurations courantes de réacteurs.

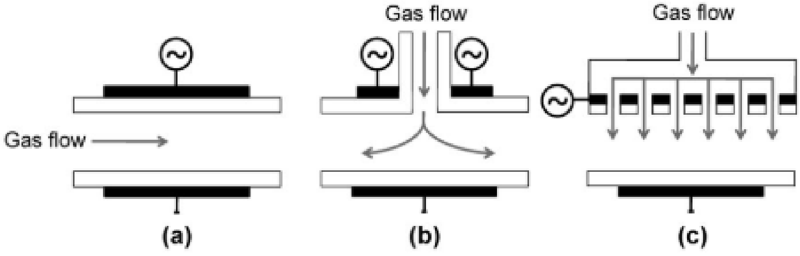


Figure 13: Exemple d'injection de gaz dans une DBD (a) latérale (b) centrale (c) au travers de l'électrode (électrode douche)[6]

La physique des DBD est étroitement liée à la fréquence d'oscillation du champ électrique ω par rapport à certaines grandeurs caractéristiques du plasma (fréquence plasma des ions ω_{pi} et des électrons ω_{pe}, fréquence de collisions des ions et des électrons). À très basses fréquences (typiquement entre 1 et 30 kHz), ω est inférieure à ωp_i et ωp_e de sorte que les deux espèces répondent au champ électrique instantané. Dans ces conditions, selon l'amplitude de l'excursion des ions et des électrons dans l'espace inter-électrodes, la multiplication électronique peut résulter des processus α (ionisation dans le volume et au voisinage des électrodes) et/ou γ (génération d'électrons secondaires par bombardement (notamment ionique) de la cathode). Selon les conditions opératoires (nature du gaz, distance inter-électrodes, amplitude et fréquence de la tension électrique appliquée, etc.), la physique des DBD peut donner lieu à différents régimes d'opération (filamentaires, Townsend, luminescentes [6]). Quelques exemples sont présentés à la Figure 14 dans le cas particulier d'une configuration plan-plan avec une injection horizontale de flux de gaz (Figure 13.a).

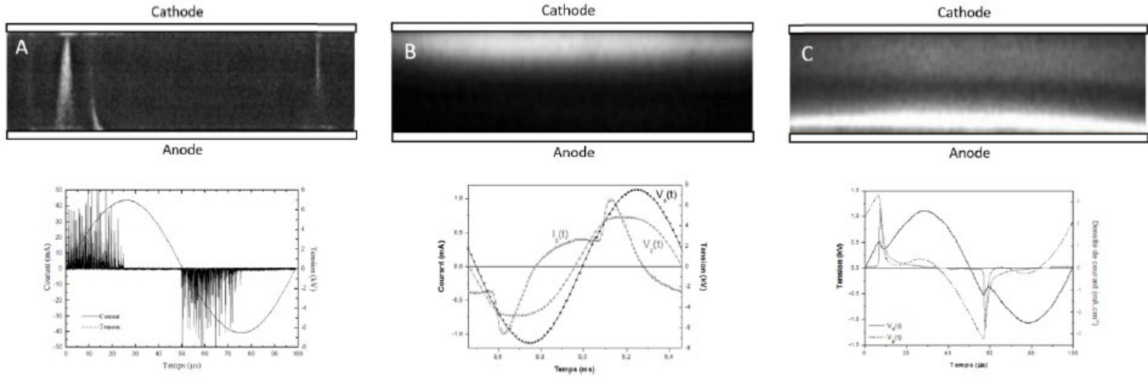


Figure 14 : Différents types de décharge DBD avec un temps de pause de 10 ns a) filamentaire, b) Townsend et c) luminescente. [90]

En régime filamentaire, le plus courant dans les DBD, l'émission lumineuse ainsi que la caractéristique courant-tension montrent la présence de microdécharges distribuées aléatoirement, spatialement et temporellement (Figure 14 a). Au contraire, selon un choix judicieux de conditions opératoires, un régime homogène (autant pour la décharge de Townsend que pour la décharge luminescente) peut être obtenu. Dans ces conditions, la distribution lumineuse devient plus uniforme et un seul pic de courant est observé par demi-cycle de la tension appliquée (Figure 14 b et c) [6]. À l'évidence, les DBD homogènes en régime de Townsend et en régime luminescent sont beaucoup plus adaptées au dépôt de couches minces [91,92]. En effet, les microdécharges observées en régime filamentaire conduisent à des dépôts de puissance locaux très importants ce qui peut s'avérer très critique pour plusieurs matériaux.

Dans les DBD homogènes en régime de Townsend ou en régime luminescent, comme la fréquence de collisions des électrons avec les particules neutres ν est largement supérieure à la pulsation du champ électrique ω, le transfert d'énergie du champ vers les neutres via les électrons s'effectue à chaque instant de la période du potentiel électrique appliqué. Les propriétés fondamentales de la DBD deviennent alors tributaires de la valeur instantanée de l'amplitude du champ électrique et varient donc fortement en fonction du temps. Ceci inclut la densité et la température des particules chargées, mais aussi la densité des particules dans des états excités. Dans les conditions typiques, les densités de puissance absorbées par les électrons du champ électrique appliqué (moyenne sur un cycle) sont de l'ordre de 0.1-1 $W.cm^{-3}$ [6].

À plus hautes fréquences (typiquement entre 3 et 30 MHz), les ions peinent à suivre l'oscillation rapide du champ électrique ($\omega > \omega p_{i)}$ de sorte que sur un cycle, peu parcourent une distance considérable. Quant aux électrons, ils répondent toujours au champ instantané. De plus, comme $\nu < \omega$, les propriétés fondamentales du plasma peuvent toujours varier en fonction du temps. Cependant, contrairement aux DBD de basse fréquence, la décharge demeure allumée sur tout le cycle de la tension appliquée et la présence des diélectriques entre les deux électrodes n'est plus nécessaire pour empêcher l'apparition d'arcs. En effet, l'inversion rapide de polarisation minimise intrinsèquement les risques d'accumulations de charges. Dans ces conditions, les densités de puissance absorbée par les électrons du champ électrique (moyenne sur un cycle) sont typiquement de l'ordre de 1-10 $W.cm^{-3}$ [6].

Le Tableau 2 présente un résumé des propriétés fondamentales des DBD pour plusieurs régimes de décharge. En régime filamentaire, les densités électroniques peuvent être très élevées (jusqu'à 10^{20} m^{-3}), mais sur de très courtes durées (typiquement 10 - 100 ns) et dans un tout petit volume (rayon d'environ 200 µm). Dans le cas de la décharge luminescente homogène, les densités de courant peuvent atteindre 10 $mA.cm^{-2}$, ce qui correspond à des maximums de densités de charges de l'ordre de 10^{16}-10^{17} m^{-3}. Tableau 2Ces maximums de densités sont évidemment plus faibles dans la décharge sombre de Townsend. Finalement, dans les plasmas RF, comme le plasma demeure toujours allumé, les densités de courant sont plus élevées ce qui fait en sorte que les densités de charges peuvent atteindre les 10^{17}-10^{18} m^{-3}.

Type de décharge	DBD en régime filamentaire	DBD en régime luminescent	DBD en régime de Townsend	Plasma RF
Durée de la décharge	10-100 ns	1-5 µs	Moitié de la période	Allumée en tout temps
Densité de courant maximale ($mA.cm^{-2}$)	10^3-10^4	1-10	0.1-5	50
Densité de puissance maximale ($W.cm^{-2}$)	10	1	10	5

Densité électronique maximale (m^{-3})	10^{20}	10^{16}-10^{17}	10^{13}-10^{14}	10^{18}
Densité d'états métastables maximale (m^{-3})	10^{19}	10^{17}	10^{19}	10^{18}
Densité ionique maximale (m^{-3})	10^{20}	10^{17}	10^{17}	10^{17-18}

Tableau 2 : Caractéristiques et densités des espèces actives dans les DBD pour plusieurs régimes de décharges. Adapté de Massines et al. [6]

I.3.2 Cinétique et polymérisation de dépôt de la matrice

a. Fragmentation du précurseur

Le dépôt de la matrice par PECVD dans les plasmas froids suit plusieurs étapes citées à la section précédente. La première étape est la création d'espèces réactives qui vont ensuite être transportées vers le substrat où s'effectue le dépôt. Les espèces dites réactives sont des fragments de précurseurs rendus actifs grâce aux espèces énergétiques du plasma (électrons, ions, espèces excitées, rayonnement). Dans les DBD, la fragmentation du précurseur menant à la création d'espèces réactives peut se faire via les collisions avec les électrons, mais aussi via les collisions avec des espèces excitées de longue durée de vie, par exemple l'état métastable N_2(A) dans les décharges de Townsend dans l'azote et l'état métastable He ^{3}S dans les décharges luminescentes dans l'hélium [6].

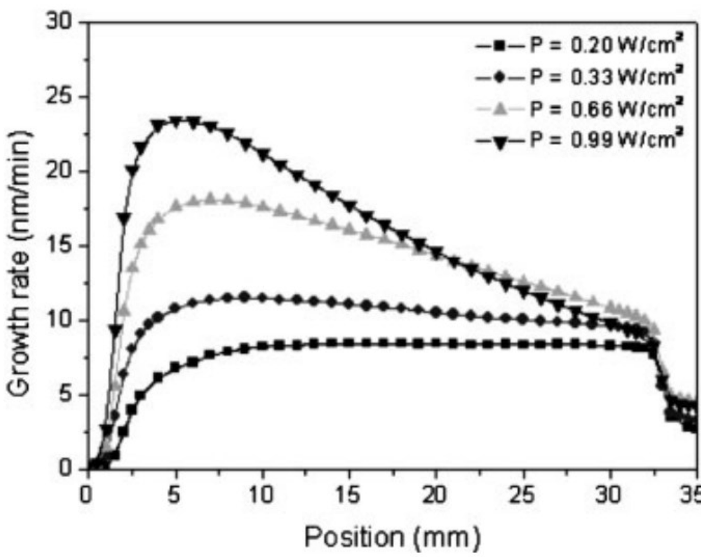


Figure 15: Vitesse de dépôt de couches de SiO_2 pour plusieurs valeurs de puissance absorbée [93].

Dans certaines conditions, par exemple en l'absence de phénomènes de transport des espèces réactives dans le gaz, de réémission et de diffusion de surface, les vitesses de dépôt sont directement liées à la conversion locale du précurseur en espèces réactives. Ainsi, pour une concentration locale de précurseur donnée, il existe un lien direct entre les vitesses de dépôt locales et les propriétés physico-chimiques du plasma au voisinage de ce point. Pour illustrer ce phénomène, la Figure 15 illustre l'influence de la densité de puissance absorbée dans une décharge de Townsend en configuration plan-plan (Figure 13.a) dans N_2-N_2O sur la vitesse de dépôt d'une couche mince de SiO_2 à partir du précurseur hexamethyldisiloxane (HMDSO). Ici, la position 0 mm correspond au début de l'électrode et 35 mm correspond à la fin. Pour une position donnée, Enache *et al.*[93] montrent qu'une augmentation de la densité de puissance absorbée engendre une augmentation de la vitesse de dépôt. Dans ces conditions, ceci s'explique par une augmentation du degré de fragmentation du précurseur avec la puissance, un effet associé à une augmentation de la population de $N_2(A)$ directement impliqués dans la cinétique de fragmentation de l'HMDSO [93].

La Figure 16 présente également un gradient de la vitesse de dépôt le long de la DBD, celui-ci variant en fonction de la puissance. Bien que les profils semblent assez uniformes à basse puissance, un maximum est observé en entrée de décharge à haute puissance. Ceci s'explique en grande partie par une diminution de la concentration locale de l'HMDSO disponible pour le dépôt

en fonction de la distance. En effet, à plus hautes puissances, la fragmentation de l'HMDSO et le dépôt correspondant sur le substrat deviennent si importants qu'il existe de moins en moins d'HMDSO disponibles pour le dépôt de la couche mince en sortie de décharge. Dans ce cas-là, une consommation importante du précurseur est responsable d'un dépôt inhomogène dans la cellule de décharge.

Pour augmenter les vitesses de dépôt d'une couche mince dans des conditions opératoires données, une approche naturelle pourrait ainsi être, en plus d'augmenter la puissance comme le montre la Figure 15, d'augmenter la concentration du précurseur. Pour discuter de cet aspect, la Figure 16 présente le degré de conversion du précurseur HMDSO obtenu par spectrométrie de masse en fonction de la concentration en ppm dans une décharge luminescente d'hélium. Les auteurs notent une diminution significative du degré de conversion lorsque la concentration de HMDSO augmente. Cela pourrait être expliqué par la quantité d'énergie fournit par précurseur afin d'avoir une fragmentation efficace [94]. À nouveau, il est toutefois difficile d'interpréter ce résultat sans des mesures de la densité et de la température des espèces impliquées dans la fragmentation.

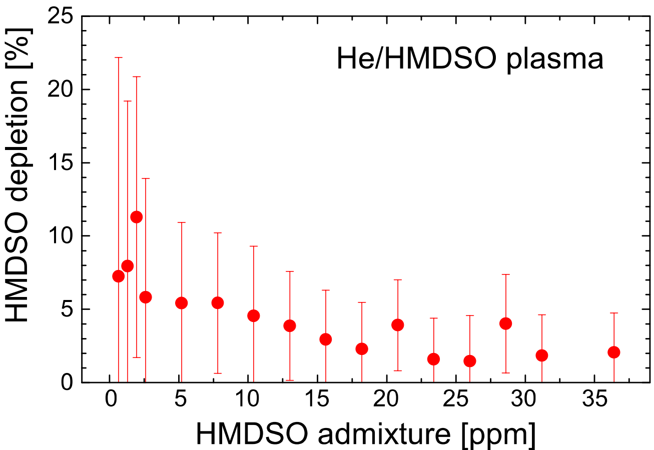


Figure 16 : Appauvrissement en HMDSO en fonction de la concentration de ce dernier [95].

Sonnenfeld et al. [96], ont proposé un schéma de procédé de fragmentation par plasma du HMDSO. Comme le montre la Figure 17, deux chemins réactionnels sont possibles selon si c'est une liaison Si-C ou Si-O qui est brisée par les espèces du plasma. Dans les DBD à la pression

atmosphérique, il est généralement admis que l'énergie injectée dans le système est suffisamment faible pour que la liaison Si-O soit conservée [93,96].

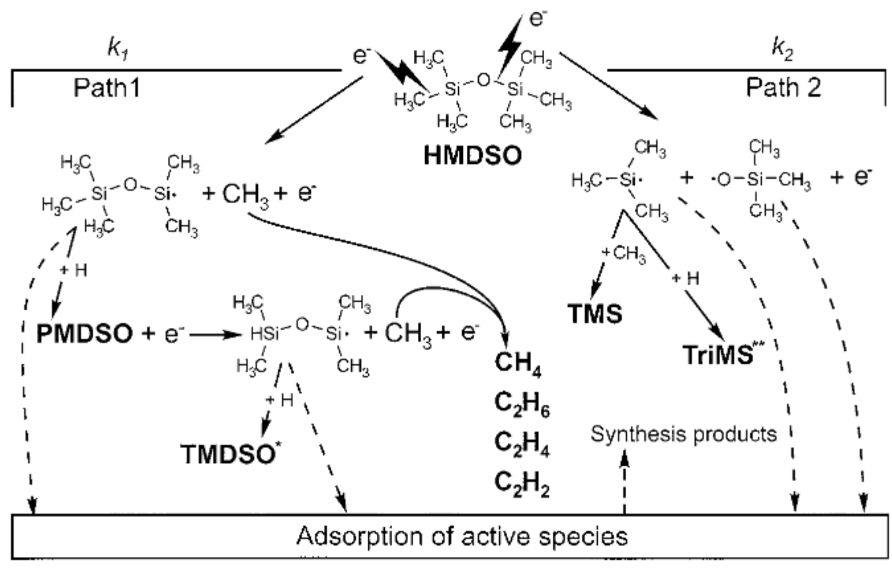


Figure 17: Schéma de la fragmentation assistée par plasma de l'HMDSO [96]

b. Transport et collage des fragments

Dans les DBD, en plus de la cinétique de fragmentation des précurseurs discutée plus haut, les dynamiques d'écoulement du gaz et des espèces réactives jouent également un rôle important sur le dépôt des couches minces. Comme le montre la Figure 13, l'injection du gaz plasmagène et des précurseurs du dépôt peut se faire selon différentes configurations. La configuration a) représente deux électrodes planes en face à face. Comme discuté plus haut (cf. Figure 15), des différences dans l'homogénéité des films déposés peuvent être observées selon les conditions opératoires. Ces inhomogénéités peuvent toutefois être contournées en ayant recours à un système de défilement du substrat [97]. La configuration b) peut être vue comme deux injections de sens opposés. Cependant la portion du substrat placé en dessous de l'injection centrée ne reçoit généralement pas les espèces activées par le plasma, mais directement les flux gazeux avant leur activation. Dans ces conditions, le dépôt est typiquement localisé de chaque côté des deux électrodes [6]. Enfin la configuration c), communément appelée électrode douche, consiste à faire passer le flux de gaz au travers de l'électrode supérieure. Cette configuration possède l'avantage de faciliter l'homogénéité du dépôt sur toute la surface du substrat situé sur

l'électrode inférieure. Les trous doivent néanmoins être suffisamment grands pour ne pas être obstrués par les espèces du dépôt et peuvent également venir perturber la stabilité de la décharge.

En plus de la fragmentation du précurseur et de la dynamique de l'écoulement, d'autres phénomènes peuvent également influencer le dépôt de couches minces. *Savin de Larclause et al.* [98] citent trois mécanismes pouvant intervenir dans le dépôt :

- Le transport direct : Le fragment du précurseur colle directement à la surface du substrat sans aucune collision avec les autres surfaces.
- Le processus de réémission : Le fragment est réémis par la surface après plusieurs collisions sans adhérer à celle-ci ou après une désorption de la surface et peut atteindre un autre site de la surface.
- La diffusion en surface : Le fragment incident est adsorbé à la surface, diffuse le long de celle-ci et vient adhérer sur un site plus stable.

Dans les DBD, c'est généralement le transport direct qui domine puisque le milieu environnant est fortement collisionnel. De plus, les coefficients de collage des fragments sont souvent très élevés, ce qui limite les effets de transport entre le point de dissociation et le point de dépôt. Dans ces conditions, les effets de bombardement ionique sont aussi assez faibles, ce qui limite les phénomènes de désorption et de re-dépôt en un autre point du substrat. Finalement, les processus de diffusion de surface deviennent importants que pour des températures du substrat plus élevées [99].

A la pression atmosphérique, il faut néanmoins porter une attention au temps de résidence des précurseurs dans la cellule de décharge. Si le temps de résidence est relativement faible, on observera alors un dépôt d'une couche mince comme nous l'avons vu à la section précédente. Cependant, si le temps de résidence devient plus important, il est possible d'observer une association en phase gazeuse des fragments donnant lieu à des plasmas poudreux et donc à des nanoparticules à la surface du substrat [92,100–103].

c. Polymérisation

Dans les paragraphes précédents, les espèces responsables de la fragmentation du précurseur ont été énoncées, de plus le transport de ces fragments jusqu'au substrat a également été abordé. Pour aller plus en détail dans la formation de couches minces, il est nécessaire de comprendre les processus mis en jeu à la surface. En particulier, l'adsorption de fragments du précurseur conduit, généralement, à des matériaux dits polymères plasmas qui sont très fortement réticulés. Pour étudier ce type de propriétés, il est courant de recourir à la spectroscopie infrarouge à transformée de Fourier [104–106]. Un exemple issu des travaux de *Kale et al.* est présenté à la Figure 18. De manière générale, on note la présence de la bande d'étirement du Si-O-Si détectée à 1030 cm^{-1}, les vibrations CH_3 dans Si-$(CH_3)_2$ à 800 cm^{-1} et dans Si-$(CH_3)_3$ à 840 cm^{-1} , et les vibrations de asymétriques et symétriques de CH_x à ~2900 cm^{-1}.

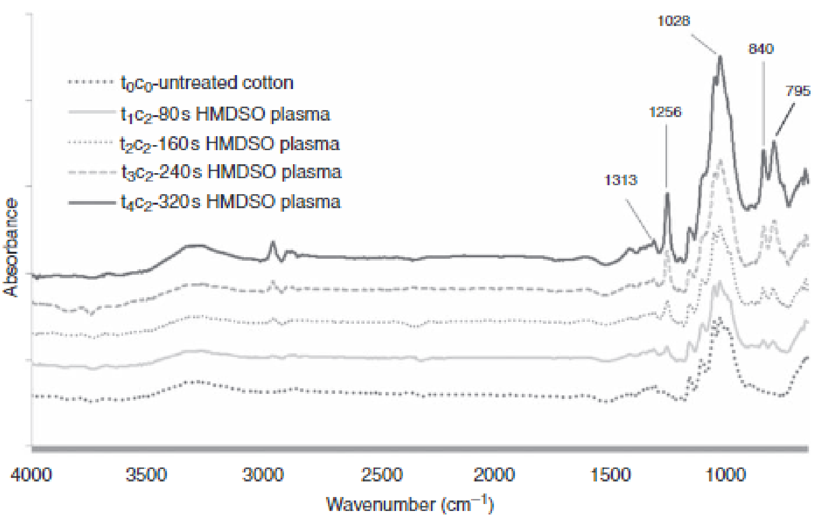


Figure 18: Spectre FTIR du coton traité par dépôt assisté par plasma d'HMDSO pour différents temps de traitements.

Dans la littérature[107,108], un degré de polymérisation est souvent défini en faisant le rapport de deux bandes d'absorption. Par exemple, le rapport $\frac{Si(CH_3)_2}{Si(CH_3)_3}$ où le dénominateur présente une bande de la molécule d'HMDSO et le numérateur une bande visible uniquement suite à la perte d'un groupe méthyl signe de la fragmentation. La polymérisation d'HMDSO peut être modifiée de plusieurs manières, par exemple, *O'neil et al.* [109] et *Siliprandi et al.*[107], obtiennent des couches moins polymérisées en augmentant la quantité de monomère injectée dans le plasma. A faibles concentrations, le précurseur est fragmenté, mais le niveau de réticulation est important.

Comme le montre la Figure 19, il existe plusieurs points de liaison inter-chaines, notamment au niveau de liaisons Si-CH2-SI, Si-Si ou Si-O-Si. Au contraire, lorsque la concentration d'HMDSO est trop élevée, l'énergie délivré par la décharge ne semble pas suffisante pour polymériser fortement le monomère. Dans ces conditions, une couche visqueuse et faiblement réticulée peut être obtenue.

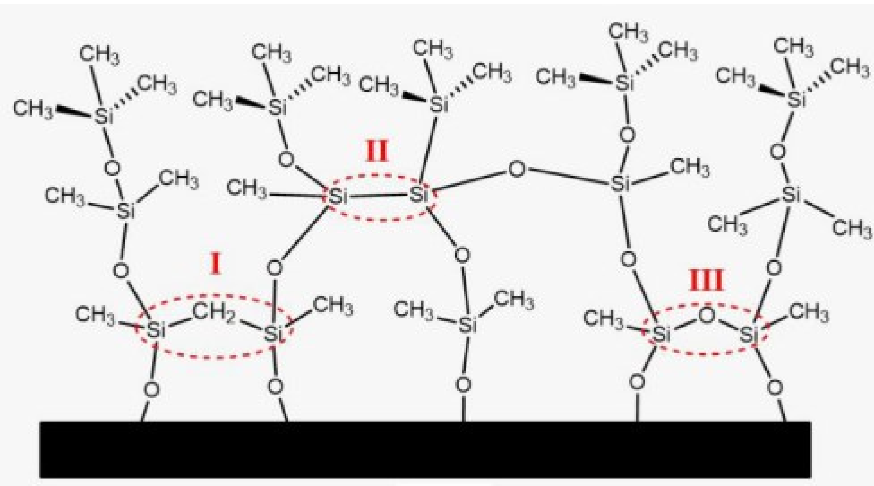


Figure 19: Représentation de la structure d'un du film polymérisé par plasma à partir d'HMDSO [110]

Le nombre d'onde d'absorbance des bandes peut également renseigner sur le degré de polymérisation du dépôt. En effet, une altération de la structure inorganique comme l'angle et la longueur de la liaison changent la fréquence de vibration [104,111].

I.3.3 Dynamique d'incorporation de nanoparticules

a. Atomisation, agrégation et chargement

Tel que discuté précédemment, une approche particulièrement séduisante pour le dépôt de couches minces nanocomposites avec inclusions particulaires consiste à coupler la PECVD décrite à la section précédente avec une injection de solutions de nanoparticules formées *ex-situ*. Pour injecter les nanoparticules à partir d'une solution colloïdale, il est nécessaire d'atomiser la solution (souvent à l'aide d'un nébuliseur). Le nébuliseur va ainsi venir former un aérosol, c'est à dire de petites gouttelettes composées du solvant et des nanoparticules. Afin de supprimer le

solvant, les gouttelettes peuvent être séchées dans une ligne de gaz chauffée (*spray-drying method*). Profili *et al.* [87] ont analysé l'atomisation d'une solution colloïdale dans une DBD. Au-delà de l'agglomération primaire pouvant se produire dans la suspension, la Figure 20 révèle un second processus d'agglomération pouvant survenir lors de l'atomisation. Ce type d'agglomération pendant le séchage par atomisation est bien connu dans la littérature sous le nom d'auto-assemblage [112]. Les nanoparticules présentes dans la gouttelette vont ainsi s'assembler lors de l'évaporation du solvant ; les résultats de cet auto-assemblage sont directement liés à la nature des forces mises en jeu et dépendent de plusieurs paramètres dont la charge et la taille de la gouttelette ainsi que la charge et la taille des nanoparticules.

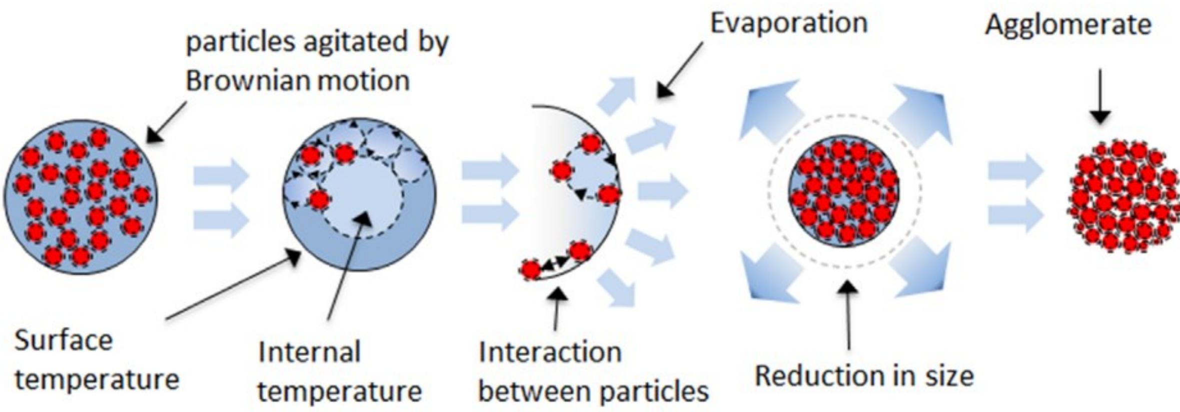


Figure 20: Schéma du processus d'agglomération lors de l'atomisation [87]

En effet, en s'appuyant sur les travaux de Profili *et al.* [113], on note que les nanoparticules obtenues après atomisation présentent une charge. La Figure 21 montre une différence notable du nombre de particules récoltées sur l'électrode inférieure d'un réacteur DBD longtemps après l'extinction de la décharge par rapport à immédiatement après l'extinction de la décharge. Ce phénomène peut être expliqué par la présence d'un champ électrique rémanent sur les diélectriques. Or, si les nanoparticules réagissent à un champ électrique rémanent, cela implique nécessairement qu'elles soient chargées.

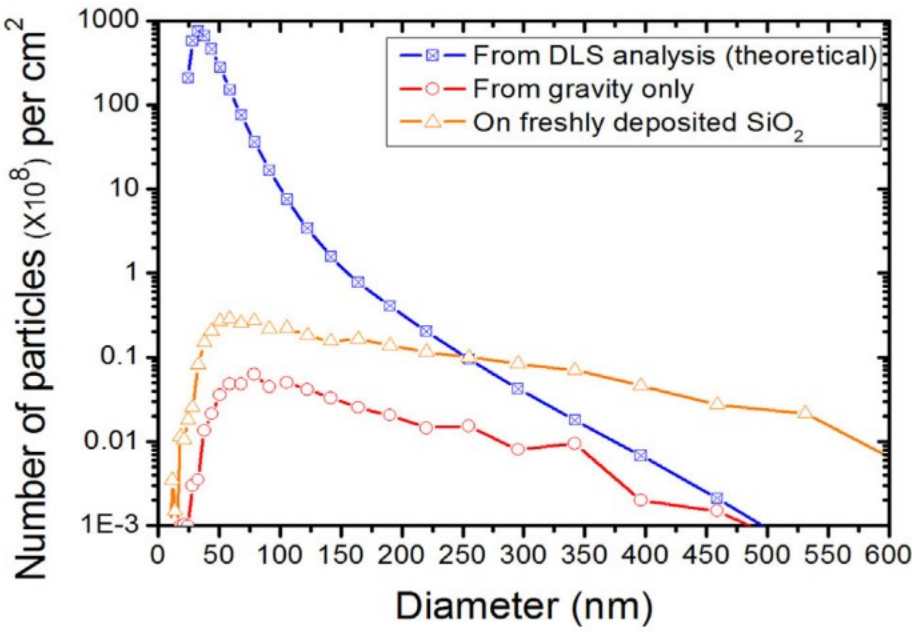


Figure 21: Distribution en taille des nanoparticules par cm² collecté sur substrat par gravité (rouge) et à la suite d'une décharge (orange) analysée par SEM. Comparé à la distribution en taille des nanoparticules par cm2 dans la solution colloïdale obtenue par DLS. [113]

Inspiré de ces résultats, quelques travaux [113,114] ont aussi pu montrer que le transport des nanoparticules après atomisation pouvait être sensible aux variations d'amplitude et de fréquence du champ électrique de la DBD (avec la décharge éteinte). En effet, pour des fréquences suffisamment élevées, il est possible de confiner les nanoparticules dans l'espace inter-électrodes tandis qu'à basse fréquence, le dépôt s'effectue à l'entrée de la cellule de la DBD (avec la décharge éteinte). De ce résultat, les auteurs ont conclu qu'il était possible de venir contrôler le dépôt des nanoparticules sur le substrat par modulation en fréquence du champ électrique appliqué [115]. Des conclusions similaires ont été obtenues par d'autres groupes [114].

Lorsque l'atomisation s'effectue directement dans une décharge ou dans un plasma, la situation devient toutefois plus complexe comme le montre Jidenko *et al.* [116]. En effet, en plus de la charge liée au processus d'atomisation de la suspension, les nanoparticules peuvent se charger par collection d'ions et d'électrons de la décharge ou du plasma. De manière générale, dans un plasma macroscopiquement neutre, la charge d'une nanoparticule est déterminée par l'équilibre des courants ioniques et électroniques à la surface de celle-ci. Les électrons ayant une mobilité plus élevée due à leur faible masse, les nanoparticules deviennent alors en majorité chargées

négativement. Dans les DBD, le phénomène de chargement devient plus complexe puisque les propriétés du plasma varient fortement dans le temps et dans l'espace. En plus, dans certaines conditions, par exemple dans la décharge de Townsend, la densité d'ions est largement supérieure à celle des électrons (milieu non macroscopiquement neutre). Il devient ainsi extrêmement difficile de déterminer la charge des nanoparticules avec précision. On admettra toutefois, comme à basse pression, que la charge d'une nanoparticule est proportionnelle à sa taille [116].

b. Transport des nanoparticules

Après atomisation de la suspension, il devient ensuite important de contrôler la dynamique de transport des nanoparticules dans l'espace inter-électrodes. Lorsque couplée à la cinétique de dépôt et la polymérisation de la matrice abordées dans la section précédente, il devient ainsi possible, en principe, de maîtriser la distribution spatiale des nanoparticules dans la matrice, et par conséquent, l'évolution des propriétés macroscopiques des couches minces nanocomposites pouvant être obtenues dans ce type de décharge ou de plasma. On note néanmoins très peu de travaux à ce sujet dans la littérature. Même si certains auteurs ont eu recours à ces procédés basés sur les plasmas à la pression atmosphérique pour synthétiser des couches minces nanocomposites [87,117], la physique de l'ensemble des processus mis en jeu demeure très peu documentée. Pour étudier, la dynamique de transport des nanoparticules, il est d'abord nécessaire d'établir un bilan des forces. Dans un premier temps, les nanoparticules chargées injectées dans une DBD, et donc soumises à un champ électrique oscillant subissent la force électrostatique :

$$\vec{F}_E = q_p.\vec{E}$$

Où q_p est la charge de la particule et E est l'intensité du champ électrique.

Comme tout corps sur Terre, les nanoparticules subissent également la force de gravité. Cette force, orientée vers le bas, est proportionnelle au rayon de la particule au cube :

$$\vec{F}_G = m_p.\vec{g} = \frac{4}{3}\pi r_p^3 \rho_p.\vec{g}$$

Où m_p est la masse de la particule, r_p est son rayon et ρ_p est sa densité massique. Enfin, g est l'accélération gravitationnelle.

Les nanoparticules peuvent subir des forces d'entrainement par les autres espèces du plasma que ce soit les ions (dans la direction du champ électrique) ou les neutres (dans la direction du flux de gaz). Ces forces dépendent du rayon de la nanoparticule au carré via la section efficace de collisions entre nanoparticules et particules entrainantes. Le flux de gaz crée une force d'entrainement sur les nanoparticules généralement donnée par [117]:

$$\vec{F}_{e,n} = \frac{4}{3}\pi r_p^2 n_g m_g v_{th,g}(\vec{v}_g - \vec{v}_p)$$

Où n_g est la densité du gaz, m_g est la masse des neutres, $v_{th,g}$ est la vitesse d'agitation thermique du gaz et v_g et la vitesse moyenne à laquelle est soustrait la vitesse moyenne des particules v_p.

Le mouvement des ions dans le plasma aura un effet similaire à celui des particules neutres du gaz, mais les ions, étant chargés positivement, auront deux types d'impact sur les nanoparticules chargées. Dans le premier cas, l'ion entre en collision avec la nanoparticule et lui donne une impulsion par transfert de quantité de mouvement. L'expression pour ce type de force est similaire à celle pour la force de trainée sur les nanoparticules neutres :

$$\vec{F}_{i,coll} = \pi b_c^2 n_i m_i \vec{v}_i^2$$

Où b_c est le paramètre d'impact, m_i est la masse des ions, n_i est leur densité et v_i est leur vitesse moyenne.

Dans le second cas, l'interaction coulombienne entre l'ion et la nanoparticule entraine une déflexion des ions et produit sur la nanoparticule une force qui s'exprime comme :

$$\vec{F}_{i,coul} = 4\pi b_{\pi/2}^2 T n_i m_i \vec{v}_i^2$$

Où $b_{\pi/2}$ est le paramètre d'impact pour une déflexion à 90° et T est le logarithme Coulombien qui limite la force coulombienne à $r_p \leq \lambda_D$

Enfin, une force de thermophorèse apparait lorsqu'il existe un gradient de température suffisant, par exemple, dû au chauffage d'une des électrodes [80] :

$$\vec{F}_{th} = -\frac{35}{15}\frac{r_p^2}{v_{th,g}}\left(1 + \frac{5\pi}{32}(1-\alpha_T)\right)\kappa_T \vec{\nabla} T_g$$

Où α_T est le coefficient d'accommodation thermique du gaz à la surface d'une particule, κ_T est la partie translationnelle de la conductivité thermique du gaz et $\vec{\nabla} T_g$ est le gradient de température.

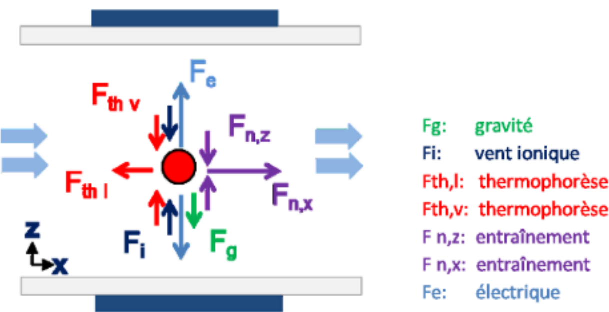


Figure 22: Schéma représentant la direction de l'ensemble des forces agissant sur une particule [118]

Chaque force décrite ici peut ainsi, en principe, agir sur la nanoparticule et donc influencer sa dynamique de transport dans la DBD. Dans le cas d'une DBD plan-plan comme celle de la Figure 13.a, l'impact des forces sur une nanoparticule est illustré à la Figure 22. Par exemple, la force de gravité est dirigée vers l'électrode inférieure du réacteur tandis que la force électrostatique est dirigée vers les deux électrodes selon la direction du champ électrique oscillant dans le cycle de la tension appliquée. Quant à la force ionique, elle a pour action de confiner les nanoparticules au centre du réacteur. Afin d'amener la particule vers le substrat et donc de créer une couche mince, une force résultante dirigée vers ce dernier est primordiale.

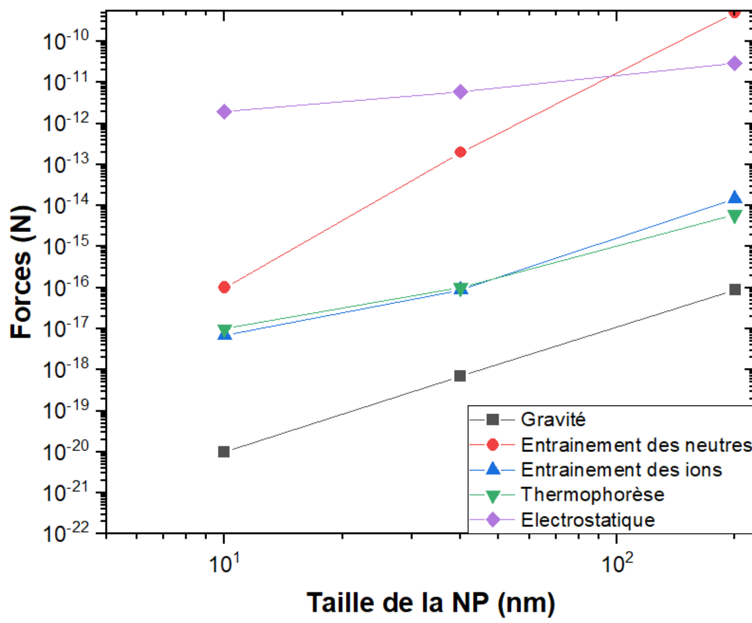


Figure 23: Valeur des forces en N pour différentes tailles de particules (d'après les valeurs de [118] dans une décharge de Townsend à pression atmosphérique)

Nous avons calculé l'amplitude de l'ensemble de ces forces en fonction de la taille des nanoparticules dans une DBD à la pression atmosphérique. Les conditions sont les mêmes que celles décrites dans l'article de Profili *et al.* [113]. Les résultats sont présentés à la Figure 23. On note que, dans ces conditions, la force électrostatique domine pour des particules de taille inférieure à 100 nm. Pour des particules de diamètre supérieur à 100 nm, en présence d'un débit de gaz, c'est la force d'entrainement des neutres qui domine. L'entrainement des ions et la thermophorèse semblent être des forces négligeables dans les conditions typiques des DBD et la gravité devient une force dominante uniquement pour des particules de l'ordre du micromètre. Selon la taille de nanoparticules désirées dans la couche mince nanocomposite, il devient alors judicieux de modifier l'une ou l'autre des forces. Pour le dépôt de nanoparticules de TiO_2 inférieures à 100 nm, Profili *et al.* ont donc mis au point une modulation en fréquence du champ électrique appliqué pour ajuster finement la force électrostatique et donc la distribution spatiale des nanoparticules à la surface du substrat [115]. Ils ont ainsi pu rapporter des dépôts homogènes sur toute la surface du substrat, sans avoir recours au défilement. Des conclusions similaires ont été obtenues par *Brunet et al.* [114]. Si l'application nécessite des nanoparticules de plus grandes

dimensions, il faudrait alors se concentrer sur l'écoulement des neutres et donc sur l'hydrodynamique du gaz plasmagène.

c. Présence de gouttelettes

Selon les conditions opératoires, les nanoparticules et /ou le précurseur de la matrice peut aussi se transporter dans la décharge sous forme de gouttelettes. Ce type de plasma en présence de gouttelettes est connu sous le nom de "misty plasma" dans la littérature [119,120]. Dans ce cas, plusieurs interactions similaires à l'interaction plasma-nanoparticules sont décrites[121]. Par exemple, la goutte, tout comme la nanoparticule, peut se charger. Elle peut donc devenir sujette à la force électrostatique. Cependant, de nombreux autres mécanismes peuvent intervenir. Tout d'abord, lorsque chauffée dans la décharge, elle peut s'évaporer, conduisant à une libération contrôlée de vapeur au cours du transport. D'autre part, étant donné leurs dimensions micro- ou millimétriques, au-delà d'une certaine charge, la goutte peut se dissocier en plusieurs gouttes de taille inférieure, selon un phénomène de rupture électrostatique. Cette séparation est principalement due aux forces de fission coulombienne permettant la rupture de la goutte au-delà d'une certaine charge seuil définie par le critère de Rayleigh[119]. La combinaison de ces deux phénomènes (c-à-d chargement et évaporation) contribue à une forte évolution de la taille de la goutte comme étudiée dans le cas des jets électrostatiques [122,123]. La Figure 24 représente des exemples de la littérature.

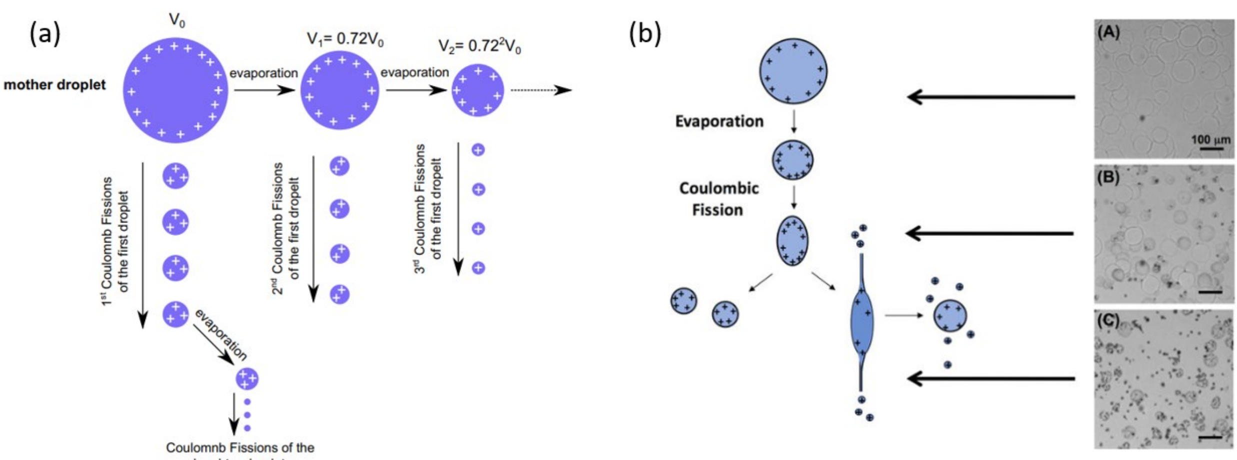


Figure 24: a) Schéma de l'évaporation et de la fission coulombienne subséquence [123] et b) effet de l'évaporation et de la fission coulombienne sur le relief du dépôt [122]

Quelques études ont été faites dans le cas des plasmas à basse pression afin de modéliser l'évaporation des gouttes. C'est le cas des travaux menés par *Ogawa et al.*[124] qui prennent en compte plusieurs phénomènes tels que la condensation, la radiation, la recombinaison, etc. pour calculer un temps d'évaporation de la goutte en fonction de son rayon. Ainsi, une goutte d'hexane d'un rayon de 20 µm mettra 3 sec pour s'évaporer totalement dans un environnement sans plasma contre 0.5 avec plasma. Cependant, ce modèle a été développé pour un plasma de basse pression et les données obtenues ne peuvent être valables dans les plasmas à pression atmosphérique étant donné le passage en milieu collisionnel. La littérature sur la physique des misty plasmas demeure donc embryonnaire, comme la soulève *Stancampiano et al.* [121].

I.4. Conclusion de chapitre

Dans ce chapitre, nous avons jeté les bases des différentes méthodes de dépôt assistées par plasma des couches minces nanocomposites à renforts particulaires. Dans les plasmas à pression réduite, ceci comprend des méthodes physiques, chimiques ou hybrides. À la pression atmosphérique, pour obtenir une meilleure souplesse au niveau des compositions des nanoparticules et de la matrice, nous avons décrit une nouvelle méthode couplant la PECVD à une injection de nanoparticules formées *ex-situ*. Au niveau de la dynamique de dépôt de la matrice, nous avons noté plusieurs lacunes dans l'état des connaissances de la physique de ces plasmas hautement réactifs. En particulier, dans plusieurs cas, il est difficile de déterminer la nature et l'impact des espèces actives impliquées dans la fragmentation des précurseurs. Par ailleurs, lorsque le précurseur est injecté dans le réacteur par l'atomisation d'une solution colloïdale, nous avons noté une agglomération importante des nanoparticules pouvant être expliquée par des effets d'auto-assemblage [112]. De plus, nous avons décrit l'ensemble des forces impliquées dans la dynamique de transport du précurseur. Bien que ces facteurs jouent des rôles cruciaux sur l'évolution des propriétés macroscopiques des couches minces multifonctionnelles pouvant être obtenues dans ce type de réacteurs, la littérature correspondante demeure peu abondante de sorte que plusieurs procédés restent sans aucun doute très loin d'être optimisés.

Dans ce travail de doctorat, une étude fondamentale de pointe sur la physique des DBD destinées au dépôt de couches minces nanocomposites avec injection pulsée de précurseurs est réalisée. Afin de créer des nanoparticules de petites tailles (<10nm) tout en évitant l'agglomération et la manipulation des nanoparticules, nous utilisons un réacteur-injecteur récemment mis au point dans les laboratoires de l'Université de Toulouse [14]. Dans ce système, les nanoparticules sont synthétisées directement à l'intérieur du réacteur-injecteur par la réaction d'un précurseur de nanoparticules avec un autre agent réactif. Afin de permettre un temps de synthèse des nanoparticules, le réacteur-injecteur utilisé fonctionne en deux temps et donc en injection pulsée. Cette injection pulsée couplée à un procédé de dépôt à pression atmosphérique est un vrai enjeu tant au niveau du fonctionnement de la décharge qu'au niveau de la dynamique de dépôt. Le travail suivant a alors pour but de répondre à la plupart des verrous scientifiques de ce nouveau dispositif de synthèse de couches minces nanocomposites. Pour cela, le réacteur-injecteur sera utilisé avec synthèse de nanoparticules (DLRI) mais également en injection directe de liquide (DLI). Auparavant, la première étape de ce travail consiste à étudier le fonctionnement de la DBD avec une injection pulsée de gaz.

Chapitre II. Fonctionnement d’une décharge à barrière diélectrique avec injection pulsée de gaz

Comme démontré dans le chapitre précédent, la synthèse de couches minces assistée par plasma à la pression atmosphérique présente un réel intérêt. Le développement d’une telle technologie couplé à une méthode d’injection sécuritaire telle que le réacteur-injecteur est d’autant plus intéressante. Cependant, ce réacteur fonctionne avec une injection pulsée. Ce chapitre se veut un travail préliminaire afin de comprendre le fonctionnement d’un plasma à la pression atmosphérique, ici la décharge à barrière diélectrique, avec une injection pulsée de gaz. Ainsi, dans un premier temps, le montage expérimental utilisé est décrit. Ensuite, les différentes méthodes de caractérisation utilisées pour analyser les effets de l’injection pulsée gaz, soit la caractérisation électrique et la spectroscopie d’émission optique, sont décrites. Enfin, les résultats apportés par cette étude sont reportés dans un article intitulé « Influence of pulsed gas injections on the stability of Townsend dielectric barrier discharges in nitrogen at atmospheric pressure » récemment publié dans *Journal of Physics D : Applied Physics* (MS# 131703).

II.1. Montage expérimental

La Figure 25 représente un schéma du réacteur utilisé dans ce chapitre. L’enceinte est un cylindre en acier inoxydable auquel sont ajoutés plusieurs canaux isolés permettant d’effectuer les connexions électriques ainsi que de connecter le système d’injection de gaz. Chaque partie du réacteur est décrite indépendamment dans les paragraphes suivants.

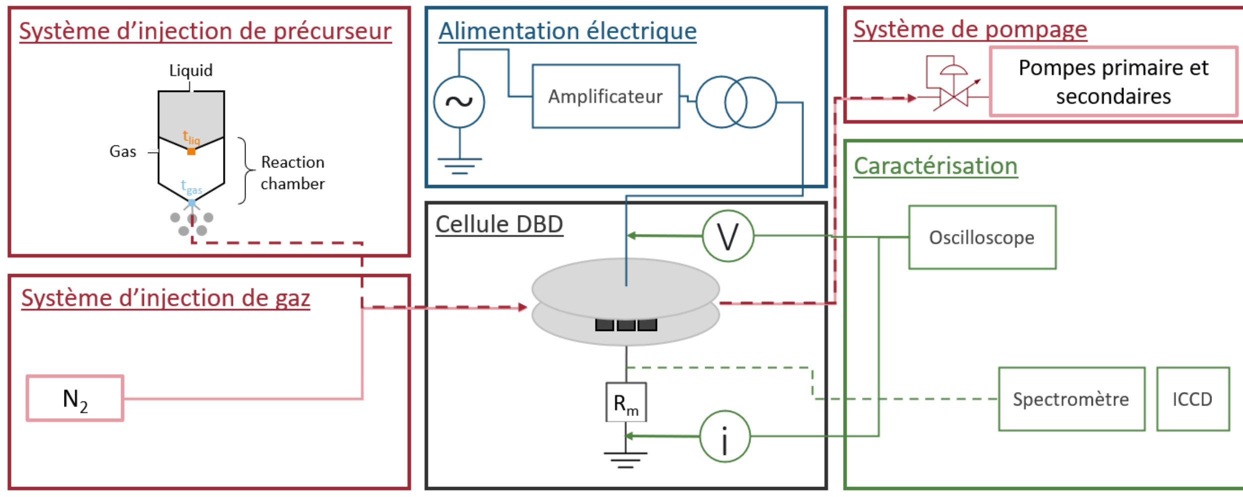


Figure 25: Schéma du procédé expérimental (adapté depuis [109])

II.1.1 Cellule de décharge

Cette enceinte de décharge a été utilisée et décrites dans des travaux précédents [92,115]. L'accès à la cellule de décharge se fait par ouverture complète du couvercle supérieur. La décharge est initiée entre deux alumines (Al_2O_3) servant de diélectriques. Les électrodes sont peintes à la peinture d'argent sur chacune des alumines. L'électrode supérieure (connectée à la haute tension) est un carré de 3x3cm^2. L'électrode inférieure (connectée à la masse) est quant à elle fractionnée en 3 rectangles égaux séparés de 400 µm perpendiculairement au flux de gaz. Une fragmentation des électrodes permet ainsi une résolution spatiale des mesures électriques. Les deux alumines peintes sont placées en vis-à-vis dans l'enceinte. Un gap de 1 mm est imposé entre les deux alumines à l'aide de demi-cercle de quartz.

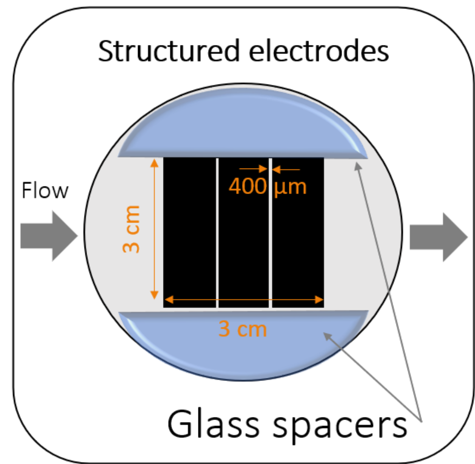


Figure 26: Schéma de l'électrode fractionnée

II.1.2 Système d'alimentation électrique

Une alimentation fournissant un signal de tension sinusoïdal à basse fréquence (1 kHz) est connectée à un amplificateur de puissance linéaire dont la sortie est reliée à l'enroulement primaire d'un transformateur élévateur. La cellule de décharge est reliée à l'enroulement secondaire du transformateur. Une tension de 13 kV crête à crête est appliquée aux électrodes et est mesurée par une sonde haute tension (Tektronix P6015A). Les sorties des trois bandes de l'électrode de masse sont reliées à trois résistances de 330 Ω pour recueillir les courants correspondants. La tension appliquée et les courants mesurés de chaque zone sont affichés sur un oscilloscope (Teledyne Lecroy WaveSurfer 3024, bande passante de 200 MHz).

II.1.3 Système de gaz

a. Système d'injection continue de gaz

L'enceinte est remplie jusqu'à la pression atmosphérique par un flux continu de N_2 (pureté 99,999% Air Liquide Alphagaz 1) à 1 L.min^{-1}. La bouteille de gaz est reliée à plusieurs vannes permettant de faire passer le gaz à travers un débitmètre ainsi qu'un régulateur de débit massique afin de contrôler le débit injecté dans la cellule de décharge.

b. Système d’injection pulsée de gaz

L'injection pulsée de gaz est faite à l'aide d'un système d'injection Atokit commercialisé par Kemstream [10]. Les impulsions de gaz sont conduites à la cellule de décharge par un tuyau en acier inoxydable de 60 cm de long et de 4 mm de diamètre intérieur. Le gaz pulsé est choisi identique au gaz de décharge injecté de manière continue (N_2, pureté 99,999%). Plusieurs paramètres d'injection peuvent être contrôlés à l'aide du système d’injection de Kemstream, notamment le temps d'ouverture du gaz (durée d'impulsion), la fréquence d'injection des impulsions et la pression du gaz en amont du dispositif d'injection pulsée.

c. Système de pompage de gaz

Afin de garder l’enceinte à un pression de 1 atm avec l’injection pulsée et continue, l’enceinte est reliée à un système de pompage primaire et secondaire. Avant chaque expérience l’enceinte est pompée jusqu’à une pression de 10^{-3} mbar pour éviter toute contamination. Par la suite, l’enceinte est remplie à 1 atm puis est maintenue à cette pression grâce à une valve auto-régulée (MKS 248D) placée en amont des pompes.

II.2. Méthodes de caractérisation

II.2.1 Caractérisation électrique

Comme indiqué précédemment, les sorties des trois bandes de l'électrode de masse ainsi que celle de la sonde de tension sont affichées sur un oscilloscope (Teledyne Lecroy WaveSurfer 3024, bande passante de 200 MHz). La décharge à barrière diélectrique peut fonctionner soit dans un régime homogène, soit filamentaire. En fonction du régime dans lequel la décharge se trouve, le courant présente des caractéristiques différentes présentées à la Figure 14. En fonction des conditions, la décharge à barrière diélectrique homogène peut se déstabiliser et transiter vers un régime filamentaire. Suite à l’apparition de micro-décharges dans un régime filamentaire, la valeur du courant est généralement plus élevée qu'en homogène. Cela se traduit inévitablement par une augmentation très rapide du courant et dans la majorité des cas par une saturation de la voie d'entrée de l'oscilloscope qui été réglé pour visualiser le courant homogène. Ainsi, la saturation du courant est synonyme de passage en filamentaire.

Le calcul de la puissance dissipée dans la décharge en régime homogène peut également être fait en utilisant l'équation suivante :

$$P(t) = \frac{1}{T}\int_0^T u(t).\, i(t)dt \qquad (1)$$

Où T est la période de la tension appliquée en seconde, u(t) et i(t) sont les signaux de la tension et du courant mesurés, respectivement. Dans le cas d'une décharge filamentaire, l'augmentation très rapide et souvent la saturation du courant induit une erreur d'échantillonnage du courant, de sorte que calcul de la puissance est impossible. Cependant, en mesurant la charge aux bornes d'un condensateur placé à la place de la résistance, la saturation du courant est évitée et il est possible d'obtenir la puissance grâce à la méthode de Lissajous [125].

II.2.2 Spectroscopie d'émission optique

La spectroscopie d'émission optique est un dispositif très utilisé permettant de caractériser la décharge de manière non intrusive. L'intensité d'une raie d'émission entre deux niveaux i et j est exprimée de la manière suivante (milieu optiquement mince) :

$$I_{ij} = f(\lambda_{ij})A_{ij}\nu_{ij}n_i \qquad (2)$$

Où f est la fonction de réponse de l'appareil à la longueur d'onde λ_{ij}, A_{ij} est la probabilité de transition pour l'émission spontanée, ν_{ij}est la fréquence de transition et n_i est la densité de particules dans le niveau excité. Le spectre classique d'une décharge à barrière diélectrique dans l'azote est présenté à la Figure 27.

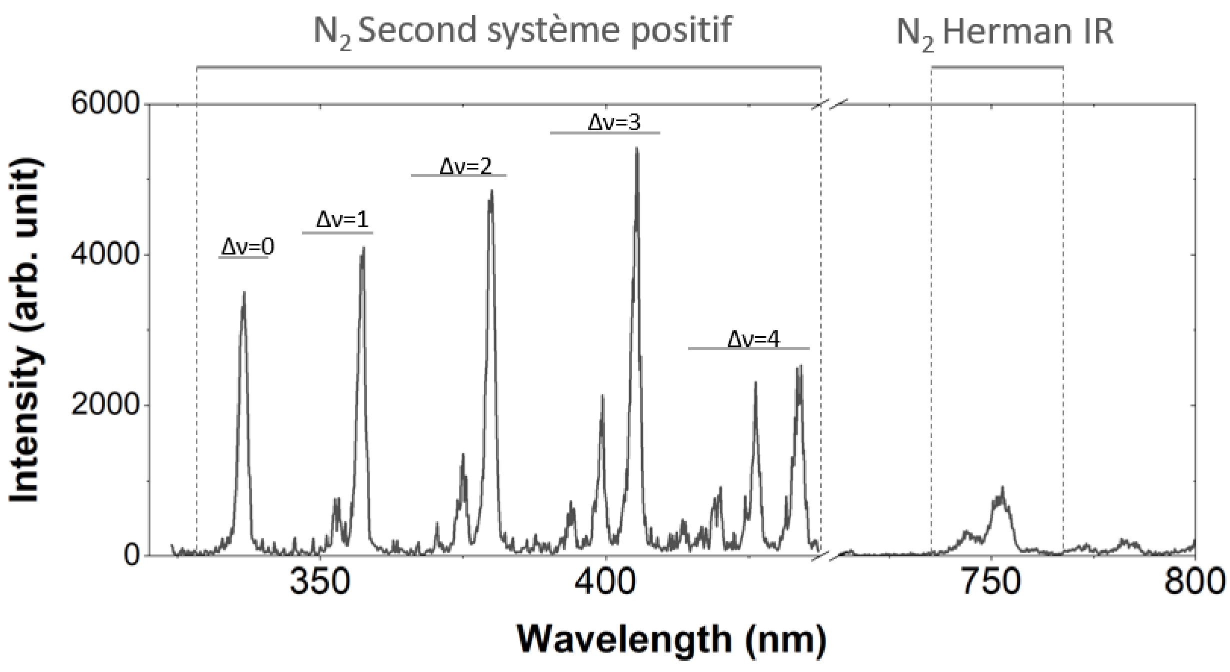


Figure 27: Spectre de bandes ro-vibrationnelles dans une DBD d'azote

L'émission observée est sous la forme de bandes plutôt que de raies étant donnée l'utilisation d'un gaz moléculaire tel que N_2. Plusieurs systèmes sont observables dont les bandes du second système positif (SPS) entre 300 et 400 nm, ainsi que celles du Herman Infrarouge (HIR) centré à 750 nm. Lors de la prise de donnée, un filtre passe-bas à 750 nm a été ajouté pour observer le HIR sans le deuxième ordre de diffraction du SPS. Les deux bandes observées sont principalement peuplées par les réactions suivantes pour le SPS et le HIR respectivement [90]:

$$N_2(X) + e^- \rightarrow N_2(C) + e^- \quad (3)$$

$$N_2(A) + N_2(A) \rightarrow N_2(C'') + N_2(X) \quad (4)$$

Il est à noter ici que l'émission d'un système est reliée à la densité d'espèce $I_{ij} = f(\lambda_{ij}) A_{ij} \nu_{ij} n_i$ (2) régulée par la différence entre les gains et les pertes de ce niveau (équation de conservation des particules). Ainsi la densité d'une espèce s'écrit comme suit :

$$\frac{dn_i}{dt} = G_i - P_i \quad (5)$$

Par exemple, pour l'intensité du $N_2(C)$, nous savons qu'il est peuplé par impact électronique sur le fondamental, ceci est un terme de gain. La première source de perte de cet état va être la désexcitation radiative du niveau $N_2(C)$ vers un niveau $N_2(B)$ en émettant un photon d'énergie $\frac{hc}{\lambda}$ dont la longueur d'onde dépend de la différence d'énergie entre les deux niveaux. Dans un plasma à pression atmosphérique, la désexcitation collisionnelle par les autres espèces du gaz ambiant N_2 et/ou O_2 est également une source de perte non négligeable. Ainsi, l'intensité de l'émission optique d'un niveau va dépendre du taux de création du niveau via les processus collisionnels de l'énergie du photon multiplié par l'efficacité optique qui quantifie la probabilité d'émission spontanée versus la probabilité de désexcitation collisionnelle.

II.3. (Article) Influence of pulsed gas injections on the stability of Townsend dielectric barrier discharges in nitrogen at atmospheric pressure

Influence of pulsed gas injections on the stability of Townsend dielectric barrier discharges in nitrogen at atmospheric pressure

L. Cacot [1,3], G. Carnide [1,2], M. L. Kahn [2], H. Caquineau [1], R. Clergereaux [1],

N. Naudé [1*] and L. Stafford [3†]

[1]LAPLACE, Université de Toulouse, CNRS, INPT, UPS, Toulouse, France

[2]LCC, CNRS (UPR 8241), Université de Toulouse, 205 route de Narbonne, 31077 Toulouse Cedex 4, France

[3]Département de physique, Université de Montréal, 1375 ave Thérèse-Lavoie-Roux, Montréal, QC, H2V 0B3, Canada

Abstract

This work investigates the effects of pulsed nitrogen gas injections on the stability of Townsend dielectric barrier discharges operated in continuous nitrogen gas flows at atmospheric pressure. For single-pulse injections with pulse durations lower than the continuous gas residence time (~50 ms), current-voltage characteristics reveal homogeneous discharges with a single current peak per half-cycle of the applied voltage. However, a sudden decrease of the discharge power over time combined with a temporary transition from homogeneous to filamentary discharge is observed for longer pulses at fixed pulsed gas flows and for higher pulsed gas flows at fixed pulse duration. In addition, for multiple pulsed gas injections with repetition frequencies between 0.1 and 10 Hz,

* Electronic mail: nicolas.naude@laplace.univ-tlse.fr

† Electronic mail: luc.stafford@umontreal.ca

discharge destabilisation increases with the number of pulses. Time-resolved optical emission spectroscopy reveals that, over the single pulse time scale, temporal variations of the emission intensities are longer than the expected residence times of the continuous and pulsed gas flows. Furthermore, a rise of oxygen impurities can be seen over both single and multiple-pulses time scales. Two-dimensional gas flow simulations reveal that pulsed injections introduce sharp and narrow temporal gas velocity profiles over the range of experimental conditions investigated, with no cumulative effects in the discharge cell from one pulse to the other. However, pulsed operation introduces significant changes in the neutral gas composition with time scales comparable to those revealed by electrical and optical diagnostics. In such conditions, the outgassing of impurities adsorbed on surfaces located upstream of the discharge cell plays a vital role in Townsend discharges' physics and characteristics.

Keywords: Dielectric Barrier Discharge, Townsend discharges, Current-voltage characteristics, Optical Emission Spectroscopy, Pulsed gas injection

1. Introduction

Non-equilibrium plasmas are routinely used in materials processing, for example, for thin film deposition and etching. For such applications, carrier and reactive gases are typically continuously injected in the plasma reactor [1,2]. For selected applications, however, pulsed gas injections are more appropriate to ensure the right set of populations of plasma-generated species [3–5]. For example, pulsed precursor injections are implemented when an additional control over deposition rate and nanostructure is required. For instance, AlO_x thin film in a pulsed injection of $Al(CH_3)_3$ in an oxygen plasma tune from low-density after precursor injection (*i.e.* when the precursor concentration is high) to dense structure shortly after the injection (*i.e* when the precursor concentration is low) due to the impingement of plasma-generated ions and reactive oxygen species on the substrate surface [6]. In hybrid plasma deposition processes relying on plasma-enhanced chemical deposition (PECVD) and sputtering, pulsed precursor injections can prevent target poisoning and can be used for the deposition of multifunctional, nanocomposite coatings [7,8]. The pulsed carrier gas injections can also be synchronized with a pulsed power supply for discharge ignition and maintenance to precisely control the precursor dissociation and plasma-surface interactions during PECVD [9]. Nowadays, pulsed injections of the carrier, precursor, and reactive gases are also used in atomic layer deposition (ALD) and atomic layer etching (ALE) processes [10–12].

Compared to continuous gas flows, pulsed gas flows inevitably lead to temporal variations of the fundamental plasma properties. For example, in Tore Supra reactor used for fusion applications, the response of the scrape-off layer to a supersonic pulsed gas

injection has shown an increase in the plasma density and a decrease in plasma temperature before returning to equilibrium after about 10 ms; in addition, the extent of such variations is proportional to the total amount of gas injected into the plasma [13]. In a capacitively-coupled, radio-frequency (RF) argon plasma at low pressure, Sadek et al. [14] have reported cyclic evolutions of the electron temperature (T_e) and electron density (n_e) following the pulsed injection of neutral gas density in an argon plasma. Cyclic evolutions of T_e and n_e have also been reported by Garofano et al. [15] with pulsed injection of hexamethyldisiloxane (HMDSO) in an argon plasma. In such conditions, variations of T_e and n_e are observed over multiple time scales: one linked to the pulsed injection of HMDSO in the argon plasma and another due to the successive formation and disappearance of nanoparticles in the dusty plasma [16,17].

The effect of airflow on the space-time distribution of filaments in dielectric barrier discharge (DBD) at atmospheric pressure has also been investigated [18]. It is found that modification of the gas flow rate changes the breakdown positions and morphology of discharge filaments, a feature linked to the combined effect of electric field and airflow on particle distribution [19,20]. While the filamentary regime of DBDs is more common, there has been significant interest in the so-called "homogeneous" regime of DBDs characterized by the absence of micro-discharges and a relatively spatially homogeneous light emission over the whole inter-electrode gap [21,22]. Of note, such micro-discharges in the filamentary regime of DBDs imply high-energy input localized over small surface areas such that their presence can be highly problematic for materials processing applications [23,24]. On the other hand, homogeneous discharges can typically be obtained through

judicious control of the voltage and current waveforms and the choice of the appropriate carrier and reactive gases [25].

A handful of studies have reported the development and use of homogeneous DBDs for advanced surface engineering applications (see, for example, [26–35]). However, most of them implement continuous gas flows (carrier and precursor gases). This work aims to examine the effects of pulsed gas injections on the stability of homogeneous DBDs operated with a continuous laminar gas flow. To study the disturbances related to a pulsed injection, experiments are carried out with the injection of carrier gas only, without precursors. The experiments are done in the specific case of a low-density Townsend discharge obtained in a plane-to-plane configuration with N_2 for both the continuous and pulsed gas injections. As reported by many authors, this Townsend discharge is typically characterized by ion density ~10^{10} cm^{-3}, electron density ~10^{7} cm $^{-3}$, electron temperature ~5 eV, neutral gas temperature ~300 K, and power density in the ~0.1-1 W.cm^{-2} [21,22]. Such Townsend discharges are relevant for the deposition of functional, nanostructured coatings on a variety of surfaces, including heat-sensitive materials [26–29,31–34,36]. Depending on the pulsed gas injection conditions, spatially-resolved current-voltage characteristics and time-resolved optical emission spectroscopy measurements reveal peculiar discharge behaviors following single and multiple pulsed gas injections.

2. Experimental set-up and diagnostics

The experimental setup used in this work was described in detail elsewhere [29,31]. The plane-to-plane DBD cell is housed in an enclosed metallic chamber (volume below 100 cm^3) to carry out experiments in a controlled pressure and atmosphere. As shown in Figure 1 (a), the gas pipes (continuous and pulsed flows, see below) and DBD cell are connected in a gas mixing chamber. Downstream of the DBD, the system is linked to the vacuum system. Prior to each experiment, the chamber is pumped down to a pressure of 10^{-3} mbar to reduce any contamination. The gas gap is then filled up to atmospheric pressure by a continuous flow of N_2 (99.999% purity) at 1 $L.min^{-1}$. The discharge cell consists of two parallel alumina plates separated by a 1 mm gap. One side of alumina plates is painted with a 3 cm×3 cm conductive silver paste acting as a metallic electrode. To collect spatially resolved electrical measurements along the gas flow lines, the ground electrode is formed of three equal-size metalized strips; this feature is shown in Figure 1 (a) [37]. Here, the middle strip is separated by 400 µm from its neighbors.

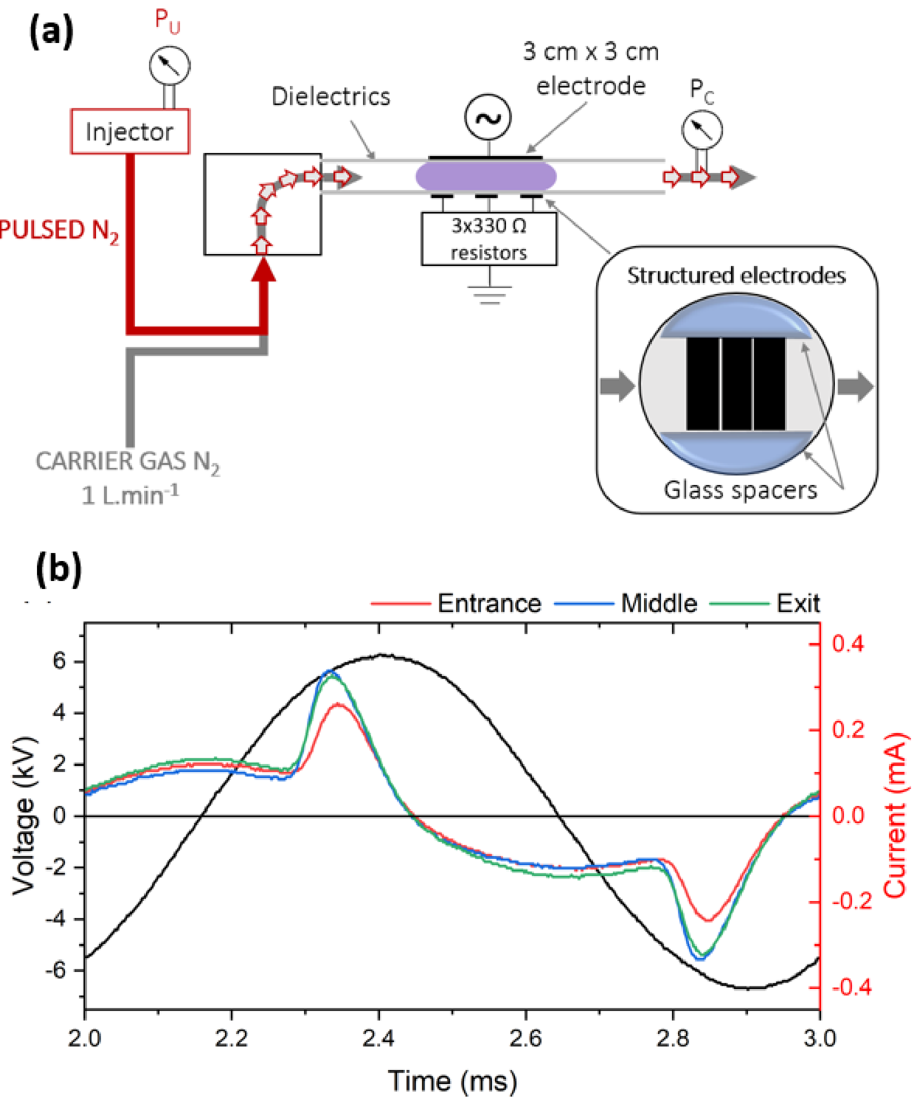


Figure 1: (a) Schematics of the experimental set-up with the multi-strip ground electrode for spatially-resolved electrical measurements; upstream of the DBD cell, the gas pipes for continuous and pulsed nitrogen gas flows arrive in a mixing chamber, (b) typical current-voltage characteristics of a Townsend discharge in N_2 at 1 kHz with a continuous gas flow.

A power supply providing a low-frequency sinusoidal voltage signal (1 kHz) is connected to a linear power amplifier whose output is linked to the primary winding of a step-up transformer. The discharge cell is connected to the secondary winding of the

transformer. A 13 kV peak-to-peak voltage is applied to the electrodes and is measured by a high-voltage probe (Tektronix P6015A). The outputs of the three strips of the ground electrode are connected to three 330 Ω resistors to gather the corresponding currents. The applied voltage and measured currents of each zone are displayed on an oscilloscope (Teledyne Lecroy WaveSurfer 3024, 200 MHz bandwidth).

Typical current-voltage characteristics of the Townsend discharge in N_2 at atmospheric pressure are presented in Figure 1 (b). Two specific features can be seen for all zones: i) the sinusoidal portion linked to the displacement current and thus to time variations of the applied voltage, and ii) the broad peak associated to the discharge current in a homogeneous Townsend discharge [38–40]. Here, current densities in each zone are in the mA/cm^2 range, which is consistent with other studies of low-frequency Townsend DBD [21,22]. To obtain a homogeneous discharge rather than a filamentary discharge formed of narrow discharge channels randomly distributed in time and space [41], a Townsend (rather than streamer) breakdown is required [21]. This condition implies a preionization of the gas but also a discharge ionization slow enough to avoid a fast avalanche development. This can be achieved through the presence of long-lived species from one half-cycle of the applied voltage to the other; this effect is commonly referred to as the "memory effect". In the specific case of N_2 discharges, long-lived metastable $N_2(A)$ states are not only involved in volume Penning ionization at low electric fields [42], but they can also induce secondary electron emission following their interaction with charged dielectric surfaces [43]. Over the range of experimental conditions examined, the very first

discharges are typically filamentary and then become homogeneous due to the onset of memory effects linked to the formation of long-lived metastable $N_2(A)$ states [42,44].

In addition to the continuous gas flow, pulsed gas injection is realized using an Atokit injection system commercialized by Kemstream. The gas pulses are led to the discharge cell through a 60 cm long stainless-steel pipe with a 4 mm inner diameter. The pulsed gas is chosen identical to the continuous discharge gas (N_2, 99.999% purity). Several injection parameters can be controlled, including the gas opening time (pulse duration), the pulse injection frequency, and the gas pressure upstream of the pulsed injection device (upstream pressure, P_U, Figure 1(a)). To maintain atmospheric-pressure conditions with both the continuous and pulsed gas flows, the pressure in the plasma chamber (P_C) recorded at the output of the DBD cell is set to atmospheric pressure using a controlled valve (MKS 248D) placed upstream of the pumping system (see Figure 1(c)). Here, the applied voltage is synchronized with the pulsed gas injection using the Transistor-Transistor-Logic (TTL) output of the injection control unit.

To determine the total amount of gas injected per pulse, the chamber pressure (P_C) is recorded without the continuous gas flow, and the inlet valve of the pumping system closed (see Figure 1(a)). The corresponding pressure rise after each pulse is shown in Figure 2(a) for different gas opening time values and upstream pressure values.

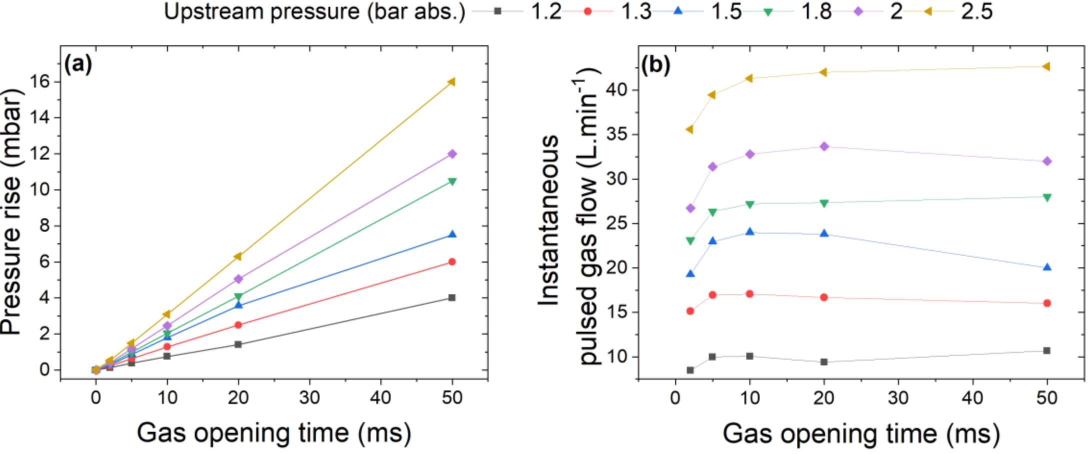


Figure 2: (a) Pressure variation (ΔP) inside the closed chamber as a function of the gas opening time (t_{gas}) for various upstream pressures (P_U). (b) Instantaneous pulsed gas flow (Q) as a function of gas opening time for various upstream pressures (P_U). In (a) and (b), lines are to guide the eye only.

As shown in Figure 2(a), the pressure rise increases linearly with the gas opening time. In addition, the rate of increase is steeper for the large upstream pressures due to the largest pressure gradient between the pulse injector and the chamber. Based on these results, the instantaneous gas flow Q during each pulse can be defined as

$$Q(L.s^{-1}) = A\frac{\Delta p\,(mbar)}{t_{gas}(s)} \qquad (1)$$

where Δp and t_{gas} are the pressure variation and the gas opening time, respectively. By recording the pressure rise as a function of time inside the closed chamber with a known continuous gas flow, a calibration curve (not shown) can be obtained to find the constant A ($L.mbar^{-1}$). The corresponding instantaneous gas flow for each pulse are presented in Figure 2(b) for various gas opening times and upstream pressures. For a fixed P_U, Figure 2(b) shows that Q remains constant regardless of the gas opening time: this confirms that

the quantity of gas injected during the gas opening time only depends on the upstream pressure. For the short gas opening times (5 ms and below), the opening and closing times of the valve inside the injection control unit become comparable to the injection time. Hence, in such cases, slightly lower Q values are observed in Figure 2(b).

Optical emission spectroscopy (OES) measurements are realized using an optical fiber with the tip placed along the middle portion of the discharge. The signal is transferred to a high-resolution monochromator (Acton SP-2500) equipped with an intensified charged coupled device (iCCD) camera (Princeton Instruments PI-MAX3). OES measurements are synchronized with the pulse injections using the TTL output of the injection control unit. A typical OES spectrum of the Townsend discharge in N_2 at atmospheric pressure is displayed in Figure 3 (same conditions as in Figure 1 (b)).

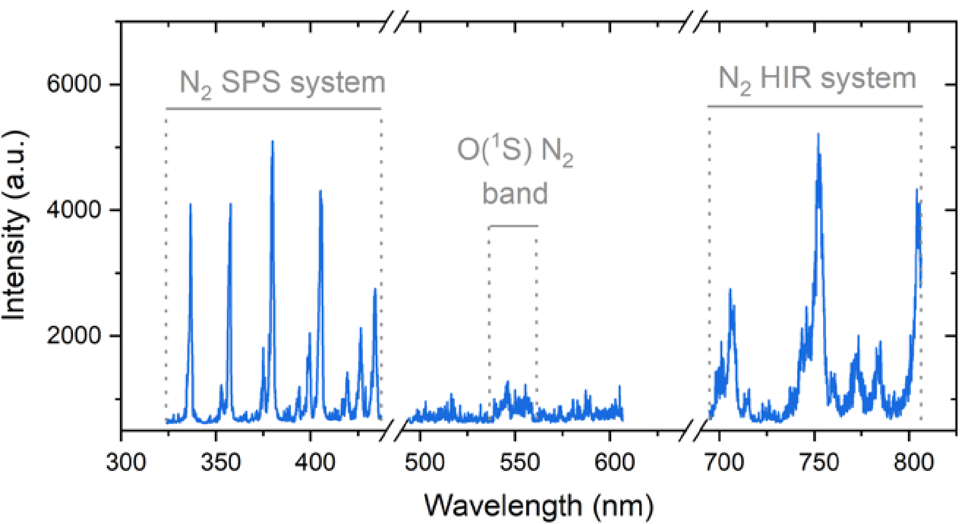


Figure 3: Typical optical emission spectrum of a Townsend discharge in a continuous nitrogen flow.

As can be seen in Figure 3, discharge emission is dominated by the Second Positive System (SPS) of N_2, the Herman Infrared system (HIR) of N_2, and the $O(^1S)N_2$ band. Here, the excited $N_2(C)$, $N_2(C'')$, and $O(^1S)N_2$ states giving rise to the observed emission bands are mostly populated according to the following reaction schemes [44–46]:

$$N_2(X) + e^- \rightarrow N_2(C) + e^- \quad (2)$$

$$N_2(A) + N_2(A) \rightarrow N_2(C'') + N_2(X) \quad (3)$$

$$\begin{cases} O(^3P) + N_2(A) \rightarrow O(^1S) + N_2(X) \\ O(^1S) + 2N_2(X) \rightarrow O(^1S)N_2 + N_2(X) \end{cases} \quad (4)$$

Based on Equations (2) and (3), the emission intensity of the SPS is typically linked to the electron population [47], whereas the emission intensity of the HIR is ascribed to the square of the population of metastable $N_2(A)$ states [48]. As for the $O(^1S)N_2$ excimer emission, Equation (4) reveals that it can be related to both $N_2(A)$ and oxygen impurities [44–46]. In presence of low oxygen concentrations into Townsend N_2 discharges, it is worth highlighting that X. Lin et al. [49] have recently shown that associative ionization reaction $N(^2P) + O(^3P) \rightarrow NO^+ + e^-$ can be the dominant process involved in the memory effect.

3. Electrical characterization of the discharge

3.1. Townsend discharge with a single pulsed gas injection

Current-voltage characteristics are used to analyze Townsend discharge with a single pulsed gas injection; Figure 4(a) to Figure 4(c) report the absolute value of the maximum current at each half period of the applied voltage for the entrance, middle, and exit zones of the DBD cell. The results are shown at two gas opening times (10 ms, Figure 4(b) and 100 ms, Figure 4(c)) for P_U=2 bar. For all experiments, the controlled valve of the pumping system is fixed to P_C=1 bar to maintain atmospheric-pressure conditions in the DBD cell with pulsed gas injections. Values without pulsed gas injections (continuous gas flow only, Figure 4(a)) are also presented. For all conditions, the discharge current is very low (< 0.5 mA); as reported in the literature [40], this is due to the ionization level not being high enough, which agrees with the behavior of the Townsend discharge in N_2. Furthermore, the maximum current at the entrance of the DBD cell is systematically lower than in the two other zones. A similar feature for continuous gas flows was reported by other authors [44,49,50]. In such conditions, the discharge first ignites at the exit, and the population of long-lived metastable $N_2(A)$ states rises between the entrance and the exit; this leads to a lower breakdown voltage and thus to a higher discharge current for the same amplitude of the applied voltage near the exit [44].

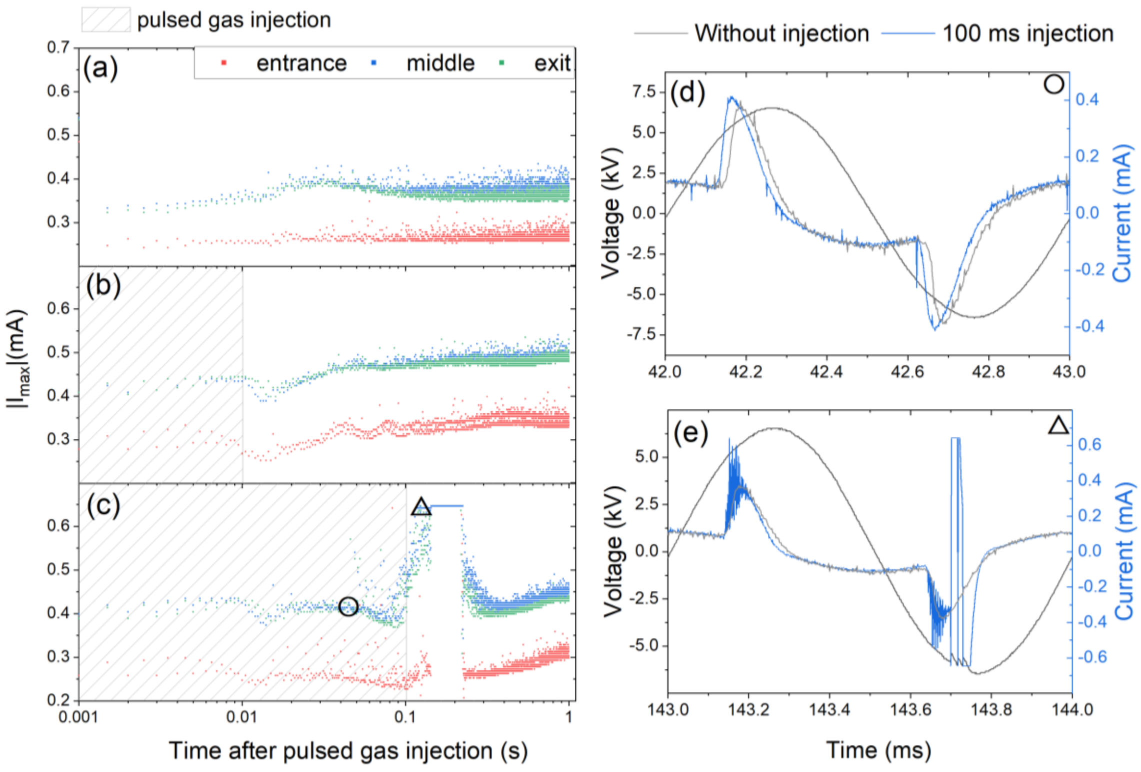


Figure 4: Absolute value of the maximum current at the entrance, middle and exit positions for each half-period of the applied voltage: (a) without pulsed gas injection (continuous gas flow only), (b) with a pulsed gas injection for a pulse duration of 10 ms, and (c) with a pulsed gas injection for a pulse duration of 100 ms. Selected current-voltage characteristics for 100 ms injection: (d) homogeneous Townsend discharge at 0.042 s (○) and (d) filamentary discharge at 0.143s (△). Here, the upstream pressure on the injection control unit is fixed to 2 bar.

Figure 4(a) further shows that regardless of the position along the gas flow lines, the absolute value of the maximum current without pulse (continuous gas flow only) remains constant over time. On one hand, for t_{gas}=10 ms, *i.e.* for pulse durations shorter than the residence time of the continuous gas flow (~50 ms), Figure 4(b) indicates that the maximum current oscillates after the pulsed gas injection up to about 100 ms and then stabilizes. This applies particularly at the entrance position, where the memory effect is weaker [44]. On the other hand, for longer pulse durations (for example, t_{gas}=100 ms),

Figure 4(c) reveals that the maximum current sharply increases after the pulse end and then oscillates before progressively returning to steady-state values. Such current variation for a pulse duration of 100 ms is linked to the formation of micro-discharges and a temporary transition from the homogeneous to filamentary discharge regime [51]. This can be confirmed by the set of current-voltage characteristics presented in Figure 4(d) and Figure 4(e) for t_{gas}=100 ms. At 42 ms after the pulsed gas injection, Figure 4(d) shows that the discharge remains in the homogenous regime but exhibits a small rise in the breakdown voltage and a slight decrease of the maximum current with respect to the ones observed for continuous gas flow only. In contrast, at 143 ms after the pulsed gas injection, Figure 4(e) reveals that the discharge transits to a filamentary regime characterized by narrow discharge channels randomly distributed in time and space [52]. In such conditions, the maximum current significantly varies over very short time scales and can even reach the saturation limit of the oscilloscope.

Discharge destabilization can also be analyzed from the time evolution of the power absorbed or dissipated by electrons in the discharge. Directly obtained from current-voltage characteristics in homogenous discharges [53], the results are presented in Figure 5 for several gas opening times (2, 10, 50 and 100 ms) for P_U=2 bar. Here, all discharge power measurements are collected on the middle electrode (similar features with different values are observed for the entrance and exit zones [50]). While the discharge power remains constant for continuous gas flows in agreement with the evolution of the absolute value of the maximum current (Figure 4(a)), two features can be seen in Figure 5 for pulsed gas flows: i) the power remains almost constant up to 10 ms after the beginning of the pulse

and then ii) depending on the gas opening time, the power in the homogeneous regime decreases down to the discharge power with only a continuous gas injection and a transition towards the filamentary regime may occur (Figure 5(c) and (d)) for the longer durations (50 and 100 ms).

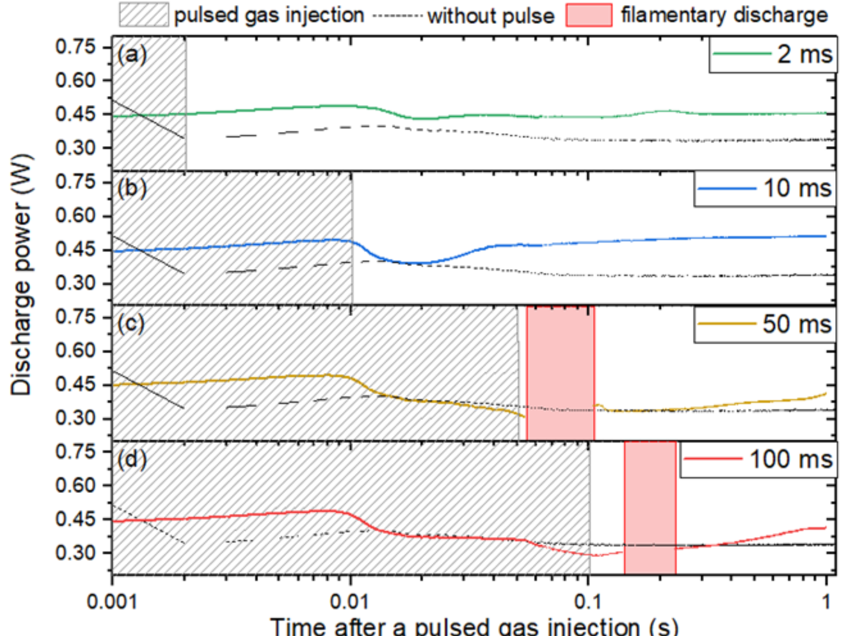


Figure 5: Discharge power (collected on the middle electrode) for various t_{gas}: (a) 2 ms, (b) 10 ms, (c)50 ms and (d)100 ms. Here, P_U is fixed to 2 bar. In the red zones, due to oscilloscope saturation in the filamentary regime, the power cannot adequately be calculated from current-voltage characteristics. A small drop is always observed for the first data point (only a few discharges in the 1-2 ms time scale); such a feature can be linked to the transition from filamentary to homogeneous discharge regime due to the time required for the buildup of the memory effect [42,44].

For P_U=2 bar, the instantaneous gas flow was estimated to 32 L.min^{-1} regardless of the gas opening time (see Figure 2). Considering the dimensions of the inlet tube, assuming that the gas flow is identical at the outlet of the pulsed injector and throughout the whole

system, the pulsed gas can be expected to reach the DBD cell after around 10 ms. Hence, the slight drop in power observed around 10 ms for all conditions can be linked to the sudden arrival of the pulsed gas in the discharge zone. Such a decrease of the discharge power is consistent with a reduction of the discharge current observed over selected time frames in Figure 4(d). For 2 ms (Figure 5(a)) and 10 ms (Figure 5(b)), the pulse duration and the total amount of gas injected per pulse are such that the discharge remains in the homogeneous regime. For injections over longer time scales (50 ms, see Figure 5(c), and 100 ms, Figure 5(d)) and thus for larger amounts of gas injected per pulse, however, the discharge becomes filamentary over selected time frames. For example, for 50 and 100 ms gas opening times, this occurs for about 50 and 100 ms, respectively.

3.2. Townsend discharge with multiple pulsed gas injections

Based on the data displayed in Figure 5, it seems that for single-pulse injections of N_2, the transition from homogeneous to filamentary discharge only occurs when the pulse durations become comparable to the residence time of the continuous gas flow (~50 ms). However, based on the results presented in Figure 2, such a trend with the pulsed gas opening time could also be linked to the total amount of gas injected per pulse. Hence, for longer pulse durations, it seems that the gas from the pulsed injection could no longer be entirely evacuated over the time scale of the continuous gas flow, suggesting a rise in the population of gaseous species. This aspect can be further examined by “multiple” pulsed injection experiments realized in the specific case of 5 injections with a gas opening time

of 10 ms and P_U=2 bar; the results for the discharge power as a function of time are displayed in Figure 6. For the specific set of injection conditions presented in Figure 6, the discharge modification becomes more prominent for successive pulsed gas injections, suggesting an accumulation effect from one pulse to the other. More specifically, the decrease of the discharge power after each pulse rises with the number of pulses such that the discharge transits from the homogeneous to the filamentary regime after several pulsed gas injections.

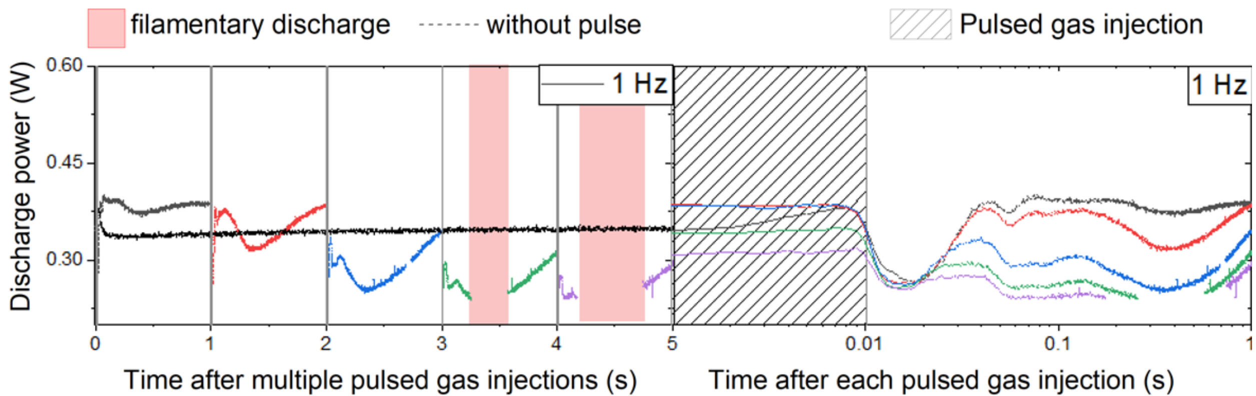


Figure 6: Discharge power for t_{gas}= 10 ms, 2 bar. The data are plotted over two-time scales: on a linear scale after multiple pulsed gas injections (left) and on a log scale after each pulsed gas injection (right). The same colour code is used in both cases: black-first pulse, red-second pulse, blue-third pulse, green-fourth pulse and purple-fifth pulse.

Based on the results in Figure 6, discharge destabilization should be more prominent for larger amounts of gas injected per pulse for a given value of t_{gas}. This aspect can be examined by plotting the discharge power variation over time for several values of the upstream pressure P_U, *i.e.* for different instantaneous flows of the pulsed gas injection (see Figure 2); the results are reported in Figure 7.

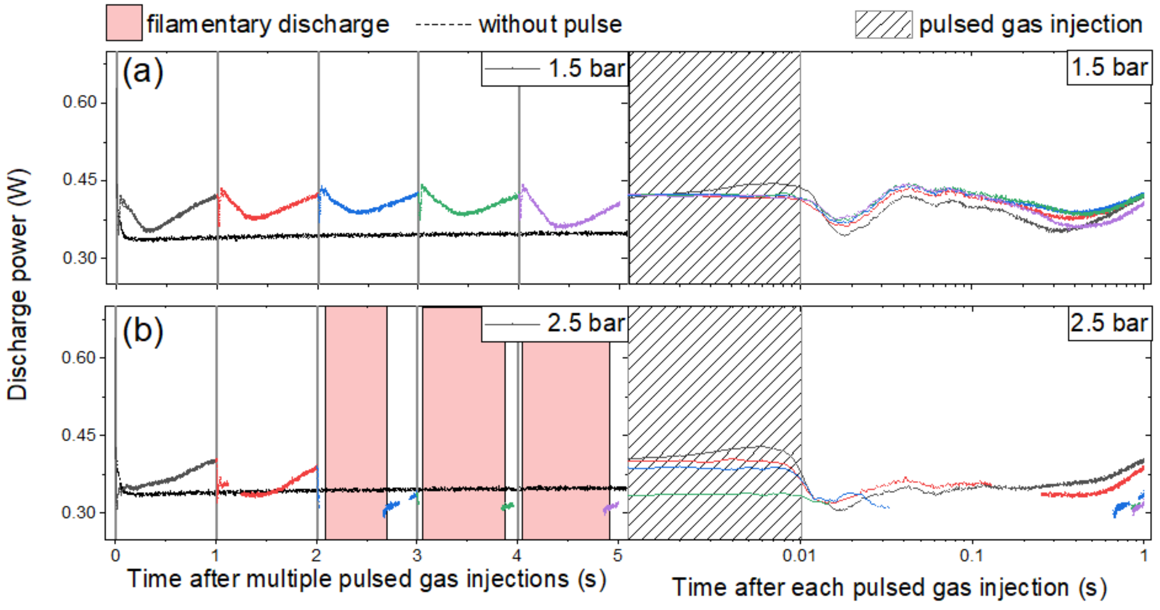


Figure 7: Discharge power for t_{gas}= 10 ms and several upstream pressure values: (a) 1.5 and (b) 2.5 bar. The data are plotted over two-time scales: on a linear scale after multiple pulsed gas injections (left) and on a log scale after each pulsed gas injection (right). The same color code is used in both cases: black-first pulse, red-second pulse, blue-third pulse, green-fourth pulse and purple-fifth pulse.

Figure 7 reveals that the slight drop in discharge power linked to the sudden arrival of the pulsed gas occurs earlier at 2.5 bar (~80 ms) than at 1.5 bar (~130 ms). Based on the results presented in Figure 2, such behavior is consistent with the corresponding rise in the instantaneous pulsed gas flow for t_{gas}=10 ms, going from about 24 L.min^{-1} at 1.5 bar to about 41 L.min^{-1} at 2 bar. Figure 7 also shows that the extent of the discharge destabilization rises with P_U. More specifically, while the discharge remains in the homogeneous regime up to at least 5 pulses for P_U=1.5 bar (Figure 7 (a)), the discharge destabilization intensifies with the number of pulses for P_U=2.5 bar (Figure 7 (b)). Such behavior is very good agreement with a cumulative effect of the pulsed gas injection on

the stability of Townsend discharge. Discharge modification is more prominent for larger amounts of gas injected per pulse, and thus for longer pulses at fixed instantaneous pulsed gas flows (Figure 5) or higher instantaneous pulsed gas flows at fixed pulsed duration (Figure 7). Of note, it can be seen from the set of data presented in Figure 6 and Figure 7 that the transition from the homogeneous to the filamentary discharge regime occurs when the discharge power reaches a critical value around 0.3 W.

A similar cumulative effect can be seen by varying the pulsed injection frequency for t_{gas}= 10 ms and P_U =2 bar (Figure 8). After the first pulse, the same decrease of the discharge power at 10 ms is observed for 0.1 Hz (Figure 8 (a)), 1 Hz (Figure 6), and 10 Hz (Figure 8 (b)); this trend is consistent with the fixed value of the instantaneous pulsed gas flow (32 $L.min^{-1}$, Figure 2). After such a temporary drop, the discharge power increases back to the value achieved without any pulsed gas injection. Depending on the injection frequency, two distinct trends can be seen: i) if the injection period ($1/f$) is long enough to retrieve power values higher than the critical one, the discharge will remain or go back to a homogeneous discharge regime, and ii) if not enough time is provided to the discharge before a subsequent pulse, the power does not increase back to the critical value and the discharge will remain filamentary.

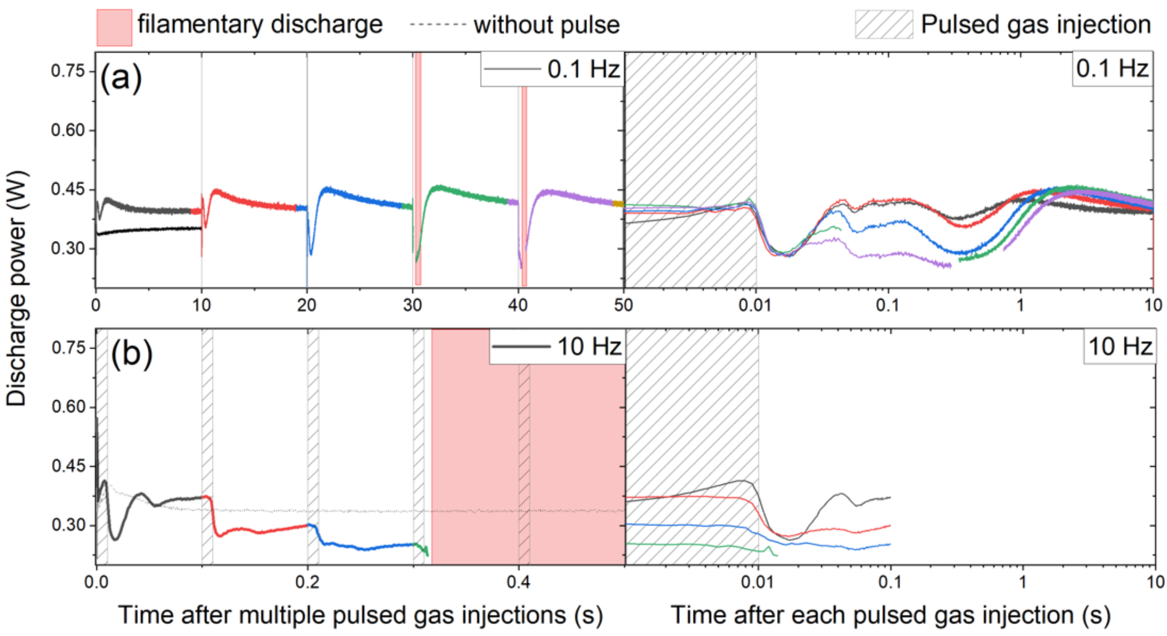


Figure 8: Discharge power for t_{gas}= 10 ms at (a) 0.1 Hz and (b) 10 Hz injection frequency. The data are plotted over two-time scales: on a linear scale after multiple pulsed gas injections (left) and on a log scale after each pulsed gas injection (right). The same color code is used in both cases: black-first pulse, red-second pulse, blue-third pulse, green-fourth pulse and purple-fifth pulse.

As mentioned previously, through selective control of the operating conditions, N_2 discharges can be homogeneous due to the presence of long-lived species from one half-cycle of the applied voltage to the other. Involved in the production of seed electrons at low electric fields [42,44], any factor leading to a net loss of metastable $N_2(A)$ states would no longer ensure conditions for homogeneous discharge formation [21]. Hence, the Townsend breakdown would be replaced by a streamer breakdown, and the discharge would transit to a filamentary regime. This is typically accompanied by an increase in the breakdown voltage [21]; this feature is consistent with the data presented in Figure 4(d). One of the phenomena leading to a net metastable loss in N_2 discharges is the quenching

of $N_2(A)$ states by gas-phase collisions [21]. Hence, additional gas-phase species arising from the pulsed gas injections and the cumulative effect can play an important role on the populations of $N_2(A)$ states and, thus on the stability of Townsend discharges. In particular, the set of current-voltage characteristics for single and multiple injections have shown that gas accumulation can be linked to many possible routes: (i) pulse durations longer than the residence time of the continuous gas flow at fixed instantaneous pulsed gas flows, (ii) larger instantaneous pulsed gas flows at fixed pulsed duration, and (iii) multiple pulsed injections with repetition frequencies between 0.1 and 10 Hz. In line with this discussion, any significant change of the neutral gas composition, for example, in the presence of impurities or precursors used for materials processing, could modify the discharge stability; we will return to this point later.

3.3. Optical emission spectroscopy of the discharge

Optical emission spectroscopy (OES) is used to examine in more detail the stability of Townsend N_2 discharges with pulsed gas injections. Here, the gas tubes and discharge chamber are flushed more than 10 times with nitrogen before the experiment to ensure a minimal contribution from outgassing and thus from impurities emanating from surfaces [55]. In such conditions, it is found that the homogeneous discharge regime can be maintained over a larger number of pulses than in the previous set of less standardized experiments (Figure 6, Figure 7, and Figure 8). Figure 9 presents the time evolution of the discharge power and selected emission intensities for 10 pulsed gas injections. Here, the gas opening time, upstream pressure, and injection frequency are fixed to 10 ms, 2 bar, and

1 Hz, respectively. Values for a Townsend discharge with a continuous flow of nitrogen are also shown for comparison.

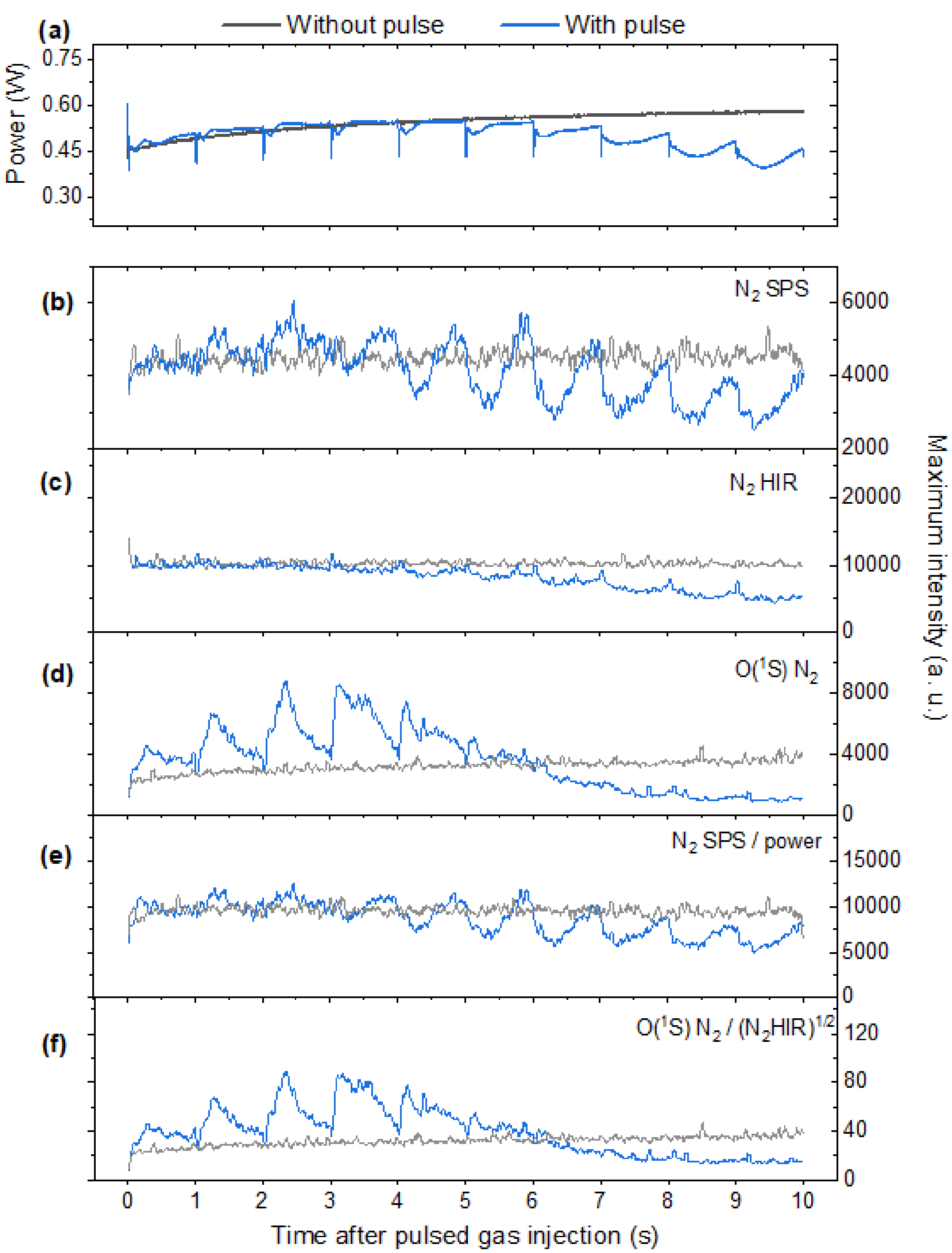


Figure 9: (a) Discharge power with and without gas injection. Evolution of the emission intensity of (b) N_2 SPS, (c) N_2 HIR, (d) $O(^1S)N_2$, (e) N_2 SPS/Power and (f) $O(^1S)N_2/(N_2HIR)^{0.5}$. Here, the gas opening time, upstream pressure, and injection frequency are fixed to 10 ms, 2 bar, and 1 Hz, respectively.

As highlighted in the previous section, Figure 9 (a) indicates that the discharge power decreases sharply with the pulsed gas injection but returns to a pre-defined value after each perturbation. After several injections, however, the power continues to decrease without returning to the value before perturbation. A similar trend is observed in Figure 9 (b) for the emission intensity of the SPS of N_2 linked to the N_2(C) state [56]. From Equation 1, N_2(C) is mainly populated by electron-impact collisions on ground state N_2(X). Therefore, the similar trend in the time evolution of the discharge power and N_2 SPS emission intensity over time can partially be linked to temporal variations of the electron density (linked to the discharge power). In this framework, the N_2(C) emission intensity is divided by the discharge power to analyze the time evolution of N_2(X) with pulsed gas injection; the results are presented in Figure 9 (e). While no significant change can be seen for the first few pulses, a slight decrease occurs following each additional pulse with an accumulative effect for a larger number of pulses. It is important to note that additional gas or any change in the gas composition can induce temporal modification of the collisional quenching of emitting N_2(C) states [21,57]: hence, the behavior observed in Figure 9 (e) can result from time variations of both N_2(X) and optical efficiency of N_2(C)-to-N_2(B) transitions (due, for example, to the incorporation of impurities, see below).

As for the N_2 HIR emission (see Figure 9 (c)), it monotonously decreases with time. For a large number of pulses, a decrease can also be seen on the time frame of each single pulse. Based on Equation (2), such short and long-time scale diminutions are a signature of N_2(A) losses [56]. In Figure 9 (d), the time evolution of the emission intensity from the

$O(^1S)$ N_2 system presents two features. First, between the first and the fourth injection, the emission intensity globally increases with a return to the pre-defined value before the next pulse. Based on Equation (3), two parameters can result in an increase in $O(^1S)N_2$ emission: i) an increase of the population of $N_2(A)$ states and ii) an increase in the population of oxygen $O(^3P)$ state [56,58]. Since the emission intensity of N_2 HIR linked to the population of $N_2(A)$ either remains either constant or shows the opposite trend in the first 4 seconds of the experiment (Figure 9 (c)), the increase in $O(^1S)N_2$ most likely arises from an increase in the number density of oxygen atoms. This can be confirmed in Figure 9 (f) by the ratio of the emission intensity of $O(^1S)$ N_2 over the square root of the emission intensity of the N_2 HIR system; this ratio is directly linked to the evolution of oxygen species. Second, after the fifth pulse, the emission intensity decreases drastically for both N_2 HIR and $O(^1S)N_2$; such trend can be explained by the net loss of $N_2(A)$ due to the expected quenching by oxygen species [54].

Through a more detailed look at a single pulsed injection (over 1 s), it can be noticed in Figure 9 (e) and Figure 9 (f) that the rate of change in $N_2(X)$ (and/or optical efficiency) and $O(^3P)$ populations is very slow considering the expected residence time of gas-phase species in the DBD cell. With an instantaneous gas flow around 32 $L.min^{-1}$ (see Figure 2), the corresponding gas residence time can be estimated to 2 ms. In addition to the pulsed gas injections, there is a continuous flow of nitrogen characterized by a residence time of about 50 ms. As can be seen in Figure 9, the more prominent variations of the $N_2(X)$ (and/or optical efficiency) and $O(^3P)$ populations occur halfway along the gas injection period, *i.e.*

0.5 s. This result suggests other mechanisms occurring over much longer time scales than those linked to continuous and pulsed nitrogen gas flows.

4. Discussion

Further characterization of the pulsed gas flow channel can be realized using the set of data presented in Figure 2. As can be seen in Figure 10, regardless of the gas opening time, the instantaneous gas flow, Q, increases with the pressure difference between the upstream and the chamber pressures, P_U-P_C (P_C being set to atmospheric pressure). In the case of a linear variation (Hagen-Poiseuille equation in a laminar gas flow [59]), the proportionality constant corresponds to the so-called fluid conductance. However, the significant departure from the linear trend displayed in Figure 10 suggests that the Hagen-Poiseuille equation is not suitable. Two hypotheses can be made to interpret this non-linearity, either a transition from laminar to turbulent gas flow or the head losses due to the specific gas flow channel [59].

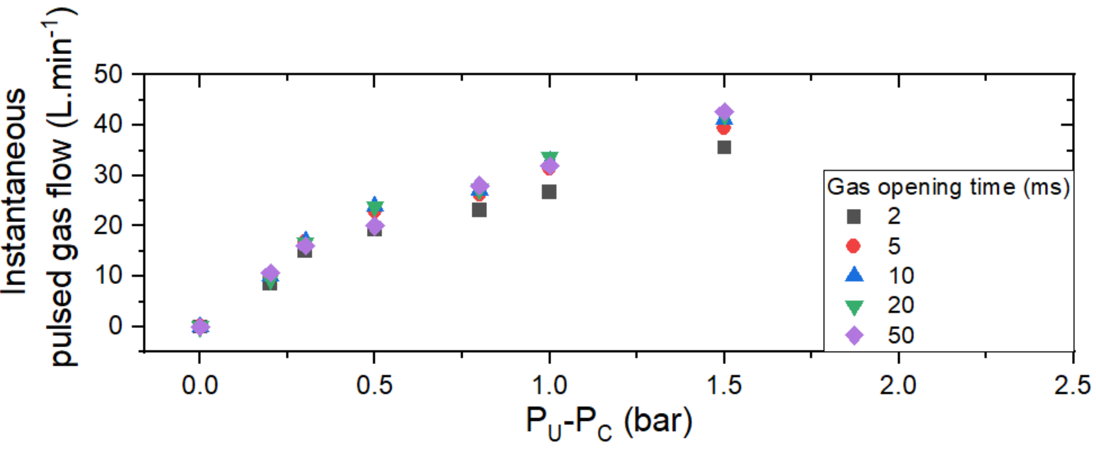


Figure 10: Correlation between the instantaneous pulsed gas flow Q and the pressure difference between the pulse injector and the chamber P_U-P_C for various gas opening times.

To analyze the possible transition from laminar to turbulent gas flow, the Reynolds number, $Re = \frac{\rho.U.D}{\mu}$, where ρ is the gas mass density, U is the gas average velocity, D is the characteristic dimension of the system, and μ is the dynamic viscosity, was calculated. Over the range of experimental conditions investigated, Re rises from about 35 for the continuous gas flow of 1 $L.min^{-1}$ to more than 1000 for an instantaneous gas flow of 32 $L.min^{-1}$; this result is consistent with an instantaneous transition from laminar to an intermediate flow regime over the time scale of the pulsed gas injection [59]. However, filamentation appears on time scales much longer than the pulse duration and not necessarily after the first injection. Furthermore, the extent of discharge destabilization varies with the injection frequency. Since these aspects are unrelated to Reynold's number and thus to a change in the gas flow regime, other issues must be involved, most likely singular head losses due to irregularities from the inlet pipe to the gas mixing chamber and then to the DBD cell (see Figure 1).

To understand the pulsed gas injection behavior over the range of experimental conditions investigated, 2D simulations are done using COMSOL Multiphysics [60] Here, simulations are performed along the discharge axis, with the mixing chamber allowing a coupling between the inlet gas pipes (continuous and pulsed gas flows) and the DBD cell (see Figure 1). The injection conditions simulated by COMSOL are as determined experimentally, i.e. a continuous flow rate of 1 $L.min^{-1}$ and a pulsed injection of 10 ms at 0.1 Hz (instantaneous flow rate of 32 $L.min^{-1}$). To prevent sharp transitions in numerical

analysis, the pulse is simulated with a rise time of 5 ms, a plateau of 10 ms, and a decay time of 50 ms. Figure 11 (a) shows the time-resolved gas velocity calculated at the center of the inter-electrode gap. As expected, the gas velocity sharply rises and then drastically decreases after each pulsed injection. No accumulation can be seen from one pulse to the other. Hence, the gas flow in the DBD cell does not seem to be modified out of the time scale of the instantaneous pulsed gas flow.

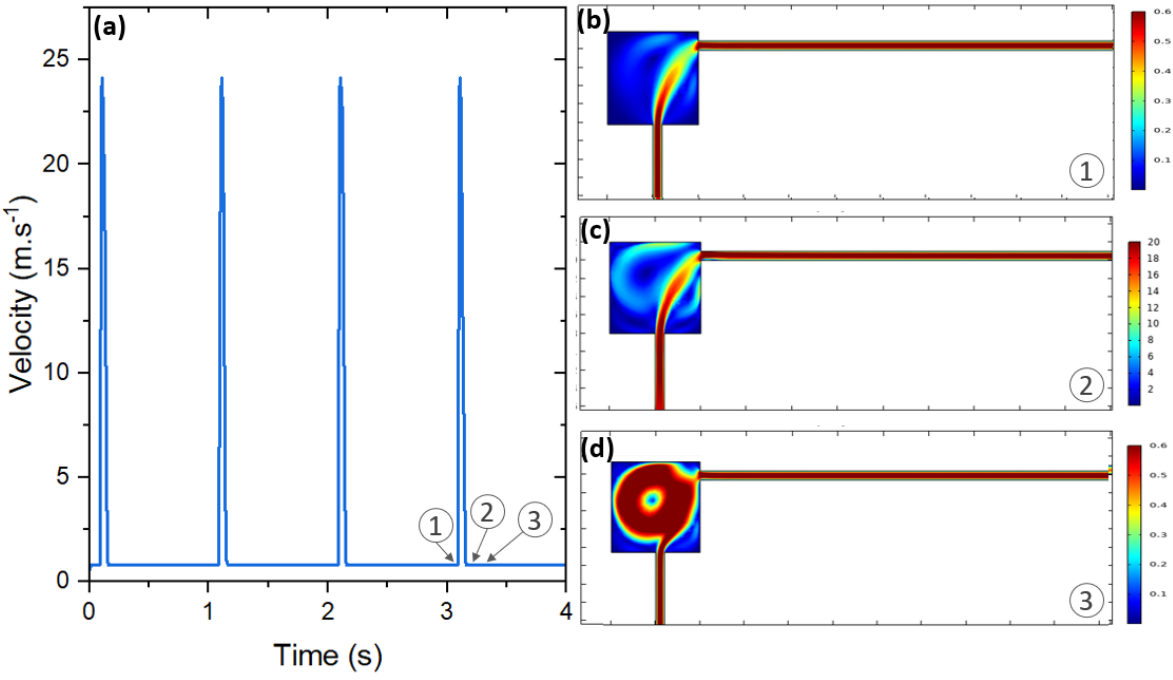


Figure 11:(a) Gas velocity profile obtained from COMSOL simulations at the centre of the inter-electrodes space. 2D mapping of the gas flow lines at (b) 3.09 (Time 1, before the 10-ms pulse), (c) 3.11 (Time 2, after the 10ms pulse) and (d) 3.20 seconds (Time 3, 10 ms after the 10ms pulse). The injection conditions simulated by Comsol are as follows: a continuous flow rate of 1 L.min^{-1} and a pulsed injection of 10 ms at 0.1 Hz (instantaneous flow rate of 32 L.min^{-1}).

Figure 11 b), c) and d) show 2D mappings of the gas velocity before the fourth 10-ms pulse (b, Time 1 (3.09 s) in a), after the fourth 10-ms pulse (c, Time 2 (3.11 s) in a), and 1 ms after the fourth 10-ms pulse (d, Time 3 (3.20 s) in a). In all cases, the gas velocity

profile with respect to height in the interelectrode space remains nearly parabolic. This behavior is consistent with the low Womersley number (from 0.2 to 2 between 0.1 and 10 Hz). In such conditions, the frequency of pulsations is sufficiently low that a parabolic velocity profile (Hagen-Poiseuille equation [59]) has time to develop during each cycle, and the flow remains nearly in phase with the instantaneous pressure gradient [61]. However, it can be seen in Figure 11 b), c) and d) that pulsed gas injection introduces recirculations in the gas mixing chamber located upstream of the DBD cell. In addition, these recirculations remain from one pulse to the other (for example, from the end of one pulse shown in Figure 11 d) to the onset of another pulse as in Figure 11 b)). Hence, due to the longer gas residence time in the mixing chamber, impurities inherently outgassing from chamber walls can accumulate in this region of the reactor, and then be released at abnormally high concentrations in the DBD cell.

This possible change in the neutral gas composition is considered by introducing in COMSOL simulations a constant oxygen desorption rate from the walls of the mixing chamber. Here the flux is estimated to 10^{-5} mol/m^{2}s to produce an oxygen molar fraction in the discharge zone of a few ppm. Figure 12 a) reveals that such feature introduces significant temporal variation of the relative oxygen content. Clearly, a sudden rise in the oxygen molar fraction occurs after each pulse, with a shape similar to the one of the gas velocity. However, while the gas velocity linked to the pulsed injection rapidly returns to the value of the continuous gas flow, a second rise in the oxygen content with much slower decay occurs between each pulse. An accumulation from the first pulse to the others with a steady-state concentration value for longer number of pulses can also be seen. As

highlighted in Figure 12 b), c), and d), such variations characterized by much longer time scales than those linked to pulsed and continuous gas flow are directly linked to surface outgassing and recirculations in the gas mixing chamber.

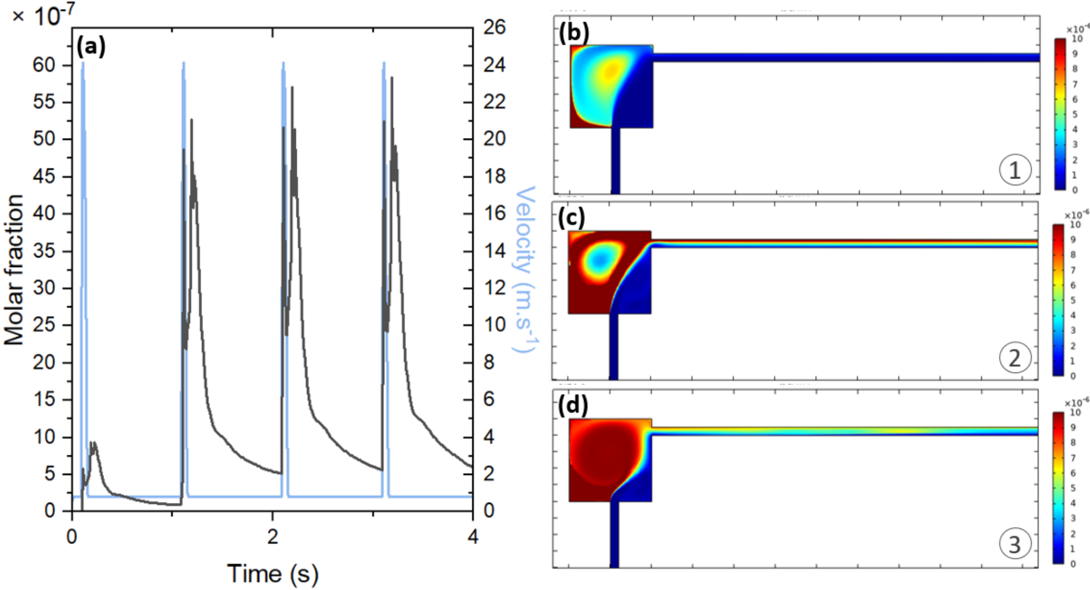


Figure 12: Oxygen molar content obtained from COMSOL simulations at the centre of the inter-electrodes space. 2D mapping of the oxygen content at (b) 3.09 (Time 1, before the 10-ms pulse), (c) 3.11 (Time 2, after the 10-ms pulse) and (d) 3.20 seconds (Time 3, 10 ms after the 10-ms pulse). The injection conditions simulated by COMSOL are as follows: a continuous flow rate of 1 L.min^{-1}, a pulsed injection of 10 ms at 0.1 Hz (instantaneous flow rate of 32 L.min^{-1}), and an oxygen desorption rate from the chamber walls of 10^{-5} mol/m^{2}s. In (a), the gas velocity is also shown for comparison.

Of note, the behaviors presented in Figure 12 are comparable to the one of the $O(^3P)$, and the opposite to the one of the $N_2(A)$ observed by time-resolved optical emission spectroscopy (Figure 9). Hence, the incorporation of oxygen impurities through surface outgassing and recirculations in the gas mixing chamber can contribute to $N_2(A)$ losses and thus to a discharge destabilization, in excellent agreement with the experiments for both single pulse and multiple pulses (Figure 4, Figure 5, Figure 7, Figure 8). Several studies have examined the influence of oxygen impurities on the fundamental properties of DBD

operated in N_2. For a low amount of oxygen (up to a few tens of ppm), the power rises with the oxygen addition. However, the opposite trend is observed at higher oxygen content [44]. In addition, high oxygen content leads to a transition from the homogeneous to the filamentary discharge regime. This set of results is again consistent with the electrical and optical characteristics presented for single pulse and multiple pulses. It is worth mentioning that the results presented in Figure 12 are obtained with an oxygen desorption rate from the walls of 10^{-5} mol/m^{2}s, yielding oxygen molar fractions in the discharge zone of a few ppm. Similar trends were observed for other desorption rates: hence, the behavior displayed in Figure 12 remains, with a linear rise of the steady-state oxygen molar concentration value with the oxygen desorption rate.

5. Conclusion

The objective of this work was to understand the behavior of Townsend DBD operated in a homogeneous regime following pulsed gas injection. Time-resolved discharge power measurements coupled with OES analysis have been realized over single and multiple pulsed injections of nitrogen in a continuous laminar nitrogen gas flow. The effects on discharge stability of three main pulsed injection parameters have been analyzed: i) gas opening time (pulse duration), ii) instantaneous pulsed gas flow (through modification of the upstream pressure P_U), and iii) pulse repetition frequency. For single pulsed gas injection, discharge power measurements revealed that gas opening times longer than 50 ms yield to a filamentary discharge regime. For larger amounts of gas injected per pulse and successive pulsed gas injections, transition from homogeneous to filamentary also occurred. In such conditions, OES revealed an increase of nitrogen and oxygen species

leading to a significant loss of metastable $N_2(A)$ species and hence of the memory effect, which is essential to obtain a Townsend discharge.

Over the range of experimental conditions investigated characterized by high instantaneous gas flows due to pulsed injection in a continuous gas flow, it was found that surface outgassing and gas recirculations in the gas mixing chamber located upstream of the DBD cell can induce oxygen impurities in the discharge over much longer time scales than the ones expected from the instantaneous and continuous gas flows. However, it can be expected that such features are directly linked to the dimension and shape of the system, in particular of the gas mixing chamber. As will be demonstrated in forthcoming papers, the operation of Townsend discharges in pulsed gas flow regimes show interest for several applications, in particular for the deposition of multifunctional thin films.

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Data availability statement

The data are available from the corresponding author upon request.

References

[1] Profili J, Levasseur O, Blaisot J-B, Koronai A, Stafford L and Gherardi N 2016 Nebulization of Nanocolloidal Suspensions for the Growth of Nanocomposite Coatings in Dielectric Barrier Discharges *Plasma Processes and Polymers* **13** 981–9

[2] Fanelli F, Mastrangelo A M and Fracassi F 2014 Aerosol-Assisted Atmospheric Cold Plasma Deposition and Characterization of Superhydrophobic Organic–Inorganic Nanocomposite Thin Films *Langmuir* **30** 857–65

[3] Biniwale R B, Mizuno A and Ichikawa M 2004 Hydrogen production by reforming of iso-octane using spray-pulsed injection and effect of non-thermal plasma *Appl Catal A Gen* **276**

[4] Kameshima S, Tamura K, Ishibashi Y and Nozaki T 2015 Pulsed dry methane reforming in plasma-enhanced catalytic reaction *Catal Today* **256**

[5] Jiménez C, de Barros D, Darraz A, Deschanvres J L, Rapenne L, Chaudouët P, Méndez J E, Weiss F, Thomachot M, Sindzingre T, Berthomé G and Ferrer F J 2007 Deposition of TiO 2 thin films by atmospheric plasma post-discharge assisted injection MOCVD *Surf Coat Technol* **201**

[6] Dingemans G, Van De Sanden M C M and Kessels W M M 2012 Plasma-enhanced chemical vapor deposition of aluminum oxide using ultrashort precursor injection pulses *Plasma Processes and Polymers* **9** 761–71

[7] Sproul W D 1987 High rate reactive sputtering process control *Surf Coat Technol* **33** 73–81

[8] Nicolas Martin, Bally A R, Hones P, Sanjines R and Levy F 2000 High rate and process control of reactive sputtering by gas pulsing : the Ti-O system *Thin Solid Films* **377–378** 550–6

[9] Kushner M J 1993 Pulsed plasma-pulsed injection sources for remote plasma activated chemical vapor deposition *J Appl Phys* **73** 4098–100

[10] KWON S J 2005 Effect of Precursor-Pulse on Properties of Al-Doped ZnO Films Grown by Atomic Layer Deposition *Japanese Journal of Applied Physics To* **44** 1062

[11] Metzler D, Bruce R L, Engelmann S, Joseph E A and Oehrlein G S 2014 Fluorocarbon assisted atomic layer etching of SiO2 using cyclic Ar/C4F8 plasma *J. Vac. Sci. Technol. A* **32** 20603

[12] Groner M D, Elam J W, Fabreguette F H and George S M 2002 Electrical characterization of thin Al2O3 films grown by atomic layer deposition on silicon and various metal substrates *Thin Solid Films* **413** 186–97

[13] Pánek R, Gunn J P, Bucalossi J, Ďuran I, Geraud A, Hron M, Loarer T, Pégourié B, Stöckel J and Tsitrone E 2005 The response of the Tore Supra edge plasma to supersonic pulsed gas injection *Journal of Nuclear Materials* **337–339** 530–4

[14] Sadek T, Carnide G, Vinchon P, Kahn M L, Clergereaux R and Stafford L 2022 Time-resolved analysis of the electron temperature in RF magnetron discharges with a pulsed gas injection *European Physical Journal - Applied Physics*

[15] V.Garofano, L.Stafford, B.Despax, R.Clergereaux and K.Makasheva 2015 Cyclic evolution of the electron temperature and density in dusty low-pressure radio frequency plasmas with pulsed injection of hexamethyldisiloxane *Appl. Phys. Letter* **107**

[16] Garofano V, Bérard R, Boivin S, Joblin C, Makasheva K and Stafford L 2019 Multi-scale investigation in the frequency domain of Ar/HMDSO dusty plasma with pulsed injection of HMDSO *Plasma Sources Sci Technol* **28** 055019

[17] Garofano V, Bérard R, Glad X, Joblin C, Makasheva K and Stafford L 2019 Time-resolved analysis of the precursor fragmentation kinetics in an hybrid PVD/PECVD dusty plasma with pulsed injection of HMDSO *Plasma Processes and Polymers* **16** 1900044

[18] Fan Z, Qi H, Liu Y, Yan H and Ren C 2016 Effects of airflow on the distribution of filaments in atmospheric AC dielectric barrier discharge *Phys Plasmas* **23**

[19] Liu F, Zhang D and Wang D 2010 Gas flow effects on the submicrosecond pulsed atmospheric pressure glow discharges *Phys Plasmas* **17** 103508

[20] Höft H, Becker M M and Kettlitz M 2016 Impact of gas flow rate on breakdown of filamentary dielectric barrier discharges *Phys Plasmas* **23** 033504

[21] Massines F, Gherardi N, Naudé N and Ségur P 2009 Recent advances in the understanding of homogeneous dielectric barrier discharges *The European Physical Journal Applied Physics* **47** 22805

[22] Massines F, Sarra-Bournet C, Fanelli F, Naudé N and Gherardi N 2012 Atmospheric pressure low temperature direct plasma technology: Status and challenges for thin film deposition *Plasma Processes and Polymers* **9** 1041–73

[23] Levasseur O, Vlad M, Profili J, Gherardi N, Sarkissian A and Stafford L 2017 Deposition of fluorocarbon groups on wood surfaces using the jet of an atmospheric-pressure dielectric barrier discharge *Wood Sci Technol* **51** 1339–52

[24] Profili J, Levasseur O, Koronai A, Stafford L and Gherardi N 2017 Deposition of nanocomposite coatings on wood using cold discharges at atmospheric pressure *Surf Coat Technol* **309** 729–37

[25] Savin de Larclause I, Paulmier T, Enache I, Caquineau H, Raynaud P, Massines F and Gherardi N 2009 Conformity of Silica-like Thin Films Deposited by Atmospheric Pressure Townsend Discharge and Transport Mechanisms *IEEE Transactions on Plasma Science* **37** 970–8

[26] Cote D R, Nguyen S V., Stamper A K, Armbrust D S, Tobben D, Conti R A and Lee G Y 1999 Plasma-assisted chemical vapor deposition of dielectric thin films for ULSI semiconductor circuits *IBM J Res Dev* **43** 5–38

[27] Avasthi D K, Mishra Y K, Kabiraj D, Lalla N P and Pivin J C 2007 Synthesis of metal – polymer nanocomposite for optical applications *Nanotechnology* **18**

[28] Levasseur O, Stafford L, Gherardi N, Naudé N, Blanchard V, Blanchet P, Riedl B and Sarkissian A 2012 Deposition of Hydrophobic Functional Groups on Wood

Surfaces Using Atmospheric-Pressure Dielectric Barrier Discharge in Helium-Hexamethyldisiloxane Gas Mixtures *Plasma Processes and Polymers* **9** 1168–75

[29] Massines F, Gherardi N, Fornelli A and Martin S 2005 Atmospheric pressure plasma deposition of thin films by Townsend dielectric barrier discharge *Surf Coat Technol* **200** 1855–61

[30] Martin S 2004 Atmospheric pressure PE-CVD of silicon based coatings using a glow dielectric barrier discharge *Surf Coat Technol* **177–178** 693–8

[31] Profili J, Levasseur O, Naudé N, Chaneac C, Stafford L and Gherardi N 2016 Influence of the voltage waveform during nanocomposite layer deposition by aerosol-assisted atmospheric pressure Townsend discharge *J Appl Phys* **120** 053302

[32] Profili J, Rousselot S, Tomassi E, Briqueleur E, Aymé-Perrot D, Stafford L and Dollé M 2020 Toward More Sustainable Rechargeable Aqueous Batteries Using Plasma-Treated Cellulose-Based Li-Ion Electrodes *ACS Sustain Chem Eng* **8** 4728–33

[33] Durán I R, Profili J, Stafford L and Laroche G 2020 Beyond microelectronics with 1,3,5,7-tetramethylcyclotetrasiloxane: A promising molecule for anti-fogging coatings *Mater Chem Phys* **242** 122508

[34] Prégent J, Vandsburger L, Blanchard V, Blanchet P, Riedl B, Sarkissian A and Stafford L 2015 Modification of hardwood samples in the flowing afterglow of N2–O2 dielectric barrier discharges open to ambient air *Cellulose* **22** 3397–408

[35] Prégent J, Vandsburger L, Blanchard V, Blanchet P, Riedl B, Sarkissian A and Stafford L 2015 Determination of active species in the modification of hardwood samples in the flowing afterglow of N2 dielectric barrier discharges open to ambient air *Cellulose* **22** 811–27

[36] Martin S 2004 Atmospheric pressure PE-CVD of silicon based coatings using a glow dielectric barrier discharge *Surf Coat Technol* **177–178** 693–8

[37] Mejanes N De, Profili J, Babaei S, Naudé N and Stafford L 2021 Refined analysis of current–voltage characteristics in Townsend dielectric barrier discharges in nitrogen at atmospheric pressure *J Phys D Appl Phys* **54** 095204

[38] Gherardi N and Massines F 2001 Mechanisms controlling the transition from glow silent discharge to streamer discharge in nitrogen *IEEE Transactions on Plasma Science* **29** 536–44

[39] Naudé N, Cambronne J P, Gherardi N and Massines F 2005 Electrical model and analysis of the transition from an atmospheric pressure Townsend discharge to a filamentary discharge *J Phys D Appl Phys* **38** 530–8

[40] Massines F, Gherardi N, Naudé N and Ségur P 2005 Glow and Townsend dielectric barrier discharge in various atmosphere *IPP Plasma Physics and Controlled Fusion* **47**

[41] Kogelschatz U 2002 Filamentary, patterned, and diffuse barrier discharges *IEEE Transactions on Plasma Science* **30** 1400–8

[42] Gherardi N, Gouda G, Gat E, Ricard A and Massines F 2000 Transition from glow silent discharge to micro-discharges in nitrogen gas *Plasma Sources Sci Technol* **9** 340–6

[43] Bosan D A, Jovanovic T V and Krmpotic D M 1997 The role of neutral metastable molecules in the breakdown probability and glow discharge in nitrogen *J Phys D Appl Phys* **30** 3096–8

[44] Tyl C, Lin X, Bouzidi M C, Dap S, Caquineau H, Ségur P, Gherardi N and Naudé N 2018 Investigation of memory effect in atmospheric pressure dielectric barrier discharge in nitrogen with small oxygen or nitric oxide addition *J Phys D Appl Phys* **51**

[45] Kossyi I A, Kostinsky A Y, Matveyev A A and Silakov V P 1992 Kinetic scheme of the non-equilibrium discharge in nitrogen-oxygen mixtures *Plasma Sources Sci Technol* **1** 207–20

[46] Brandenburg R, Maiorov V A, Golubovskii Y B, Wagner H-E, Behnke J and Behnke J F 2005 Diffuse barrier discharges in nitrogen with small admixtures of oxygen: discharge mechanism and transition to the filamentary regime *Journal of Physics D: Applied Physics J. Phys. D: Appl. Phys* **38** 2187–97

[47] Kogelheide F, Offerhaus B, Bibinov N, Krajinski P, Schücke L, Schulze J, Stapelmann K and Awakowicz P 2020 Characterisation of volume and surface dielectric barrier discharges in N 2 –O 2 mixtures using optical emission spectroscopy *Plasma Processes and Polymers* **17** 1900126

[48] Simek M, Babický V, Clupek M, Sunka P, Šimek M, Babický V, Člupek M and Šunka P 2001 Observation of the N 2 Herman infrared system in pulsed positive streamer induced emission at atmospheric pressure *J Phys D Appl Phys* **34** 3185–90

[49] Lin X, Tyl C, Naudé N, Gherardi N, Popov N A and Dap S 2020 The role of associative ionization reactions in the memory effect of atmospheric pressure Townsend discharges in N2 with a small O2 addition *J Phys D Appl Phys* **53** 205201

[50] Mejanes N de, Profili J, Babaei S, Naudé N and Stafford L 2021 Refined analysis of current–voltage characteristics in Townsend dielectric barrier discharges in nitrogen at atmospheric pressure *J Phys D Appl Phys* **54** 095204

[51] Naudé N, Cambronne J-P, Gherardi N and Massines F 2005 Electrical model and analysis of the transition from an atmospheric pressure Townsend discharge to a filamentary discharge *J Phys D Appl Phys* **38** 530–8

[52] Kogelschatz U 2002 Filamentary, patterned, and diffuse barrier discharges *IEEE Transactions on Plasma Science* **30** 1400–8

[53] Pipa A and Brandenburg R 2019 The Equivalent Circuit Approach for the Electrical Diagnostics of Dielectric Barrier Discharges: The Classical Theory and Recent Developments *Atoms* **7** 14

[54] Gherardi N and Massines F 2001 Mechanisms controlling the transition from glow silent discharge to streamer discharge in nitrogen *IEEE Transactions on Plasma Science* **29** 536–44

[55] Levasseur O, Stafford L, Gherardi N, Naudé N, Beche E, Esvan J, Blanchet P, Riedl B and Sarkissian A 2013 Role of substrate outgassing on the formation dynamics of either hydrophilic or hydrophobic wood surfaces in atmospheric-pressure, organosilicon plasmas *Surf Coat Technol* **234** 42–7

[56] Kossyi I A, Kostinsky A Y, Matveyev A A and Silakov V P 1992 Kinetic scheme of the non-equilibrium discharge in nitrogen-oxygen mixtures *Plasma Sources Sci Technol* **1** 207–20

[57] Pancheshnyi S v, Starikovskaia S M and Starikovskii A Y *Collisional deactivation of N 2 (C 3 P u , v ˆ 0, 1, 2, 3) states by N 2 , O 2 , H 2 and H 2 O molecules*

[58] Brandenburg R, Maiorov V A, Golubovskii Y B, Wagner H-E, Behnke J and Behnke J F 2005 Diffuse barrier discharges in nitrogen with small admixtures of oxygen: discharge mechanism and transition to the filamentary regime *Journal of Physics D: Applied Physics J. Phys. D: Appl. Phys* **38** 2187–97

[59] LAFFERTY J M 1998 *Foundations of Vacuum Science and Technology* (John Wiley & Sons, Inc. (US))

[60] Anon COMSOL Multiphysics®

[61] San O and Staples A E 2012 An improved model for reduced-order physiological fluid flows *J Mech Med Biol* **12**

Chapitre III. Dépôt de couches minces par injection de précurseur liquide

Dans le chapitre précédent, en ayant recours à des mesures électriques et optiques, et a des simulations numériques, il a été montré qu'une injection pulsée de gaz peut déstabiliser fortement la décharge en fonction des conditions opératoires et de la géométrie du réacteur. Il est important de noter que dans la suite de ce travail, le réacteur a été modifié afin d'éviter toute recirculation engendrant la modification de la composition du gaz au cours du temps. Il devient ainsi possible de garder un régime homogène avec une injection pulsée de gaz dans les mêmes conditions de décharge que les travaux précédents.

Dans ce contexte, nous souhaitons maintenant examiner d'abord la cinétique de dépôt, puis le comportement de la polymérisation, avec une injection pulsée de précurseur liquide. Après une brève description du réacteur, nos contributions sont présentées sous la forme de deux articles. La premier « Kinetics driving thin-film deposition in dielectric barrier discharges using a direct liquid injector operated in a pulsed regime » a récemment été accepté pour publication dans *Journal of Physics D: Applied Physics* (MS# 131902). Quant au second, « Soft polymerization of HMDSO droplets obtained by coupling pulsed aerosol injection with dielectric barrier discharge », il a récemment été soumis à *Plasma Processes and Polymers* (MS# 202200165).

III.1. Montage expérimental

III.1.1 Réacteur à plasma

Afin de s'affranchir des recirculations dans la chambre de mélange présentée au paragraphe II.3, les expériences pour le dépôt de couches minces sont effectuées dans une enceinte de plus grand volume avec un système d'injection du gaz directement dans la cellule de décharge (sans chambre de mélange). Ce réacteur à plasma est illustré à la Figure 28. Plus précisément, la décharge à barrière diélectrique est initiée entre deux électrodes en appliquant une tension sinusoïdale de fréquence 1 kHz et d'amplitude crête à crête égale à 13 kV_{pp} en

utilisant le même principe d'alimentation que celui décrit dans la Figure 25. Les diagnostics électriques sont également identiques à ceux présentés précédemment. La décharge est toujours alimentée en N_2 (Alphagaz 1, Air Liquide), le flux est contrôlé via un contrôleur de débit massique. La pression dans la chambre est fixée à 750 Torr par une vanne auto-régulée.

La cellule de décharge est composée de deux alumines de 7 cm sur 11.5 cm sur lesquelles sont peintes les électrodes de 3 cm x 6 cm. Les électrodes sont fixées sur un porte-électrodes, installé sur un rail dans l'enceinte du réacteur. À nouveau, les deux électrodes sont espacées de 1 mm grâce à des cales en verre. Lors d'un dépôt, l'échantillon de silicium est disposé sur l'électrode inférieure comme représentée à la Figure 28. Les cales en verre sont dans cette situation placées au-dessus du substrat pour maintenir un espace de 1 mm entre le substrat et l'électrode supérieure.

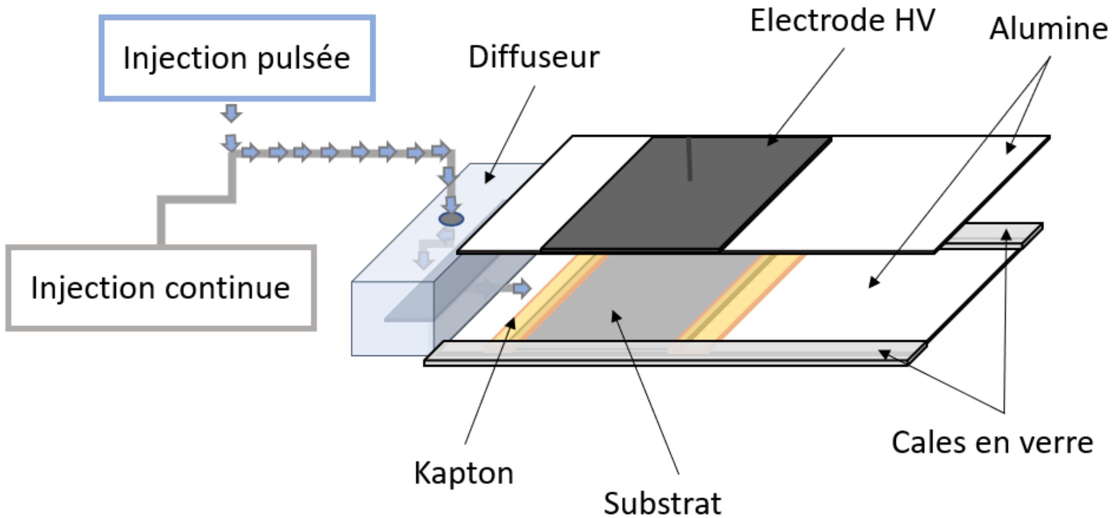

Figure 28: Schéma de l'espace de décharge et du système d'injection continu et pulsé

L'injecteur de liquide est monté en amont de la cellule de décharge et son fonctionnement est décrit dans la partie suivante. Afin de voir l'effet de l'injection pulsée du précurseur liquide sur le dépôt, dans certaines parties de ce travail, la durée du plasma est modifiée. Pour cela, le générateur est synchronisé sur le réacteur-injecteur. Ainsi, un délai entre l'injection et l'initiation du plasma peut être mis en place. De plus, le générateur peut envoyer un certain nombre de cycles à la suite du signal de synchronisation, ce qui permet d'allumer la décharge uniquement

sur une certaine partie de la période d'injection. Le temps de délais et le temps d'allumage de la décharge sont deux notions illustrées dans les schémas suivants :

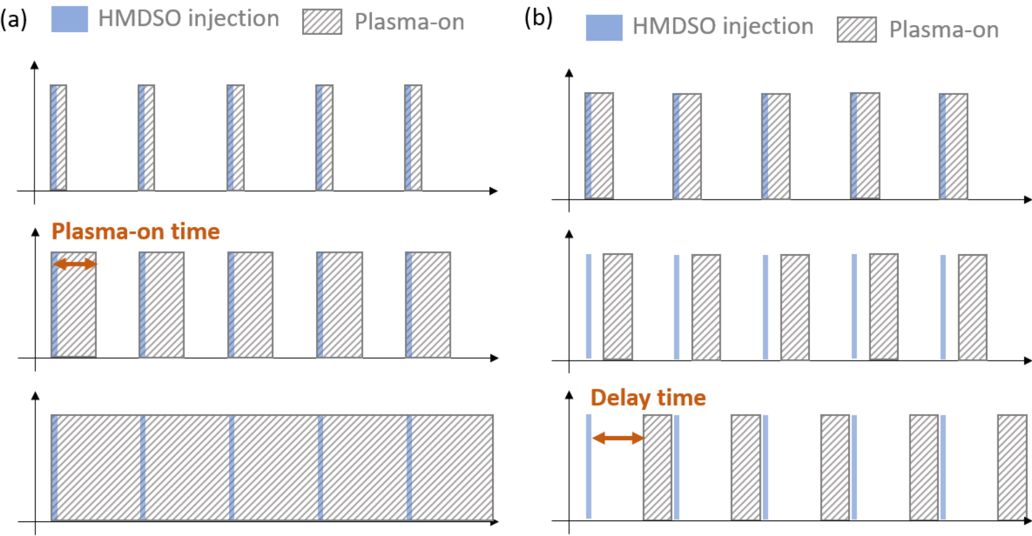

Figure 29: Représentation du temps de plasma allumé et du temps de délai

Un tel procédé de modulation du plasma a été utilisé dans la littérature pour contrôler le mécanisme de croissance des couches minces. Par exemple, *Manakhov et al.* [126] observe que la morphologie du dépôt ainsi que la vitesse de dépôt sont principalement liées au dépôt assisté par plasma pendant le temps allumé et à la polymérisation par radicaux libres durant le temps de délai entre deux décharges. *Hilt et al.*[127] montrent que la cinétique de dépôt dépend également du facteur cyclique (*duty cycle*) défini tel que $DC(\%) = \frac{t_{ON}}{(t_{ON}+t_{OFF})} \times 100$. Cependant comme décrit dans ces travaux, l'effet du temps de délai et du temps d'allumage de la décharge sur le dépôt dépend fortement du transport du précurseur pendant le temps de délai ainsi que de la durée de vie des espèces créées pendant le temps d'allumage de la décharge.

III.1.2 Injection directe de liquide

L'injection directe de liquide se fait via l'atomiseur Atokit de la compagnie Kemstream. L'injecteur est monté en amont de la décharge. Il est composé de deux chambres toutes deux reliées à deux bouteilles d'azote. La première ligne d'azote est gardée à une pression de 250 kPa et la deuxième à 200 kPa. Pour l'injection de liquide, la première ligne d'azote est reliée à un Fischer porter contenant le précurseur sous forme liquide, ici de l'HMDSO. Par surpression, le gaz

va pousser le liquide jusqu'à la première chambre. Le temps d'injection de liquide, et donc la quantité, vers la deuxième chambre est contrôlé par le t_{liq}. Ceci est l'étape 1 représentée à la Figure 30. L'étape 2 décrit le t_{off} qui est le temps durant lequel le liquide reste dans la seconde chambre. Cette chambre étant connectée à une ligne d'azote, un mélange azote + liquide sera injecté à l'étape 3. En effet, l'étape 3 correspond au t_{gaz} qui contrôle le temps d'ouverture entre la chambre de mélange et la sortie de l'injecteur, ici vers le procédé de dépôt par plasma. Enfin, ces trois étapes peuvent se répéter à une certaine fréquence choisie par l'opérateur pouvant aller de 0.1 à 50 Hz.

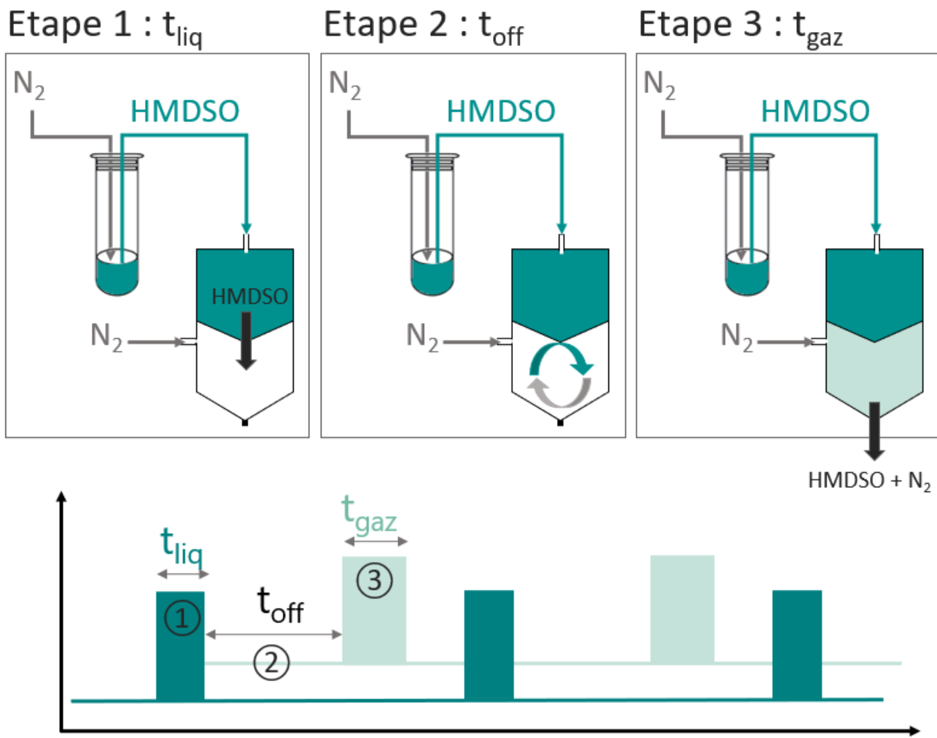

Figure 30: Schéma de fonctionnement de l'injecteur liquide.

III.2. Caractérisation ex-situ des couches minces par FTIR

La spectroscopie Infrarouge à Transformée de Fourier (FTIR) a été utilisée pour analyser la composition chimique des dépôts de manière non intrusive. Deux principales méthodes d'analyse FTIR existent, soit en réflexion (ATR) ou en transmission. Le principal inconvénient de l'ATR est la composante inconnue de la distance de pénétration dans la couche. De plus, l'échantillon doit être serré entre deux points lors de la mesure, ce qui peut affecter la couche. Pour ces deux

raisons, les dépôts sont analysés en transmission. Cela est également rendu possible, car les dépôts sont effectués sur des substrats optiquement transparent en silicium poli des deux côtés. Chaque spectre d'absorption représenté entre 400 et 4000 cm^{-1} est la moyenne de 16 scans avec une résolution spectrale de 4 cm^{-1}. Pour tous les spectres, le background est fait sur un substrat sans dépôt de sorte que l'absorbance de ce dernier n'est pas prise en compte dans les spectres. Les données sont extraites en transmittance pour être ensuite post-traitées avec un tableur afin de représenter l'absorbance. Pour cela, pour chaque spectre, une ligne de fond est générée passant par les minimums d'absorbance. La ligne de fond est ensuite retirée du spectre. Enfin le spectre d'absorbance est calculé à partir de la transmittance par la relation $A = -\,log_{10}T$.

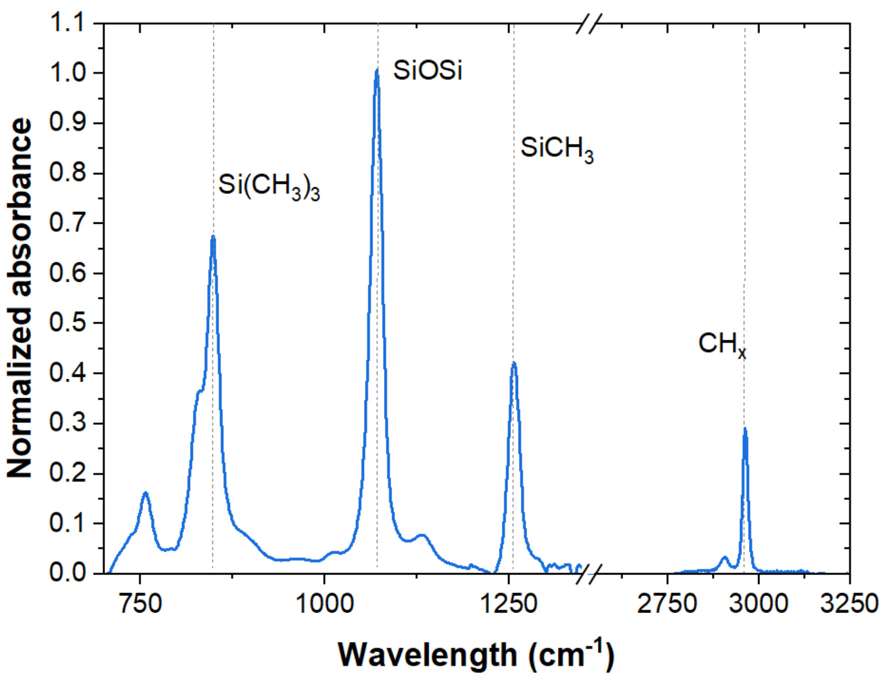

Figure 31: Spectre FTIR d'HMDSO liquide

Les bandes d'absorption typiques de l'HMDSO liquide sont présentées dans la Figure 31. Par apport d'énergie, la molécule d'HMDSO peut se briser et créer de nouvelles liaisons. Dans ces conditions, de nouvelles bandes d'absorption et des décalages spectraux vont apparaître. Parmi ces bandes, certaines sont analysées afin d'être reliées à un degré de polymérisation. Quelques bandes seront analysées plus en profondeur dans le travail qui suit telles que :

- L'aire et la position de la bande de SiOSi [111] ;

- L'aire de la bande de SiH ;
- Le ratio $\frac{Si(CH_3)_2}{Si(CH_3)_3}$ aussi appelé dans la littérature, degré de polymérisation [107].

III.3. (article) Kinetics driving thin film deposition in plane-to-plane dielectric barrier discharges using a direct liquid injector operated in a pulsed regime

Kinetics driving thin-film deposition in dielectric barrier discharges using a direct liquid injector operated in a pulsed regime

L. Cacot [1,3], G. Carnide [1,2], M. L. Kahn [2], R. Clergereaux[1],

N. Naudé[1‡] and L. Stafford[3§]

[1]Département de physique, Université de Montréal, Montréal, Québec, Canada

[2]LAPLACE, Université de Toulouse, CNRS, INPT, UPS, Toulouse, France

[3]LCC, CNRS (UPR 8241), Université de Toulouse, Toulouse, France

Abstract

This work investigates the effects of process parameters on thin-film deposition by Direct Liquid Injection in a low-frequency Dielectric Barrier Discharge (DBD). The precursor, hexamethyldisiloxane (HMDSO), is introduced as micrometer-size liquid droplets with nitrogen carrier gas in a pulsed mode and the discharge is produced at atmospheric pressure in a pulsed regime. No significant deposit is observed during plasma-off time and outside the discharge region. Despite the pulsed injection, this reveals that the precursor content in the plasma zone remains constant over much longer time scales and that thin-film deposition results from droplets charging and their transport towards the dielectrics by the low-frequency electric field. Over the range of experimental conditions investigated, it is

‡ Electronic mail: nicolas.naude@laplace.univ-tlse.fr

§ Electronic mail: luc.stafford@umontreal.ca

found that pulsed, aerosol-assisted plasma deposition is limited by the amount of energy provided to precursor droplets, and not by precursor insufficiency.

Keywords: Dielectric Barrier Discharge, Atmospheric Pressure Plasma Processes, Pulsed Direct Liquid Injection, Aerosol-Assisted Plasma Deposition, Organosilicon Coatings.

1. Introduction

Atmospheric-pressure plasmas operated in reactive gas mixtures are widely used for (multi)functional thin-film deposition. Among them, Dielectric Barrier Discharges (DBD), one of the most well-developed non-equilibrium plasmas, are frequently used to deposit thins films on large area surfaces [1,2]. Considering their broad range of applications, including anti-fogging capacity, corrosion protection ability, biocompatibility, moisture barrier and water-repellent properties [3–13], organosilicon thin films have been extensively researched, and the parameters controlling their deposition kinetics, structure, and morphology have been widely investigated. Based on the available literature, the so-called Yasuda's parameter, a parameter equivalent to the ratio of discharge power to precursor flow rate (W/F), is an important factor affecting plasma-deposited thin films [14]. *Park et al.* [15] reported that this parameter influences the chemical structure, density, and yield of the material deposited by plasma polymerization of hexamethyldisilazane using a radio frequency capacitive discharge. Similarly, *Petersen et al.* [16] reported that at low W/F, plasma-assisted polymerization of hexamethyldisiloxane (HMDSO) is dominated by oligomerization, leading to polydimethylsiloxane thin films, whereas at high W/F, cross-linked SiO_x thin films are formed. *Bardon et al.* [17] also assessed the effects of plasma power and precursor flow rate on acrylate thin-film deposition by semi-dynamic DBD operated in helium with 1,6-hexanediol dimethacrylate precursor. Their results indicate that these parameters have a strong influence on the energy supplied to precursor molecules, and thus on the plasma-assisted precursor conversion rate.

In addition to Yasuda's parameter, the plasma deposition kinetics and precursor polymerization dynamics depend on the plasma power injection controlled, for example, by the plasma-on time (duty cycle) [18–20]. In such pulsed plasma conditions, *Manakhov et al.*[19] proposed that plasma-assisted deposition occurs only during plasma-on time, whereas free radical polymerization occurs during plasma-off time. The studies conducted on thin-film deposition by plasma polymerization at atmospheric pressure further show that the morphology of the deposited material depends on the nature and flow of the precursor, which is usually introduced into the plasma chamber either directly as a gas (for

example, silane) or as a vapor from the liquid phase through an atomizing system (for example, HMDSO) [21–25]. In a study conducted on the deposition and polymerization of HMDSO by corona discharge, *O'Neil et al.* [26] showed that the surface morphology of the deposited material changes upon increasing the flow of the injected HMDSO precursor. The authors concluded that at low monomer flow rate, the precursor is fully vaporized, and deposition is due to the plasma polymerization of the gas-phase monomer. Meanwhile, at high flow rate, the precursor is not fully vaporized, and liquid droplets are introduced into the plasma chamber in the form of aerosols. Hence, droplets can interact with the plasma and contribute to the thin-film deposition process. The morphology of the organosilicon coatings deposited at high flow rate in the so-called misty plasma (combination of liquid, gas, and plasma states [27]) is different from the one achieved at low flow rate in a purely gas-phase plasma process. Despite the available studies, the effect of liquid droplets on plasma-assisted thin-film deposition at atmospheric pressure remains poorly understood due to the complexity of biphasic liquid-plasma interactions [28]. A better understanding of such features could bring new opportunities for material processing.

In this study, the effects of process parameters, namely, duty cycle, delay between precursor injection and discharge ignition, and the amount of injected HMDSO microdroplets on the plasma-assisted deposition of organosilicon thin films in low-frequency Townsend DBDs operated in nitrogen are assessed. In contrast to other studies based on aerosols and atmospheric-pressure plasmas reported in literature, direct-liquid injection and the discharge are both pulsed. This approach offers a wide parameter space for fundamental studies of misty plasmas at atmospheric pressure applied to thin-film deposition. Selected experiments are also done by varying the continuous flow of the N_2 gas used to carry along the discharge cell the precursor droplets injected and to underline the contributions of transport phenomena. Based on this complete set of data, the influence of the energy injected in the plasma per precursor molecule is explored and the predominant role of plasma-droplet interactions is highlighted.

2. Experimental setup and diagnostics

The experimental setup used in this study has been described previously [29–31]. It consists of a metallic chamber containing two horizontally mounted alumina plates coated with conductive silver paste to serve as plasma electrodes (3 cm × 6 cm). A silicon wafer substrate (4 cm × 7 cm) was fixed on the bottom alumina plate with Kapton tape, and two glass spacers were placed on top of the silicon substrate to keep the gas gap distance at 1 mm. In all experiments, the chamber was first filled with a continuous flow of N_2 gas (Alphagaz 1, Air Liquide) at atmospheric pressure. In this system, gas injection occurs through a diffuser located at the entrance of the plane-to-plane DBD cell, and a self-regulating valve located between the outlet of the plasma chamber and the vacuum pump is used to maintain the pressure at 750 Torr. Here, the diffuser and glass spacers ensure a longitudinal flow of the carrier gas and precursor through the DBD cell between the two alumina plates. DBD was ignited between the two metallic electrodes by applying a 1 kHz, 13 $kV_{peak\ to\ peak}$ sinusoidal signal that is generated using a Tektronix AFG3021C power supply connected to a linear power amplifier whose output is linked to the primary winding of a step-up transformer. A high-voltage probe (TektronixP6015A) connected between the high-voltage electrode (top electrode) and ground was used to measure the applied voltage. The flowing current and charge were deduced from the voltage values measured across a 100 Ω shunt resistor and a 220 nF capacitor, respectively; both were placed in parallel between the low-voltage electrode (bottom electrode) and ground. Meanwhile, the power injected into the DBD was calculated from Lissajous plots, based on the electrical signals acquired using an oscilloscope (TELEDYNE Lecroy HD06104A) and the approach described in [32–34].

The liquid HMDSO precursor (SigmaAldrich) along with a nitrogen carrier gas was injected into the discharge using a commercialized, two-stage, direct-liquid-injection system purchased from Kemstream. More specifically, the liquid contained in the precursor chamber (first stage) is injected in a pulsed mode in the mixing chamber of the device (second stage) filled with N_2 (Alphagaz 1, Air Liquide). The content of the mixing chamber (HMDSO precursor droplets and nitrogen carrier gas) is then injected in pulsed mode

through the diffuser in the plasma chamber. Injection, i.e. the quantity of liquid and gas injected in the DBD was controlled by the frequency and duration of the pulses. In this work, only the duration of the pulsed liquid injection (from stage 1 to stage 2) was varied between 2 (lower limit recommended by the manufacturer is 1.5 ms) and 6 ms; the pulse duration of precursor droplets and carrier gas was kept constant to 10 ms. As for the pulse repetition frequency, it was fixed to 0.1 Hz; hence, over the range of experimental conditions investigated, the discharge "sees" a new pulse every 10 s. In some cases, a continuous nitrogen carrier gas flow (between 0.07 and 1.4 $L.min^{-1}$), in addition to the pulsed HMDSO aerosol in nitrogen, was applied while maintaining atmospheric-pressure conditions. Such flow was used to examine the role of continuous precursor transport (and thus of the precursor residence time) across the inter-dielectric space.

To characterize the aerosol, the spray was illuminated with a blue light and observed at 45° using a FastCAM camera (APX RS Photron, 1500 fps). The aerosol was analyzed by post processing the recorded images with a MATLAB program to assess the time evolution of the light intensity scattered by liquid microdroplets. As an example, images of an aerosol of HMDSO in nitrogen produced with a pulsed liquid injection of 5 ms under atmospheric pressure conditions is reported in Figure 1a along the pulse injection period. As can be seen, this aerosol is composed of microdroplets that expand at the outlet of the injector. Over the range of experimental conditions investigated, the expansion rate along the longitudinal axis is about 5 $m.s^{-1}$. In addition, the variation of the total light scattering (integrated over the whole images of Figure 1a) was calculated over time and plotted in Figure 1b. Microdroplets are observed for 10 ms after the liquid is first detected, which confirms that the entire process of liquid injection into the DBD reactor occurs within the opening time of the second stage of the direct-liquid injection device, with no significant injection afterwards.

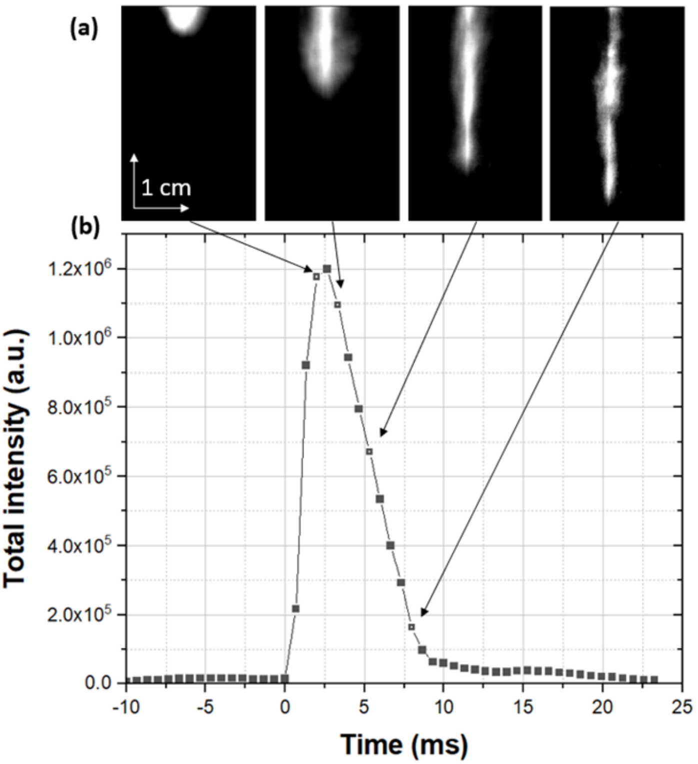

Figure 1: a) Fast camera images of the liquid precursor recorded at different times during the injection process. Of note, on each image, even if the maximum intensity decreases with time, the contrast was adjusted for aerosol visualization. b) Variation of the total light intensity scattered by liquid droplet as a function of time for 10 ms injection.

After plasma deposition, the silicon substrate was removed for thin-film thickness measurements. However, the plasma-deposited layers are soft and thus not easily measurable by profilometry. In addition, the composition and structure of the film are unknown to use a reliable spectroscopic ellipsometry model. Therefore, they were analyzed by Fourier Transform InfraRed (FTIR) in a transmission mode (Bruker). Of note, FTIR spectra emphasize the typical bands reported in the literature of plasma-polymerized HMDSO with the main feature of Si–O–Si (1200–1000 cm^{-1}) bands [35–37]. Hence, considering Beer-Lambert law, FTIR is used to extract a relative thickness of the deposited thin film (in arbitrary unit) by integrating the area of the Si-O-Si absorption band.

3. Dielectric barrier discharge with direct liquid injection

The electrical characteristics (voltage, current, and charge) of nitrogen discharge with and without direct liquid injection are presented in Figure 2. As shown in Figure 2a, the electrical characteristics of the DBD generated with pulsed flow of N_2, in the absence of liquid HMDSO precursor, are representative of a homogeneous Townsend discharge [38]. Of note, depending on the experimental conditions, pulsed nitrogen gas injection in a Townsend discharge operated with a continuous nitrogen gas flow can destabilize the discharge [39]. Such effect is not linked to the sharp and narrow temporal gas velocity profiles, but rather to gas recirculations in presence of singular head losses. In a previous study [39], it was shown that these flow perturbations arising from irregularities from the inlet pipe to the gas mixing chamber and then to the DBD cell combined with impurities outgassing from the walls introduce significant changes in the neutral gas composition. In particular, the release of oxygen impurities with abnormal concentrations over time scales much longer than the pulse duration was shown to plays a vital role on the Townsend discharges' physics and characteristics. Here, to prevent gas recirculations and changes in the neutral gas composition, the gas and precursor inlet line were simplified to minimize singular head losses. Consequently, identical current-voltage characteristics are recorded with continuous N_2 flow and pulsed N_2 gas injections.

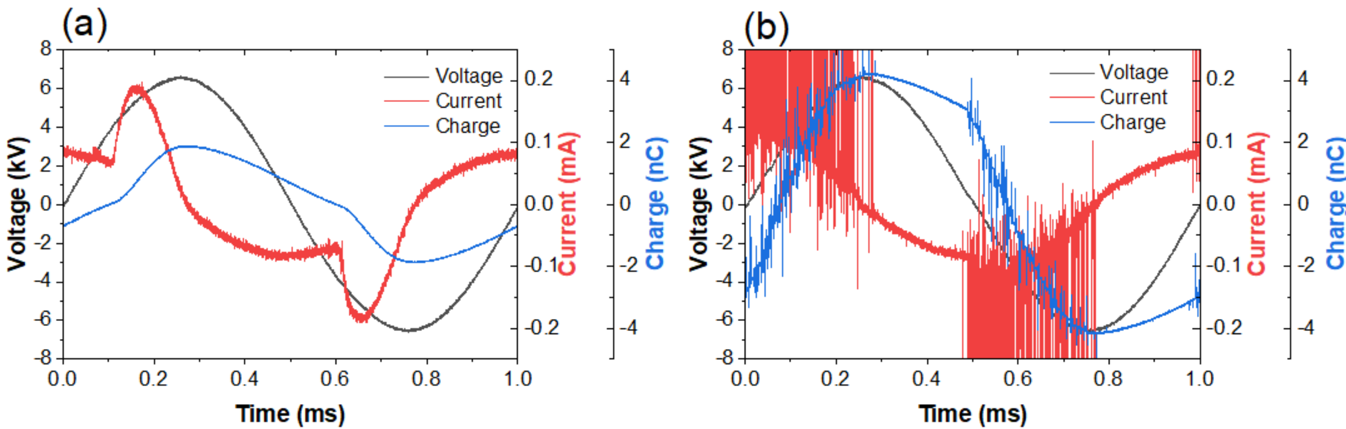

Figure 2: Applied voltage, current, and charge profiles recorded with pulsed N_2 flow (a) without and (b) with direct liquid HMDSO injection at 10 ms pulse duration and 0.1 Hz pulse frequency.

In the presence of a pulsed aerosol of HMDSO with nitrogen carrier gas, sudden current increase (shown by a saturation of the input channel of the oscilloscope) and increased charge values are detected (Figure 2b). This confirms that micro-discharges appear, and that the discharge transits from homogeneous to filamentary regime following direct injection of micrometer droplets [1,40]. Such features most likely arise due to the loss of long-lived metastable $N_2(A)$ states that are involved in the production of seed electrons by secondary electron emission [38], but also by associative ionization between excited nitrogen atoms and atomic oxygen [41,42].

4. Interaction between Townsend discharge and injected liquid

Figure 3 presents the spatial distribution of the organosilicon deposit collected after 2 min. of plasma discharge exposure for a 10 ms direct liquid injection duration and a 0.1 Hz liquid injection frequency. Considering the scheme of the deposition process, the deposit is observed only where the discharge occurs, i.e., between the two metallic electrodes that do not cover the whole surface of the two alumina plates. Pre- and post-discharge deposits are not visible to the naked eye. To confirm this observation, FTIR spectra of the substrate surface were recorded at five different positions along the gas flow lines. The graph in Figure 3 presents the spatial variation of the film relative thickness: it is higher between the electrodes, without deposition before and after the electrode area. Polymerization and deposition thus occur only in the presence of plasma. To corroborate this hypothesis, the same experiment was carried out at an applied voltage lower than the breakdown voltage. No deposition was observed, even if an electric field is present. This indicates that deposition results from plasma-droplet interactions.

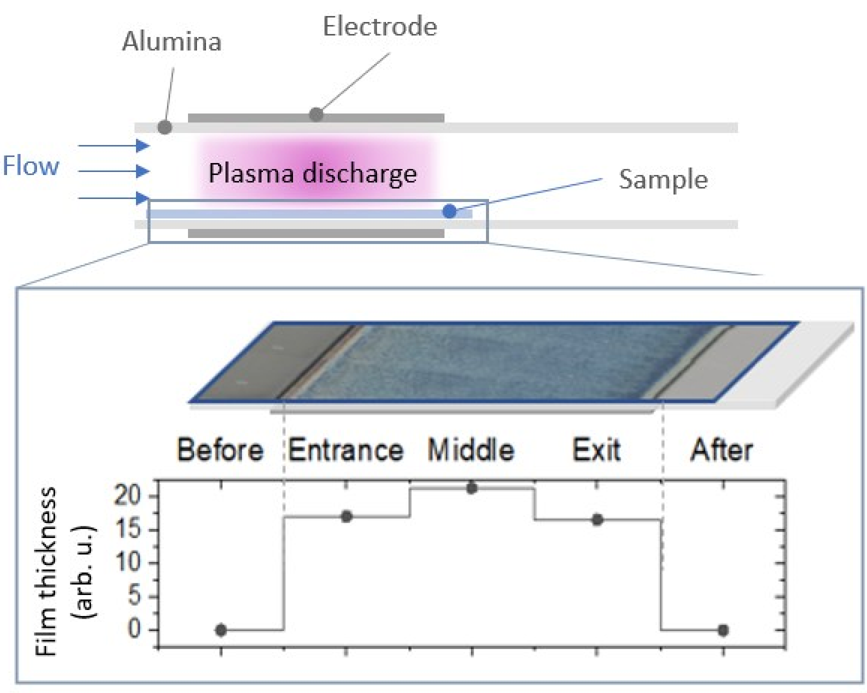

Figure 3: Scheme of the deposition process and spatial distribution of the organosilicon deposit. The results for the film thickness are obtained from the Si-O-Si band area recorded by FTIR analysis. As a rough estimate, a film thickness of about 20 arb. unit throughout this work corresponds to about 1 µm.

5. Thin-film deposition with direct liquid injection

5.1. Influence of plasma-on time

To understand the kinetics driving organosilicon thin film deposition with direct liquid injection, the discharge was pulsed in synchronization with each pulsed, 10 ms, 0.1 Hz injection of liquid. In the first set of experiments, the plasma-on time during which a voltage is applied between the two electrodes of the DBD cell was varied between 10 ms (during pulsed liquid injection with no time delay) and 10 s (referring to a continuous plasma) (Figure 4a). The material deposited on the substrate under different conditions for a total process duration of 4 min. (24 pulses of HMDSO) was analyzed by FTIR, and the variation of the film thickness was extracted and plotted as a function of plasma-on time. In Figure 4b, the result for each condition corresponds to an average over all positions

along the gas flow lines, and the error boxes represents the inhomogeneity of the film. Each experiment were repeated several times and standard deviation were low compared to thickness variations along the gas flow lines. As can be seen, the thickness of the deposited film linearly increases with plasma-on time up to 10 s. Hence, enhanced deposition rates over the total process duration of 4 min. are observed at longer plasma-on times, even though liquid injection occurs for only 10 ms. From this set of data, it seems that the amount of liquid injected within 10 ms interacts with the plasma for at least 10 s, and that the precursor remain confined in the plasma zone between the two electrodes over this whole timescale. Such conclusion reveals that the precursor is charged upon exposure to charged species as expected for micrometer droplets [43,44] and that thin-film deposition results from the transport of charged droplets towards the dielectrics by the low-frequency electric field. In such conditions, charged droplets in the misty plasma [27] behave as charged solid particles in a dusty plasma [27,45].

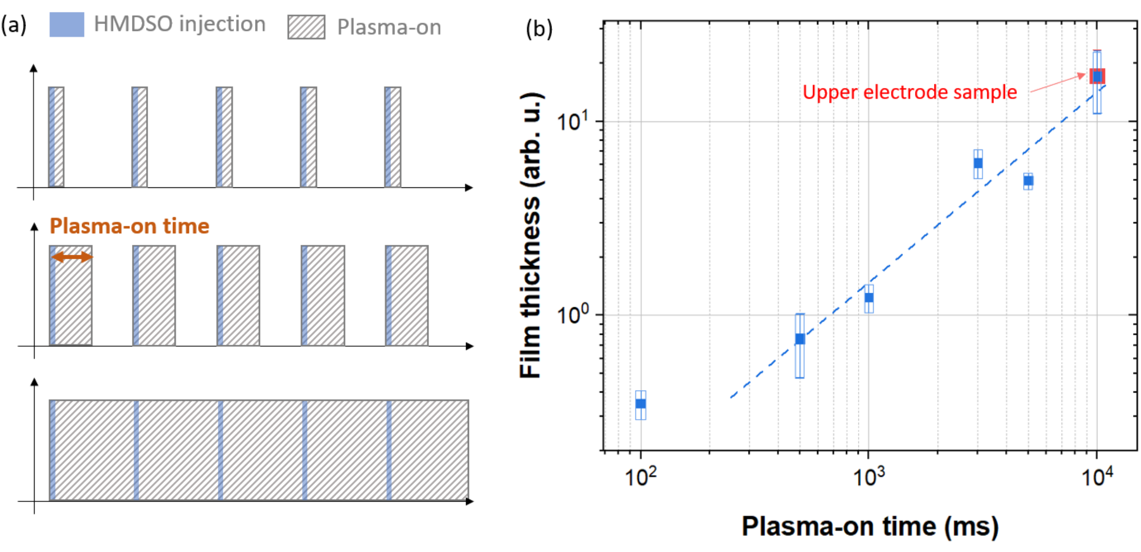

Figure 4: a) Schematics of the plasma-on time with respect to the pulsed HMDSO injection. The plasma-on time rises from the top to the bottom. b) Variation of the film thickness for a total process time of 4 min. (linked to the deposition rate) as a function of plasma-on time. Pulsed injection time of 10 ms, pulsed injection frequency of 0.1 Hz. Here, 10 s corresponds to a continuous plasma deposition. All measurements were recorded on a sample placed on the bottom dielectric, except for one condition highlighted in red as "Upper dielectric sample" which completely overlap the one obtained for the same treatment on the bottom electrode.

Knowing that the injected droplets can be deposited on both dielectrics, the top as well as the bottom one, an experiment was conducted to ensure that the material on the bottom dielectric is fully attributed to plasma processing and does not form over time due to other mechanisms such as gravity. In this experiment, the substrate was placed on the top dielectric, and the thickness of the film deposited on this substrate after 4 min. of continuous plasma processing (plasma-on time = 10 s) was measured (red square symbol in Figure 4b). Taking the error margins into account, the deposited film has the same thickness (and thus the same deposition rate) as the one deposited on the bottom dielectric under the same conditions. This indicates that the top dielectric is not a source of precursor and therefore of plasma deposition. It further underlines that the low-frequency electrostatic force induces a motion of charged droplets towards both the top and bottom dielectrics and play a very important role in aerosol-assisted plasma deposition with respect to other ones such as gravitational, thermophoresis, and dielectrophoresis forces [45]. Notably, the film thickness measured at very short plasma-on times seems higher than the linearity line seen at longer times. However, recall that the films deposited at short plasma-on times are quite thin, and so, their measured thickness is largely uncertain. At plasma-on times greater than 500 ms, the ratio of film thickness to plasma-on time is constant. This confirms that the precursor is always present in the gas gap, even at liquid injection pulse durations as low as 10 ms.

5.2. Influence of the delay between liquid injection and discharge ignition

According to previous studies, thin-film deposition in pulsed plasmas can also occur during plasma-off time [19,20,46]. Herein, the impact of plasma-off time was assessed by varying the delay period between liquid injection and discharge ignition (Figure 5a). The plasma-on time was fixed at 500 ms and the delay time was varied from 0 to 5 s (a half time of the injection period). As shown in Figure 5b, the film thicknesses at 0, 100, 500, 1000, and 5000 ms delay times for a total process time of 4 min. are in the same range. This means that the deposition rate is independent of the delay time. Hence, the quantity of precursor

does not change during the period between two pulses (i.e., 10 s for a liquid injection frequency of 0.1 Hz). Based on these results, the deposition occurring during plasma-off time seems negligible compared to the one achieved during plasma-on time. This last observation further confirms a strong interaction between the injected droplets and the plasma. Upon plasma exposure, HMDSO droplets are charged such that they can become confined in the gas gap by the low-frequency electric field. The latter is also responsible for their transport towards the dielectric allowing the thin-film deposition. In line with this result, the transport of the droplets and their residence time in the inter-dielectric space can play a critical role in the deposition process. It is therefore proposed in the next section to analyse plasma assisted deposition in the presence of a continuous carrier gas flow of nitrogen, in addition to the pulsed HMDSO aerosol in nitrogen.

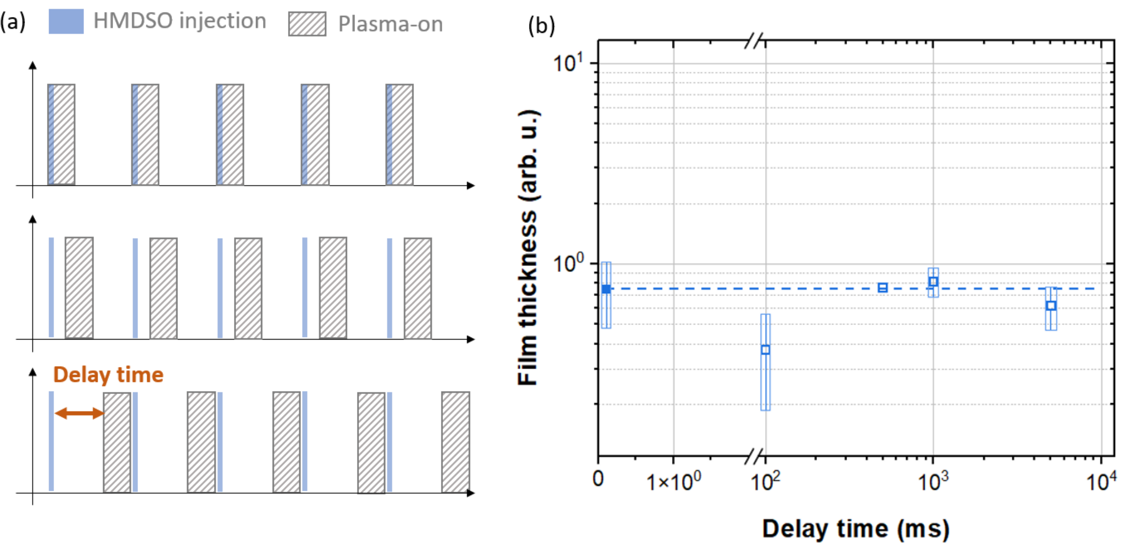

Figure 5: a) Schematics of the delay time with respect to the pulsed HMDSO injection. The delay time rises from the top to the bottom. b) Variation of the film thickness for a total process time of 4 min. (linked to the deposition rate)) as a function of delay time between liquid injection and discharge ignition. Pulsed injection time of 10 ms, pulsed injection frequency of 0.1 Hz, plasma-on time is fixed at 500 ms.

5.3. Influence of a continuous nitrogen gas flow

Most plasma processing studies involving continuous vapors or aerosols injection make use of a continuous carrier gas flow to transport the precursor towards the discharge zone. Modification of this flow rate induces variations in the residence time of the precursor because of drag forces between carrier gas and precursor droplets, thereby affecting the thickness of the plasma-deposited film. The film thicknesses for a total process duration of 4 min. are determined and reported on Figure 6a over the range of carrier gas flow of 0–2 $L.min^{-1}$. Clearly, the film thickness, and thus the film deposition rate significantly decreases with increasing rate of continuous gas flow. This can readily be explained by a lower residence time of HMDSO droplets in the plasma.

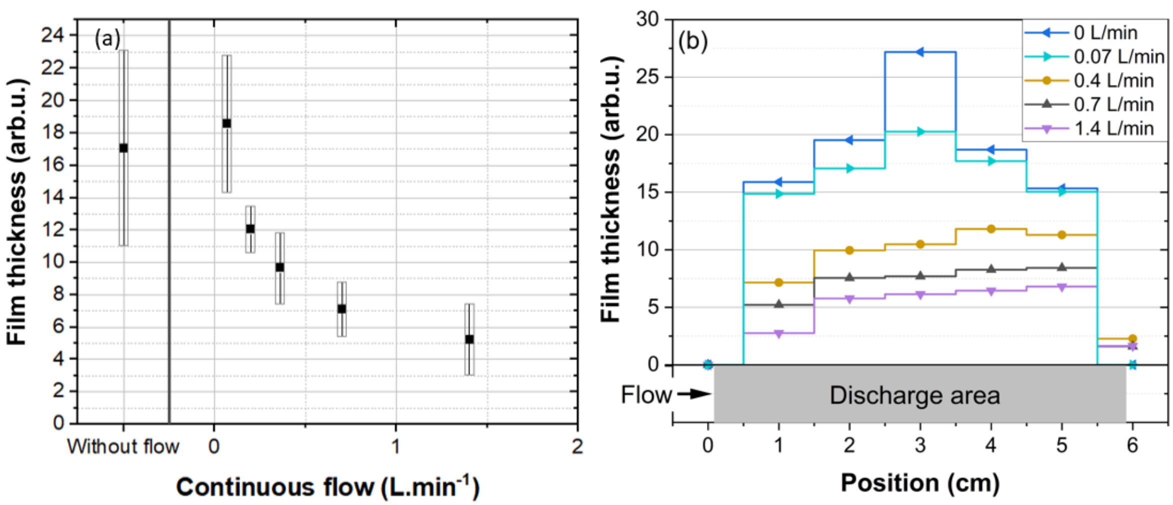

Figure 6: (a) Variation of the film thickness for a total process time of 4 min. (linked to the deposition rate) as a function of continuous N_2 gas flow rate. (b) Spatial deposition profiles along the gas flow lines recorded at different continuous flow rates. Pulsed injection time of 10 ms, pulsed injection frequency of 0.1 Hz, plasma-on time is fixed at 500 ms.

To further assess the role of carrier gas, coatings were analysed at seven different positions along the gas flow, under varying conditions of continuous N_2 flow rate. As shown in Figure 6b, when the flow rate of N_2 is lower than 0.1 $L.min^{-1}$, maximum deposition occurs at the centre of the substrate. As the flow rate is increased beyond 0.1 $L.min^{-1}$ (up to ~2 $L.min^{-1}$), the maximum thickness of the deposited film decreases and moves closer to

the outlet [47]. Notably, for this range of continuous gas flow, a small deposit is observed after the discharge compared to the absence of post discharge deposition without a continuous carrier gas. This result is consistent with the results reported by *Sarra-Bournet et al.* [48] which observe the appearance of a post discharge deposit by increasing the continuous flow in classical vapor-assisted plasma deposition conditions. Overall, these results indicate that the force on droplets linked to the presence of a nitrogen flow rate in the $L.min^{-1}$ range can compete with the electrostatic force on charged droplets leading to thin-film deposition on the substrate surface. This explains the displacement of the deposit towards the exit at higher continuous N_2 gas flow rates. In addition, when the continuous flow rate increases, the residence time of the species in the inter-dielectric space decreases, and interactions between the plasma and the droplets are restricted, resulting in the deposition of thinner films.

In line with these findings, it can be proposed that thin-film deposition with direct-liquid injection in a DBD results from the mechanisms illustrated in Figure 7. Upon exposure to the low-frequency DBD, HMDSO droplets are rapidly charged. Considering average ion and electron number densities of $\sim 10^{12}$ cm^{-3} in filamentary discharges operated in nitrogen [1] and assuming that the droplet charging time is given by the inverse of the ion plasma frequency [49], charging of HMDSO droplets most likely occurs within ~5 ns. Hence, droplets become charged over times much shorter than (i) the time scales of microdischarges (~100 ns) in filamentary DBDs [34], (ii) the period of the applied electric field (1 ms at 1 kHz), and (iii) the gas residence times linked to pulsed (~3 ms) and continuous gas flows (~150 ms at 0.7 L/min).

Once charged, without continuous nitrogen gas flow, it was highlighted that the electrostatic force controls the droplet motion and thus the thin-film deposition over both top and bottom dielectrics. For a steady-state charge of $\sim 10^4$ electrons per 10 m HMDSO droplet (and thus a mass-to-charge ratio $\sim 10^2$ kg/C) [44,50], the amplitude of oscillations of charged droplets in a 7.5 $kV.mm^{-1}$ electric field at 1 kHz is comparable to the gas gap (~1 mm). This indicates that the collection of HMDSO droplets on the dielectrics leading

to organosilicon thin-film deposition strongly depends on their size: droplets much smaller than 10 μm are easily collected within half-period of the applied electric field whereas droplets much larger than 10 μm remain trapped over multiple low-frequency cycles until they become pushed out of the DBD cell by the carrier gas. As the flow of continuous nitrogen gas increases, the contribution of the neutral drag force increases such that the transport of droplets along the gas flow lines becomes more important. For example, the ratio of neutral drag-to-Coulomb force amplitude on 10 μm HMDSO droplets with $\sim 10^4$ electrons is 1% at 0.07 $L.min^{-1}$ and 17% at 1.4 $L.min^{-1}$.

In the collection criterion discussed above, HMDSO droplets immersed in the filamentary DBD were assumed to acquire a charge uniformly distributed over the whole surface (see Figure 7). However, over the range of experimental conditions investigated, the Debye length in microdischarges is comparable to the droplet size. Thus, spatially inhomogeneous charging of HMDSO droplets can modify the balance between the inward surface tension of the liquid and the outward electrostatic and liquid pressure forces. This can cause the droplet to become unstable and undergo Coulomb fission [44,51], before reaching the so-called Rayleigh condition [52]. The result is the formation of smaller progeny droplets from unstable parent droplets. Because of the high amplitude of oscillations of progeny HMDSO droplets, they can more easily be collected on the substrate following their interaction with the low-frequency electric field. Hence, thin-film deposition using direct-liquid injection of HMDSO in the filamentary DBD may become linked to the amount of energy provided to precursor droplets for charging, electrostatic deformation, and fission; this aspect is examined in more details in the next section. Of note, as highlighted by *Coppins* [27], the time scales for droplet electrostatic deformation in misty plasma processes are usually much shorter than the one for droplet evaporation, both in and out of the plasma. Thus, for the Coulomb fission phenomenon of interest here, evaporation kinetics can be neglected.

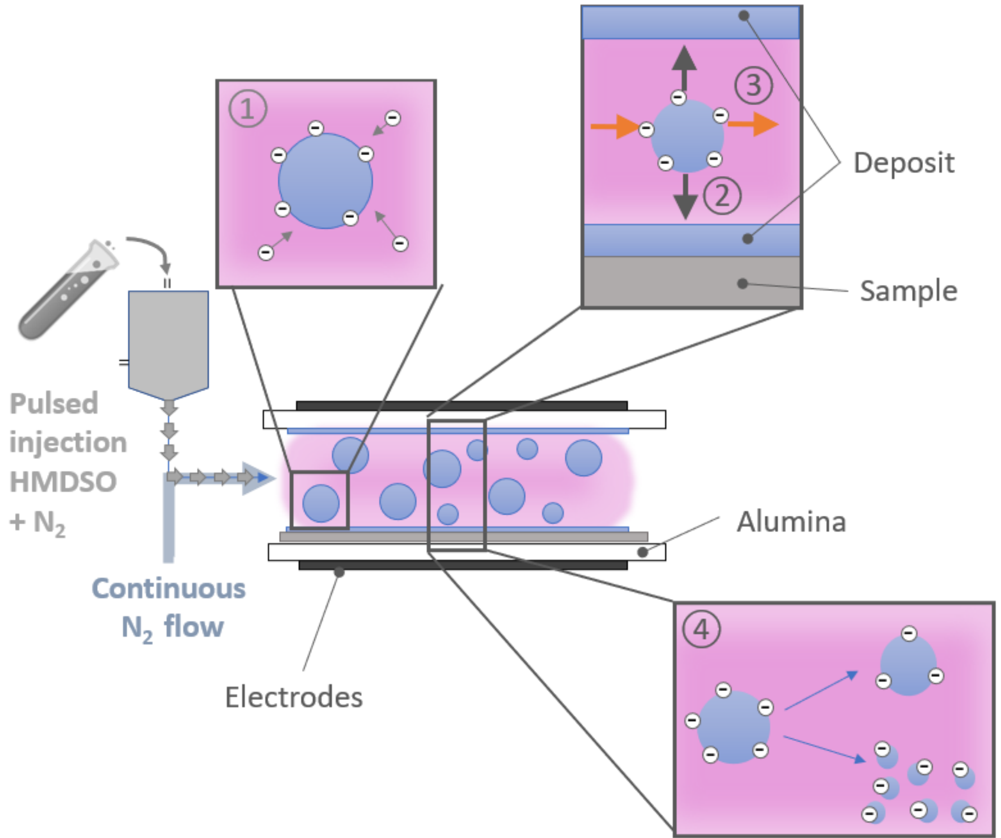

Figure 7:Scheme of the different mechanisms involved in thin-film deposition of organosilicon coatings by pulsed injection of HMDSO droplets into a DBD. Mechanisms include (1) droplet charging, (2) Coulomb and (3) Neutral drag forces on droplets, and (4) Electrostatic deformation leading to Coulomb fission.

5.4. Influence of the energy injected into the discharge

It is well-established that the Yasuda parameter relating plasma power to precursor flow rate is one of the most important factors affecting the plasma-precursor interaction and thus plasma deposition and polymerization kinetics. These studies make use of a continuous gas flow to transport the precursor vapor into the plasma. Considering that in some experiments conducted herein no continuous gas flow was used, we interpret the Yasuda parameter as the ratio of power injected into the DBD to precursor residence time. In such case, the energy parameter can be defined as follow (also called by some authors Specific Energy Input (SEI) [53]):

$$E = P \times t_{residence} \times Duty\ Cycle \qquad (1)$$

where P is the power determined from electrical analysis of the DBD, $t_{residence}$ is the average time during which the gas remains in the discharge (calculated based on the dimensions of the inter-dielectric space and the continuous N_2 gas flow rate), and *Duty Cycle* is the ratio between the plasma-on time and the liquid injection time. At zero continuous gas flow, the residence time of the precursor seems infinite. However, since the pressure in the chamber is maintained at 750 Torr by pumping, the liquid precursor flows inside the plasma chamber. Looking at Figure 6a, the thickness of the film obtained for a N_2 gas flow rate of 0.1 $L.min^{-1}$ is comparable to the one of the films obtained in the absence of a continuous N_2 gas flow. If the average thickness of the deposit depends mainly on the residence time of the species in the discharge, it may be hypothesized that the pumping system generates a flow equivalent to ~0.1 $L.min^{-1}$ continuous gas flow.

To assess the effect of the energy parameter provided by Equation (1) on the kinetics driving organosilicon thin-film deposition by direct liquid injection into nitrogen DBDs, the thickness profile extracted from Si-O-Si peak area as a function of energy was plotted for a total process duration of 4 min. As shown in Figure 8, the thickness of the deposited film, linked to the deposition rate, increases linearly with the energy in the early stages. Hence, the deposition rate is limited by the amount of energy provided to precursor molecules, and not by precursor insufficiency [16,17,54]. However, beyond ~0.05 $J.cm^{-2}$, the increase becomes less significant with a departure from the proportional curve, which suggests either a saturation in conversion or a limitation in the precursor quantity; we will come back to this point later on.

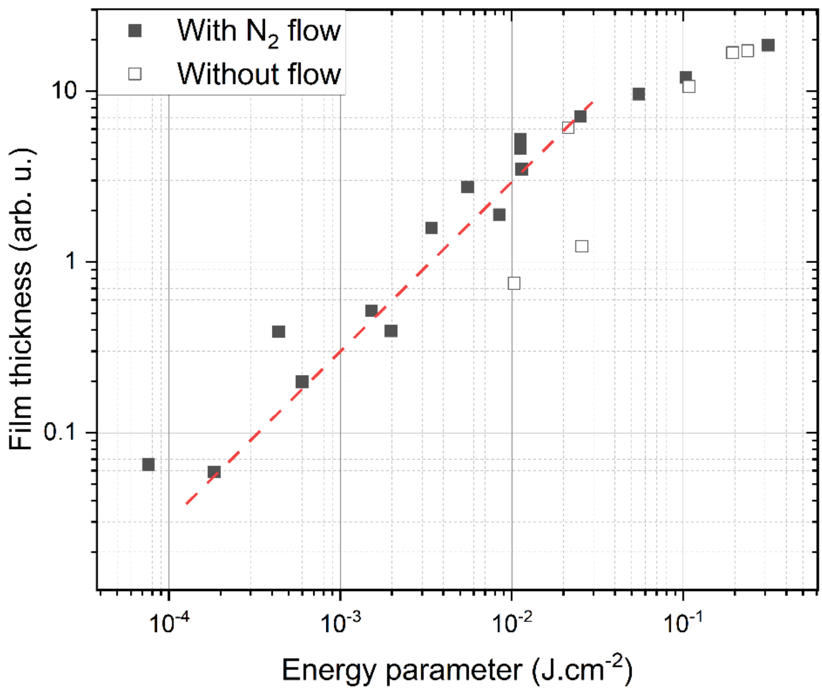

Figure 8: Variation of film thickness recorded for a total process time of 4 min. (linked to the deposition rate) as a function of the energy parameter. Pulsed injection time of 10 ms, pulsed injection frequency of 0.1 Hz. The results are shown for various plasma-on times and delay times between precursor injection and plasma ignition with or without a continuous N_2 gas flow.

5.5. Influence of the quantity of liquid injected into the discharge

In the previous sub-section, we have shown that the thickness of the deposited organosilicon film depends only on the plasma-on time and not on the delay between pulsed liquid injection and discharge ignition. Furthermore, by plotting the variation of film thicknesses as a function of the energy parameter, we have seen that the plasma deposition rate is first energy-limited and then deviates from this trend at higher energies. To examine the effect of the quantity of liquid injected into the discharge on the amount of plasma-deposited material, the liquid opening time of the direct-liquid injector (time during which the liquid flows from the liquid chamber of the injector to the injection chamber)

was varied. Of note, all results presented previously were recorded at 5 ms liquid opening time and 10 ms injection duration. Figure 9a and b show the variation of liquid flow, film thickness, and mean power density injected into the DBD, respectively, as a function of liquid opening time (t_{liq}) between 2 and 6 ms, at constant injection duration (10 ms) and frequency (0.1 Hz). As expected, the results presented in Figure 9a reveal that the amount of liquid injected into the DBD cell increases linearly with t_{liq}. Such feature is linked to an increase in the number and/or size of the HMDSO droplets. Over the same range of experimental conditions, the power density injected into the DBD remains almost constant at around 0.2 $W.cm^{-2}$ (Figure 9c). As for the film thickness, also shown in Figure 9b, despite the significant rise in liquid flow, it does not increase with t_{liq}. As previously discussed from the data presented in Figure 8, this confirms that the discharge is saturated with precursor. In other words, the power provided by the discharge enables the deposition of the same quantity of precursor, irrespective of the amount of precursor injected. Here, in addition to plasma deposition and plasma polymerization, the energy is also used to induce droplet charging, electrostatic deformation, and Coulomb fission. As for the departure from the linear trend observed at high energy parameters in Figure 8, since it cannot be linked to a precursor insufficiency, other mechanisms must be involved, for example, the gas phase coalescence of droplets because of mutual interactions [43,55] or different plasma polymerization processes.

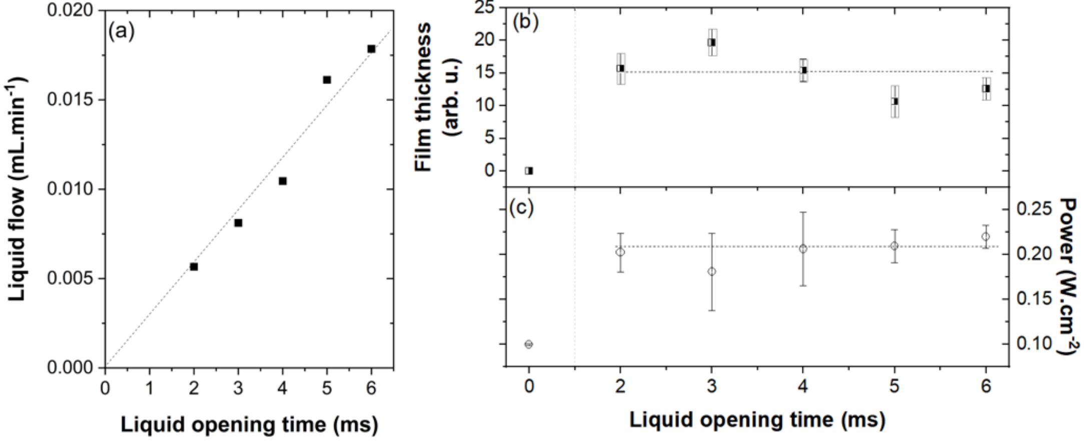

Figure 9: Variation of (a) liquid flow, (b) film thickness recorded for a total process time of 4 min. (linked to the deposition rate), and (c) mean power density injected into the DBD as a function of liquid opening time.

6. Conclusion

This study investigates the kinetics driving the plasma-assisted deposition of organosilicon thin films using pulsed HMDSO aerosols with nitrogen into a DBD at atmospheric pressure. The effects of plasma-on time, delay between precursor injection and plasma ignition, continuous gas flow, and liquid quantity on the thickness (or rate) of the plasma-deposited film were assessed. The obtained results show that the deposit thickness (or rate) is proportional to the plasma-on time; however, it is independent of the plasma delay time. This indicates that the precursor is always present in the inter-dielectric gap, even if injection only occurs over a short time scale with respect to the pulsed injection frequency. In such conditions, thin-film deposition results from droplets charging and their transport towards the dielectrics by the low-frequency electric field. Moreover, the use of a nitrogen carrier gas flow leads to thinner films whose maximum thickness is shifted towards the exit of the substrate. Hence, the transport of droplets with the nitrogen carrier gas flow along the gas flow lines competes with the thin-film deposition as a result of plasma-droplet interactions on the substrate surface. Finally, the deposition is favored by an increase in the energy provided per precursor molecule. In addition to plasma deposition and polymerization, such energy is also used for droplet charging, electrostatic deformation, and fission. Future studies will aim at exploring the physico-chemical structure of such films, in particular the extent of plasma polymerization and retention of the initial monomer structure for technological applications.

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Data availability statement

The data are available from the corresponding author upon request.

References

[1] Massines F, Sarra-Bournet C, Fanelli F, Naudé N and Gherardi N 2012 Atmospheric pressure low temperature direct plasma technology: Status and challenges for thin film deposition *Plasma Processes and Polymers* **9** 1041–73

[2] Merche D, Vandencasteele N and Reniers F 2012 Atmospheric plasmas for thin film deposition: A critical review *Thin Solid Films* **520** 4219–36

[3] Vautrin-Ul C, Boisse-Laporte C, Benissad N, Chausse A, Leprince P and Messina R 2000 Plasma-polymerized coatings using HMDSO precursor for iron protection *Prog Org Coat* **38** 9–15

[4] Saloum S Ã, Naddaf M and Alkhaled B 2008 Properties of thin films deposited from HMDSO / O 2 induced remote plasma : Effect of oxygen fraction **82** 742–7

[5] Profili J, Levasseur O, Koronai A, Stafford L and Gherardi N 2017 Deposition of nanocomposite coatings on wood using cold discharges at atmospheric pressure *Surf Coat Technol* **309** 729–37

[6] Gherardi N, Maechler L, Naudé N and Massines F 2009 APGD and APTD for the deposition of silicon based thin films from N 2 O / HMDSO mixtures : application to gas-barrier layers *Ispc 19* pp 1–4

[7] Fanelli F 2010 Thin film deposition and surface modification with atmospheric pressure dielectric barrier discharges *Surf Coat Technol* **205** 1536–43

[8] Meunier L, Profili J, Babaei S, Asadollahi S, Sarkissian A, Dorris A, Beck S, Naudé N and Stafford L 2020 Modification of microfibrillated cellulosic foams in a dielectric barrier discharge at atmospheric pressure *Plasma Processes and Polymers* **2000158**

[9] Kale K H and Palaskar S 2010 Atmospheric pressure plasma polymerization of hexamethyldisiloxane for imparting water repellency to cotton fabric *Textile Research Journal* **81** 608–20

[10] Frari D Del, Bour J, Bardon J, Buchheit O, Arnoult C and Ruch D 2009 Hybrid Layers Deposited by an Atmospheric Pressure Plasma Process for Corrosion Protection of Galvanized Steel **9** 1–9

[11] Asadollahi S, Farzaneh M and Stafford L 2019 On the Icephobic Behavior of Organosilicon-Based Surface Structures Developed Through Atmospheric Pressure Plasma Deposition in Nitrogen Plasma *Coatings* **9** 679

[12] Lin Y-C and Wang M-J 2019 Fabrication of hydrophobic/hydrophilic HMDSO films by atmospheric pressure plasma jet deposition *Jpn J Appl Phys* **58** SAAC01

[13] Meshkova A S, Elam F M, Starostin S A, van de Sanden M C M and de Vries H W 2018 The role of carrier gas flow in roll-to-roll AP-PECVD synthesized silica moisture barrier films *Surf Coat Technol* **339** 20–6

[14] Lin Y and Yasuda' H 1995 Effect of Plasma Polymer Deposition Methods on Copper Corrosion Protection *J Appl Polym Sci* **60**

[15] Park S Y, Kim N, Kim U Y, Hong S I and Sasabe H 1990 Plasma Polymerization of Hexamethyldisilazane *Polym J* **22** 242–9

[16] Petersen J, Bardon J, Dinia A, Ruch D and Gherardi N 2012 Organosilicon Coatings Deposited in Atmospheric Pressure Townsend Discharge for Gas Barrier Purpose: Effect of Substrate Temperature on Structure and Properties *ACS Appl Mater Interfaces* **4** 5872–82

[17] Bardon J, Dieden R, Grysan P, Mertz G, Martin A, Delmée M and Ruch D 2019 Mechanical properties of thin plasma polymer coatings from hexanediol dimethacrylate and relations with their chemical properties *Surf Coat Technol* **358** 320–30

[18] Moreno-Couranjou M, Guillot J, Audinot J-N, Bour J, Prouvé E, Durrieu M-C, Choquet P and Detrembleur C 2020 Atmospheric pulsed plasma copolymerization of acrylic monomers_ Kinetics, chemistry, and applications *Plasma Processes and Polymers* **17**

[19] Manakhov A, Moreno-Couranjou M, Boscher N D, Rogé V, Choquet P and Pireaux J-J 2012 Atmospheric Pressure Pulsed Plasma Copolymerisation of Maleic Anhydride and Vinyltrimethoxysilane: Influence of Electrical Parameters on Chemistry, Morphology and Deposition Rate of the Coatings *Plasma Processes and Polymers* **9** 435–45

[20] Hilt F, Duday D, Gherardi N, Frache G, Didierjean J and Choquet P 2015 Plasma polymerisation of an allyl organophosphate monomer by atmospheric pressure pulsed-PECVD: insights into the growth mechanisms *RSC Adv* **5** 4277–85

[21] Starostin S A, Premkumar P A, Creatore M, van Veldhuizen E M, de Vries H, Paffen R M J and van de Sanden M C M 2009 On the formation mechanisms of the diffuse atmospheric pressure dielectric barrier discharge in CVD processes of thin silica-like films *Plasma Sources Sci Technol* **18**

[22] Raballand V, Benedikt J, Hoffmann S, Zimmermann M and von Keudell A 2009 Deposition of silicon dioxide films using an atmospheric pressure microplasma jet *J Appl Phys* **105** 083304

[23] Levasseur O, Stafford L, Gherardi N, Naudé N, Beche E, Esvan J, Blanchet P, Riedl B and Sarkissian A 2013 Role of substrate outgassing on the formation dynamics of either hydrophilic or hydrophobic wood surfaces in atmospheric-pressure, organosilicon plasmas *Surf Coat Technol* **234** 42–7

[24] Palumbo F, lo Porto C, Fracassi F and Favia P 2020 Recent Advancements in the Use of Aerosol-Assisted Atmospheric Pressure Plasma Deposition *coatings* **10**

[25] Mitev D, Radeva E, Peshev D, Cook M and Peeva L 2016 PECVD polymerised coatings on thermo-sensitive plastic support *Journal of Physics: Conference Series* vol 682 (Institute of Physics Publishing)

[26] O'Neill L, Herbert P A F, Stallard C and Dowling D P 2010 Investigation of the effects of gas versus liquid deposition in an aerosol-assisted corona deposition process *Plasma Processes and Polymers* **7** 43–50

[27] Coppins M 2010 Electrostatic Breakup in a Misty Plasma *Phys Rev Lett* **104** 065003

[28] Stancampiano A, Gallingani T, Gherardi M, Machala Z, Maguire P, Colombo V, Pouvesle J-M and Robert E 2019 Plasma and Aerosols: Challenges, Opportunities and Perspectives *Applied Sciences* **9** 3861

[29] Mejanes N de, Profili J, Babaei S, Naudé N and Stafford L 2021 Refined analysis of current–voltage characteristics in Townsend dielectric barrier discharges in nitrogen at atmospheric pressure *J Phys D Appl Phys* **54** 095204

[30] Profili J, Levasseur O, Naudé N, Chaneac C, Stafford L and Gherardi N 2016 Influence of the voltage waveform during nanocomposite layer deposition by aerosol-assisted atmospheric pressure Townsend discharge *J Appl Phys* **120** 053302

[31] Babaei S, Profili J, Asadollahi S, Sarkassian A, Dorris A, Beck S and Stafford L 2020 Analysis of transport phenomena during plasma deposition of hydrophobic coatings on porous cellulosic substrates in plane-to-plane dielectric barrier discharges at atmospheric pressure *Plasma Processes and Polymers* **17** 2000091

[32] Naudé N, Cambronne J-P, Gherardi N and Massines F 2005 Electrical model of an atmospheric pressure Townsend-like discharge (APTD) *The European Physical Journal Applied Physics* **29** 173–80

[33] Pipa A and Brandenburg R 2019 The Equivalent Circuit Approach for the Electrical Diagnostics of Dielectric Barrier Discharges: The Classical Theory and Recent Developments *Atoms* **7** 14

[34] Naudé N, Cambronne J-P, Gherardi N and Massines F 2005 Electrical model and analysis of the transition from an atmospheric pressure Townsend discharge to a filamentary discharge *J Phys D Appl Phys* **38** 530–8

[35] Li K, Gabriel O and Meichsner J 2004 Fourier transform infrared spectroscopy study of molecular structure formation in thin films during hexamethyldisiloxane decomposition in low pressure rf discharge *J Phys D Appl Phys* **37** 588–94

[36] Babaei S, Profili J, Asadollahi S, Sarkassian A, Dorris A, Beck S and Stafford L 2020 Analysis of transport phenomena during plasma deposition of hydrophobic

coatings on porous cellulosic substrates in plane-to-plane dielectric barrier discharges at atmospheric pressure *Plasma Processes and Polymers* **17** 2000091

[37] Levasseur O, Stafford L, Gherardi N, Naudé N, Blanchard V, Blanchet P, Riedl B and Sarkissian A 2012 Deposition of Hydrophobic Functional Groups on Wood Surfaces Using Atmospheric-Pressure Dielectric Barrier Discharge in Helium-Hexamethyldisiloxane Gas Mixtures *Plasma Processes and Polymers* **9** 1168–75

[38] Massines F, Gherardi N, Naudé N and Ségur P 2009 Recent advances in the understanding of homogeneous dielectric barrier discharges *The European Physical Journal Applied Physics* **47** 22805

[39] Cacot L, Carnide G, Kahn M L, Caquineau H, Clergereaux R, Naudé N and Stafford L 2022 Influence of pulsed gas injections on the stability of Townsend dielectric barrier discharges in nitrogen at atmospheric pressure *J Phys D Appl Phys*

[40] Gherardi N, Gouda G, Gat E, Ricard A and Massines F 2000 Transition from glow silent discharge to micro-discharges in nitrogen gas *Plasma Sources Sci Technol* **9** 340–6

[41] Tyl C, Lin X, Bouzidi M C, Dap S, Caquineau H, Ségur P, Gherardi N and Naudé N 2018 Investigation of memory effect in atmospheric pressure dielectric barrier discharge in nitrogen with small oxygen or nitric oxide addition *J Phys D Appl Phys* **51**

[42] Lin X, Tyl C, Naudé N, Gherardi N, Popov N A and Dap S 2020 The role of associative ionization reactions in the memory effect of atmospheric pressure Townsend discharges in N2 with a small O2 addition *J Phys D Appl Phys* **53** 205201

[43] Iqbal M M and Turner M M 2015 Investigations of Droplet-Plasma Interaction using Multi-Dimensional Coupled Model *Contributions to Plasma Physics* **55** 627–42

[44] Bennet E D, Mahony C M O, Potts H E, Everest P, Rutherford D, Askari S, McDowell D A, Mariotti D, Kelsey C, Perez-Martin F, Hamilton N, Maguire P and

Diver D A 2016 Precision charging of microparticles in plasma via the Rayleigh instability for evaporating charged liquid droplets *J Aerosol Sci* **100** 53–60

[45] Profili J, Dap S, Levasseur O, Naude N, Belinger A, Stafford L and Gherardi N 2017 Interaction of atomized colloid with an ac electric field in a dielectric barrier discharge reactor used for deposition of nanocomposite coatings *J Phys D Appl Phys* **50** 075201

[46] Bour J, Bardon J, Aubriet H, Frari D del, Verheyde B, Dams R, Vangeneugden D and Ruch D 2008 Different Ways to Plasma-Polymerize HMDSO in DBD Configuration at Atmospheric Pressure for Corrosion Protection *Plasma Processes and Polymers* **5** 788–96

[47] Enache I, Caquineau H, Gherardi N, Paulmier T, Maechler L and Massines F 2007 Transport Phenomena in an Atmospheric-Pressure Townsend Discharge Fed by N2/N2O/HMDSO Mixtures *Plasma Processes and Polymers* **4** 806–14

[48] Sarra-Bournet C, Gherardi N, Turgeon S, Laroche G and Massines F 2009 Deposition of functional hydrogenated amorphous carbon-nitride film (a-CN : H) using C 2 H 4 / N 2 townsend dielectric barrier *The European Physical Journal Applied Physics* **22820** 1–6

[49] Coppins M 2004 The critical droplet size in a misty plasma *31st EPS Conference on Plasma Phys. Lindon*

[50] Maguire P D, Mahony C M O, Kelsey C P, Bingham A J, Montgomery E P, Bennet E D, Potts H E, Rutherford D C E, McDowell D A, Diver D A and Mariotti D 2015 Controlled microdroplet transport in an atmospheric pressure microplasma *Appl Phys Lett* **106** 224101

[51] Li K-Y, Tu H and Ray A K 2005 Charge Limits on Droplets during Evaporation *Langmuir* **21** 3786–94

[52] Rayleigh, Lord 1882 XX. *On the equilibrium of liquid conducting masses charged with electricity The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science* **14** 184–6

[53] Hegemann D, Bülbül E, Hanselmann B, Schütz U, Amberg M and Gaiser S 2021 Plasma polymerization of hexamethyldisiloxane: Revisited *Plasma Processes and Polymers* **18** 2000176

[54] Shelemin A, Choukourov A, Kousal J, Slavínská D and Biederman H 2014 Nitrogen-doped TiO2 nanoparticles and their composites with plasma polymer as deposited by atmospheric pressure DBD *Steel Res Int* **11** 864–77

[55] Turner M M, Iqbal M M and Turner M M 2013 Behaviour of HMDSO Liquid Precursor Droplets in Atmospheric Pressure Discharge Plasma and Gas Mixture

III.4. (article) Soft polymerization of hexamethyldisiloxane by coupling pulsed direct-liquid injection with dielectric barrier discharge

Soft polymerization of hexamethyldisiloxane by coupling pulsed direct-liquid injections with dielectric barrier discharge

L. Cacot [1,2], G. Carnide [2,3], M. L. Kahn [3], N. Naudé[2],

L. Stafford[1] and R. Clergereaux[2]

[1]Département de physique, Université de Montréal, 1375 av. Thérèse-Lavoie-Roux, Montréal, QC, H2V 0B3, Canada

[2] LAPLACE, Université de Toulouse, CNRS, INPT, UPS, Toulouse, France

[3] LCC, CNRS (UPR 8241), Université de Toulouse, 205 route de Narbonne, 31077 Toulouse Cedex 4, France

Abstract

This work examines the combination of pulsed direct-liquid injections with dielectric barrier discharge at atmospheric pressure for the deposition of organosilicon coatings using HMDSO as the precursor and nitrogen as the carrier gas. In such conditions, deposition relies on the charging of micrometer droplets and their transport toward the substrate by the Coulomb force. The thin-film morphology and extent of precursor fragmentation are strongly linked to the amount of energy provided by the filamentary discharge to HMDSO droplets. While cross-linked and smooth coatings were achieved at low energies as in standard gas phase plasma polymers, viscous and droplet-like structured thin films were deposited at higher energies. The latter material is attributed to the soft polymerization of HMDSO droplets related to plasma-droplet interactions.

Keywords: Thin Films, Atmospheric Pressure Plasma Deposition, Dielectric Barrier Discharge, Pulsed Direct Liquid Injection, Aerosols, Organosilicon Coatings

1. Introduction

Thin films obtained from dry processes have garnered great attention due to their wide scope of functionalities [1–8]. For applications requiring low-cost deposition over large areas, atmospheric-pressure plasma processes, including those based on Dielectric Barrier Discharges (DBDs), are relevant [9–12]. In most systems, reactive precursors used for plasma deposition are injected either as gases (for example, silane) or vapors (for example, hexamethyldisiloxane, HMDSO) [13–16]. For the latter, injection of precursor vapors in atmospheric pressure plasma can rely on a carrier gas bubbling in a liquid [15], direct vaporization using a warm water bath [17], or a vapor source controller [18]. However, these methods involving gases and vapors can only be used with low precursor flow rates [19,20]. In addition, only volatile and thermally stable precursors can be injected.

Aerosol-assisted methods are a relevant alternative to inject a larger quantity and variety of liquids, regardless of their composition and properties [8]. Such processes involve the injection of liquid precursors in the form of droplets with a carrier gas used to transport the aerosol towards the reactor. These methods have been extensively applied in the field of chemical vapor deposition (CVD) and atomic layer deposition (ALD) [21] and has attracted increasing interest in plasma-enhanced chemical vapor deposition (PECVD) [22–29]. In addition to single-phase liquid precursors for CVD and PECVD, aerosol-assisted methods can also inject multicomponent solutions such as mixtures of liquids, dispersions of nanoparticles or colloidal solutions; such route is then promising to deposit nanocomposite (multi)functional thin films. For example, nanocomposites were produced using a solution of metal (gold) salts dissolved in a polymerizable solvent (isopropanol) [30] or colloidal solutions with metal-oxide (ZnO, TiO_2) nanoparticles injected in low- [31] and atmospheric-pressure plasmas [12,32–34].

In all studies based on aerosols and plasmas reported in literature, precursors for thin-film deposition are injected in a continuous way. Depending on the substrate temperature, applied power conditions (continuous or pulsed), reactant partial pressure and flow rate, and location of the substrate along the gas flow lines, the so-called “soft plasma polymerization” (SPP) can be achieved [35]. In such conditions, the plasma can deposit a solid film with a minimal precursor fragmentation such that the deposited coating retains

the molecular complexity, functionality, and value of the monomer [27,36–39]. The benefits of SPP processes are significant and relatively well documented in the literature, in particular for biomedical applications [40,41].

Recently, the combination of pulsed direct-liquid injection with pulsed DBDs was explored for deposition of organosilicon coatings using HMDSO as the precursor and nitrogen as the carrier gas [42]. This approach offers a wide parameter space for fundamental studies of the so-called misty plasma (combination of liquid, gas, and plasma states [43]) at atmospheric pressure and their application to (multi)functional thin-film deposition. By investigating the effects of process parameters, namely, plasma-on time, delay between HMDSO precursor injection and plasma ignition, and precursor amount on film thickness, it was found that the deposition process results from the charging of micrometer droplets and their transport towards the dielectrics of the DBD cell by the low-frequency electric field [42,44]. In such conditions, the addition of a continuous carrier gas flow to the pulsed HMDSO aerosol significantly reduced the deposition rate due to a prominent decrease of the precursor residence time [42,45]. Finally, it was found that pulsed, aerosol-assisted plasma deposition is limited by the amount of energy provided to precursor droplets, and not by precursor insufficiency [16,42,46–48].

In this study, we examine the physico-chemical structure of such films, in particular the morphology and the extent of precursor fragmentation. It is demonstrated that these aspects are strongly linked to the amount of energy provided to precursor droplets and that polymers, i.e., linear macromolecules with repeating subunits, can be achieved through judicious control of the process conditions. The work is divided into two parts. In the first section, the aerosol assisted PECVD process is analyzed by injecting a pulsed aerosol of HMDSO without continuous nitrogen carrier gas flow. In the second section, the role of the droplet's residence time is examined through variations of the continuous nitrogen gas flow rate.

2. Experimental setup and diagnostics

As illustrated in Figure 1, the setup used in this work consists of a plane-to-plane DBD and a two-stage pulsed direct-liquid injection (DLI) device (Atokit from Kemstream™) for the introduction of HMDSO aerosol with nitrogen carrier gas [49]. The apparatus for DBD ignition and charge-current-voltage diagnostics were described in previous publications [13,50,51]. The power injected in the DBD is calculated based on the measured charge and voltage values, with Lissajous figure [52]. Here, the discharge is sustained by the application of a low-frequency sinusoidal voltage (1 kHz, 13 $kV_{peak\ to\ peak}$) between two dielectrics separated by a 1 mm gas gap. Of note, the plasma chamber is first vacuum pumped to eliminate contaminants, then it is filled with N_2 (Alphagaz 1, Air Liquide) to a pressure of 1 bar. Constant pressure in the chamber is maintained using a self-regulating valve (MKS 248D) that is coupled to a pressure regulation system. In some cases, a nitrogen continuous flow between 0.7 and 1.4 $L.min^{-1}$ is added to the pulsed aerosol. HMDSO (≥ 98%; Sigma Aldrich) is placed in a Fisher-Porter tube that is plugged to the first stage of the DLI that is pressurized with 2.5 bar absolute N_2 (Alphagaz 1, Air Liquide). From the first stage, the liquid is injected into a second stage chamber as pulses (5 ms opening time and 0.1 Hz injection frequency), where it is mixed with 2 bar absolute of N_2 (Alphagaz 1, Air Liquide). The mixture is then injected as pulses (10 ms opening time and 0.1 Hz injection frequency) into the gas pipe and diffuser connecting the DLI to the DBD chamber. Over the range of experimental conditions investigated, the HMDSO aerosols injected into the DBD cell consist in a fog of micrometer size droplets [42] and the liquid injection rate is 2.7 µL per pulse, i.e., 16.0 $\mu L.min^{-1}$.

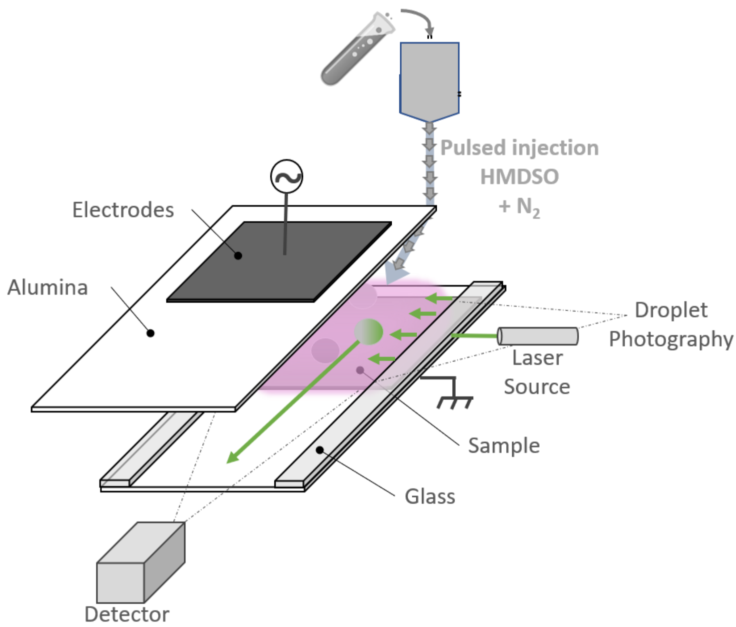

Figure 1 Schematic view of the experimental setup coupling pulsed HMDSO aerosols with DBD for thin film deposition. The laser source and detector used for droplet scattering measurements are also shown.

While this low-frequency DBD operated in nominally pure nitrogen exhibits homogeneous behavior in both current-charge-voltage and optical characteristics [10], the injection of HMDSO with the DLI induces discharge destabilization and thus a filamentary DBD [42]. In agreement with the literature [27,28], the average diameter of the filaments observed by fast optical imaging (Princeton Instruments PI-MAX3, 1000 frames per s, not shown here) were in the 200 μm range.

A silicon sample is placed on the bottom dielectric for ex-situ measurements of organosilicon thin-film deposition. The morphology is first observed by optical microscopy (OMAX) and analyzed on several images by ImageJ software [free software: https://imagej.nih.gov/ij/]. For each microstructure, two perpendicular sizes, denoted D_1 and D_2, are measured and processed using the 2D size plot method developed by *Zhao et al.* [53]. This approach aims to point out the various types of microstructures on the coating and their shape. Here, it is used to emphasize the isotropic nature of the microstructures formed on the substrate through plasma droplet interactions. The coatings are also analyzed by FTIR spectroscopy (Vertex 70; Bruker®) in transmission mode. The spectra are recorded in the range of 500–4000 cm^{-1}, with a spectral resolution of 4 cm^{-1}. Each spectrum corresponds to the average of 16 scans.

Finally, for selected experimental conditions, laser light scattering measurements are conducted to image the presence of droplets in the discharge cell. To avoid interferences with the emission of a nitrogen plasma, a 532 nm laser is used and installed perpendicular to the gas flow lines (see Figure 1). Light scattering is detected at 90º with respect to the laser beam using a monochromator and a detector centered at 532 nm. Images are also taken on the side of the discharge cell, through a glass spacer.

3. Characterization of the organosilicon coatings deposited without continuous nitrogen carrier gas

Figure 2 depicts typical optical microscope images of the coatings deposited on silicon wafers for 1, 2, and 4 min of plasma treatment without continuous nitrogen carrier gas flow added to the pulsed HMDSO aerosol in nitrogen. As can be seen, the coatings are different from those generally produced with a N_2 Townsend discharge with HMDSO [48,54,55].

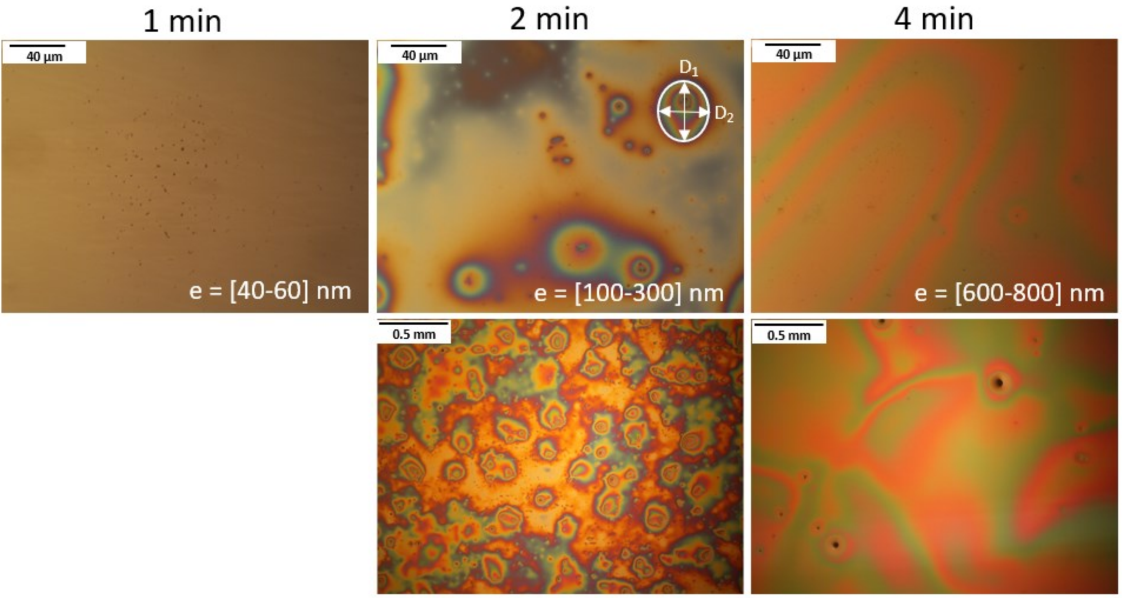

Figure 2: Optical microscopy images of the coatings obtained after 1, 2, and 4 min. The results are shown at high (top row) and low (bottom row) magnifications.

For 1 min, the image displayed in Figure 2 show that the coating consists in micrometer spots dispersed on the substrate surface. While the films obtained with continuous injection of fully vaporized HMDSO are generally smooth [56,57], Figure 2 reveals that the ones obtained with pulsed HMDSO injection at longer times are viscous and macroscopically inhomogeneous. After 2 min., a microscale coating with surface irregularities is observed, as suggested by the thin-film interferences. Such iridescence, linked to thin-film thickness variations, are not linked to gradients along the gas flow lines [58–60], but rather indicates a deposition of droplets as observed for fuel droplets on top of water. Similar droplet-like morphologies were observed by *O'Neil et al.* [57] in a corona discharge produced in helium at higher HMDSO flow rates (80 µL.min^{-1} versus 16 µL.min^{-1} in our conditions) using a

continuous precursor injection method (vapor source controller). This aspect seems even more prominent after 4 min, with features characterized by much larger dimensions.

Of note, similar coatings and size distributions were observed with the silicon substrate placed on either the top or the bottom dielectric (not shown). This reveals that, over the range of experimental conditions investigated, the top dielectric is not a source of precursor. More precisely, this means that the film deposited on the bottom electrode does not result from an accumulation of matter on the top electrode and its release toward the bottom one by gravity. It further confirms that the coatings result from HMDSO droplets, and that thin-film deposition occurs following the transport of charged droplets by the low-frequency electrostatic force towards both the top and bottom dielectrics. This force thus plays a very important role in aerosol-assisted plasma deposition processes with respect to other ones such as gravitational, thermophoresis, and dielectrophoresis forces [42].

The dimensions of the microstructures observed in Figure 3 are extracted by post-processing, and the obtained values are shown in Figure 3 in the form of a typical 2D-plot [53]. Figure 3 clearly shows that the type and the average size of those microstructures vary with plasma deposition time. A single point cloud is observed for the shortest time with size <10 □m. This indicates that for 1 min, the coatings are composed of isotropic structures, with an average diameter of about 1 µm. It is worth mentioning that these microstructures observed for short plasma deposition times cannot be attributed to the impact of filaments on the surface, since their average diameter of about 200 µm [61,62] is much larger than the microstructures observed in the 2D plots (Figure 3). It underlines that the deposit is only made up of droplets with only diameters in the low micrometer scale and below. As a rough estimation, for a steady-state charge of $\sim 10^4$ electrons on a 10 µm HMDSO droplet (and thus a mass-to-charge ratio $\sim 10^2$ kg/C) [44,50], at 1 kHz, the amplitude of oscillations of the charged droplet in a 4 $kV.mm^{-1}$ electric field (recall that the electric field is linked to the gas gap voltage after discharge breakdown [63]) becomes comparable to the gas gap (~1 mm). Therefore, droplets much smaller than 10 µm are easily collected within half-period of the applied voltage whereas droplets much larger than 10 µm are trapped in the gas gap by the oscillating electric field [42].

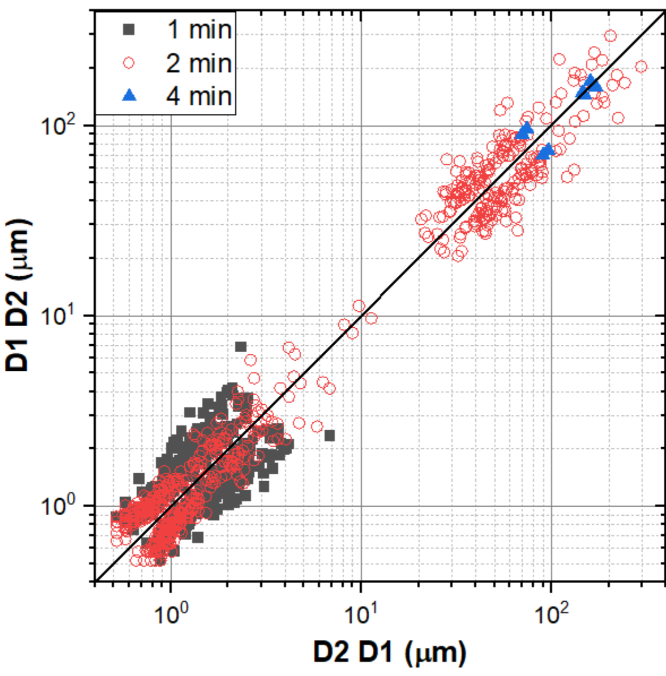

Figure 3: 2D-plots of the microstructures observed on the substrate after 1, 2, and 4 min of plasma deposition.

For the intermediate time, the 2D plot comprising two-point clouds underlines the presence of two populations, one as for short time with size <10 □m and an additional one ranging from 30 up to 300 □m, is observed. Finally, for the longest time, only a few points are observed with value below 10 µm but most of the microstructures are above 100 □m with a deposit more homogeneous. Since thin-film deposition results from the deposition of charged HMDSO droplets with a dimension of ~1 □m [42], the presence of larger features indicates droplet association on the substrate surface, as discussed in 3D deposition processes [64]. Such association reactions is typically observed during droplet condensation on a hydrophilic surface [65].

Though the filaments do not directly contribute to the film microstructure, they play an important role in the deposition process at multiple levels. First, the interaction of ions and electrons from the filaments with the aerosol induces HMDSO droplets surface charging over very short time scales (~5 ns with average ion and electron number densities of ~10^{12} cm^{-3} in filamentary discharges operated in nitrogen [10]). Since this charging time is much shorter than (i) the duration of microdischarges (~100 ns) in filamentary DBDs [66],

(ii) the period of the applied voltage (1 ms at 1 kHz), and (iii) the gas residence times (>3 ms), one can safely assume that all HMDSO droplets become charged. In the absence of continuous gas flow, and thus of a significant neutral drag force, droplets remain between the two electrodes for relatively long-time scales. Since the neutral gas temperature seems insufficient to induce droplet evaporation [67], numerous filaments-droplets interactions can make the droplet instable and initiate Coulomb fission [68,69].The result is the formation of smaller droplets that can more easily be transported toward the substrate following their interaction with the low-frequency electric field [42], as observed for short plasma deposition times.

Imaging and light scattering are used to observe the droplet transport following pulsed direct-liquid injections. A typical picture recorded at 4 min. on the side of the DBD cell along the gas flow lines is presented in Figure 4a. Clearly, in addition to the relatively weak background signal, large features can be seen in some spots of the DBD cell by laser scattering, which is consistent with the presence of HMDSO droplets in the gas gap as well as their growth as larger-scale features [70–73].

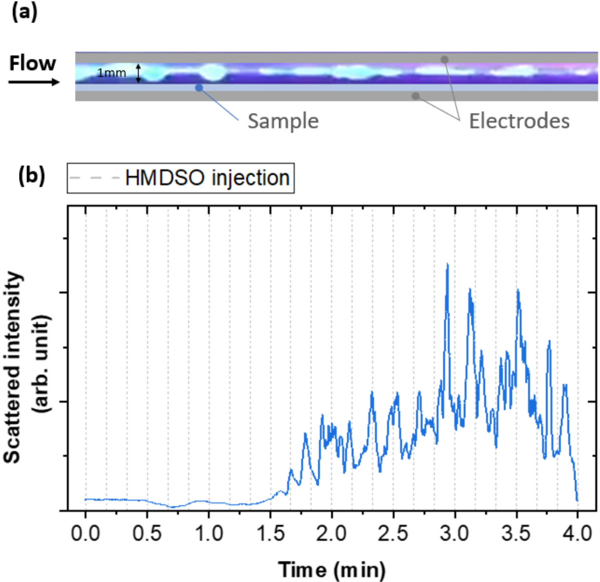

Figure 4:a) Typical laser backscattering image of the gas gap without continuous gas flow rate after 4 min of plasma deposition and b) Temporal evolution of the intensity of light scattered at 90° with respect to the laser beam for experiments without continuous gas flow rate.

The time evolution of the light emission scattered at 90° with respect to the laser beam (see Figure 1) is presented in Figure 4b as a function of plasma deposition time. The first observation is that the intensity progressively increases and reaches a saturation after several pulse injections (the "noise" around the saturation value is attributed to the "local" measurement of the laser beam dimension across the width of the DBD cell). Such temporal evolution of scattered light intensity may be attributed to an increase in the number and/or size of droplets over time. Higher numbers and larger sizes reveal that the HMDSO droplets injected by the pulsed direct-liquid injections are efficiently confined in the plasma region by the electrostatic force. In the absence of a carrier gas flow (and thus with a minimal contribution from the neutral drag force), they can therefore accumulate in the gas gap. Quantitatively, assuming a minimal gas flow of 0.07 $L.min^{-1}$ (without continuous carrier gas flow, this gas flow results from the constant pressure operation in the DBD cell maintained using a self-regulating valve located upstream of the pumping system [42]), the ratio of neutral drag-to-Coulomb force amplitude on 10 m HMDSO droplets with ~10^4 electrons is only 1%, which is consistent with a significant droplet confinement. In Figure 4b, the presence of the saturation for longer plasma deposition times reveals that the system reaches an equilibrium between: (i) the input of HMDSO droplets by pulsed direct-liquid injections, (ii) the deposition of small-scale droplets on both dielectrics following their

transport by the low-frequency electric field, and (iii) the output of large scale HMDSO droplets being confined by the electric field and transported away from the DBD cell by the small neutral drag force.

As indicated in Figure 2, the film thickness measured by stylus profilometry after 1 min of plasma deposition is in the 40-60 nm range. After 2 min., this coating is 2–3 times thicker and after 4 min., the film thickness reaches 600-800 nm. Thin-film deposition rate thus increases from 40-60 $nm.min^{-1}$ to 150-20 $nm.min^{-1}$ between 1 and 4 min.; such evolution of the deposition rate is consistent with the 3D island deposition and/or the accumulation of HMDSO droplets in the gas gap observed by laser scattering. Beyond 4 min., no significant change in the thin-film deposition rate was observed, which is consistent with the saturation seen in Figure 4b. Of note, deposition rates in the 150-200 $nm.min^{-1}$ range are among the upper limits for organosilicon coatings using HMDSO in atmospheric pressure plasmas [10,74].

Considering that thin-film deposition is limited to the discharge region (18 cm^2) due to droplet charging and trapping between the two electrodes, and that the film thickness (600-800 nm) remains relatively homogeneous along the gas flow lines, the process yields after 4 min to a coating of $1.0\text{-}1.4 \cdot 10^{-3}$ cm^3. With a liquid injection rate of 16.0 $\mu L.min^{-1}$, and thus a total injection volume of 64.0 µL, the conversion yield of HMDSO droplets into organosilicon thin film (ratio of the coating volume with the liquid injected one) is 1.5-2.2 vol%. This yield confirms that many droplets do not contribute to the film deposition; this results from their trapping in the gas gap over multiple low-frequency cycles before being evacuated out of the DBD cell. Thin-film deposition thus becomes limited by the amount of energy provided to precursor droplets not only for charging, but also for fission to promote the transport of smaller droplets towards the substrate [42].

Plasma-deposited coatings are further investigated by transmission FTIR spectroscopy. The spectra recorded at the middle of the sample as a function of plasma deposition time are reported in Figure 5a. As a comparison, a FTIR spectrum from liquid HMDSO is also presented. Si-O-Si stretching band detected at 1000–1150 cm^{-1} indicates that the central skeleton of HMDSO is not significantly broken by the discharge. This hypothesis is in good agreement with the CH_3 rocking vibrations in $Si\text{-}(CH_3)_3$ at 840 cm^{-1} and the

asymmetric and symmetric bending vibrations of CH_x at ~2900 cm^{-1}. Indeed, the main difference between liquid HMDSO and the plasma-deposited film corresponds to the CH_3 rocking vibrations in Si-$(CH_3)_2$ at 800 cm^{-1} as observed in polydimethylsiloxane that suggests weak plasma dissociation as well as soft polymerization. Furthermore, a change in the relative intensity of these two peaks can be observed over time. According to *Siliprandi et al.* [20], the ratio of these two bands is related to the degree of polymerization: in highly-fragmented deposits, Si-$(CH_3)_2$ relative absorbance increases, while in low-fragmented deposits, there is a high retention of Si-$(CH_3)_3$. Of note, previous works on plasma polymerized droplet-like coatings with corona discharge in helium [57] do not show either Si-$(CH_3)_3$ nor Si-$(CH_3)_2$ bands in the FTIR spectra suggesting that pulse aerosol plasma processes involve specific plasma deposition mechanisms.

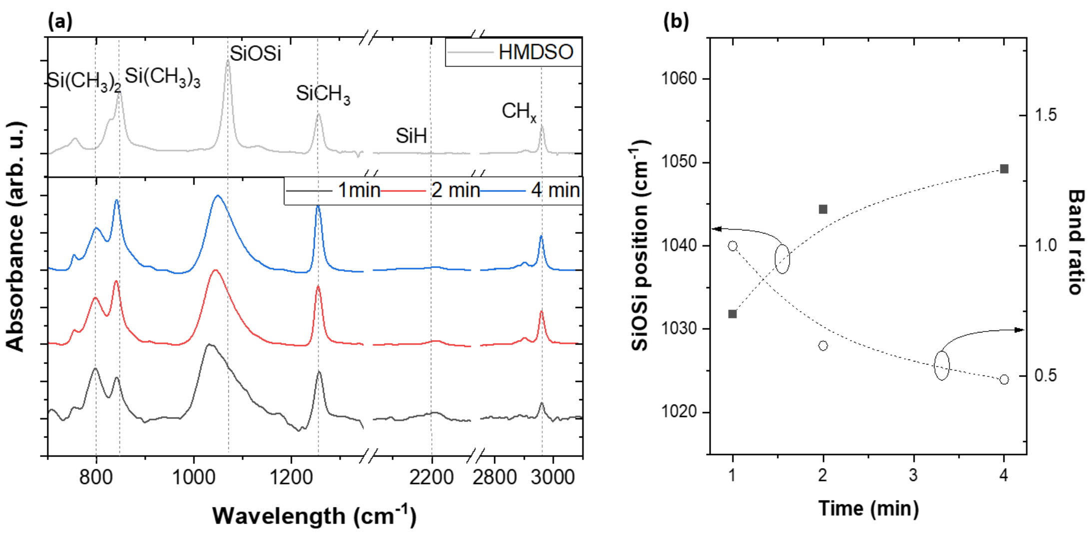

Figure 5: a) FTIR spectra taken in the middle of the sample for various time and compared with the one of liquid HMDSO. b) on the left scale Si-O-Si peak position and on the right scale degree of polymerization Si-$(CH_3)_2$-to- Si-$(CH_3)_3$ band ratio) as a function of time.

The influence of the plasma deposition time on the Si-$(CH_3)_2$-to-Si-$(CH_3)_3$ band ratio is plotted in Figure 5b. Clearly, even if the thin-film deposition rate increases between 1 and 4 min. (as reported in the inset of Figure 5), the degree of polymerization decreases with increasing deposition time, in good agreement with the viscous aspect of the deposited films. Plasma polymerization can also be monitored by plotting the position of the Si-O-Si band observed by FTIR (from 1000 to 1100 cm^{-1}). As can be seen in Figure 5b, an

important shift in the position of the Si-O-Si band is observed, from 1032 cm^{-1} at 1 min. to almost 1050 cm^{-1} at 4 min. Of note, this latter value approaches the one of liquid HMDSO without plasma polymerization (see Figure 5a). Hence, a large amount of matter probed by transmission FTIR after 4 min. of plasma deposition tends towards a polymer formed by linear macromolecules with repeating subunits [35]. The aerosol-assisted process thus consists in a soft polymerization assisted by plasma. On the other hand, early in the process, a higher fragmentation of the monomer is seen, with features typically reported for plasma-polymerized organosilicon coatings with fully vaporized HMDSO [56,57,75].

4. Characterization of the organosilicon coatings deposited with continuous nitrogen carrier gas

Considering that the thin-film deposition process is strongly influenced by the droplet residence time, plasma polymerization and the deposition of a polymer may be further controlled by varying this parameter. Herein, the residence time of HMDSO droplets in the plasma volume is changed by introducing a continuous flow of nitrogen used as carrier gas into the inter-electrode space. Figure 6 depicts the optical microscope images corresponding to deposits obtained under varying gas flow conditions after 4 min. of plasma treatment. Clearly, the morphology of the plasma-deposited layers varies with continuous gas flow rate, and the deposits become less “mushy” at higher flow rates. Moreover, while the liquid injection rate remains constant (16 $\mu L.min^{-1}$), the film thickness and, consequently, the deposition rate decreases (by about a factor of 2 between 0 and 0.7 $L.min^{-1}$). This lower deposition rate at high carrier gas flows was observed in other studies and results from the lower specific energy inputs [42].

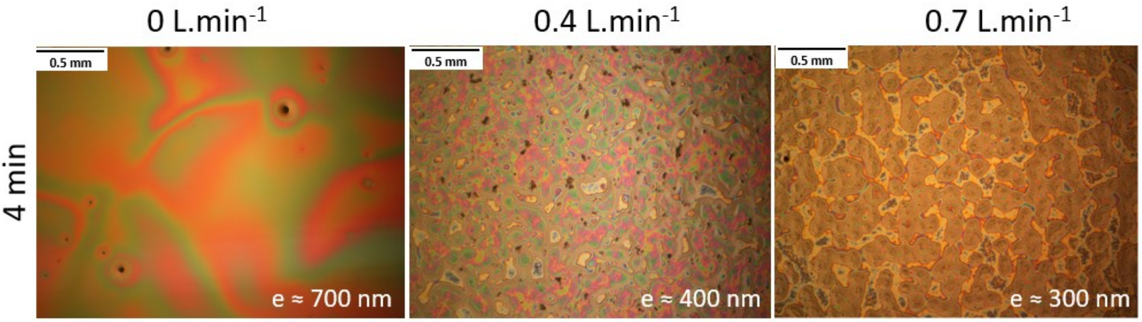

Figure 6: Optical images of the deposits obtained after 4 min. for different gas flow conditions.

As highlighted in the previous section, the collection of HMDSO droplets on the substrate leading to organosilicon thin-film deposition strongly depends on their motion in the low-frequency electric field [42]. As the flow of continuous nitrogen gas increases, the contribution of the neutral drag force increases such that the transport of droplets along the gas flow lines becomes more important, i.e. that their residence time decreases. Quantitatively, the ratio of neutral drag-to-Coulomb force amplitude on 10 m HMDSO droplets with ~10^4 electrons is 1% at 0.07 L.min^{-1} (without continuous carrier gas flow, recall that this gas flow results from the constant pressure operation in the DBD cell maintained using a self-regulating valve located upstream of the pumping system [42]), and 10% at 0.7 L.min^{-1}. For larger droplets, the contribution of the neutral drag force becomes even more important. In line with this consideration, the effect of a continuous gas flow rate on droplets transport is examined in more details by light scattering. The results presented in Figure 7 show that in the presence of a continuous gas flow, no light scattering is observed. In sharp contrast with the data set displayed in Figure 7, this suggests that droplets present in the gas gap are less abundant. Droplets that remained trapped in the gas gap over multiple low-frequency cycles in the absence of a continuous gas flow are now pushed out of the DBD cell by the neutral drag force [42].

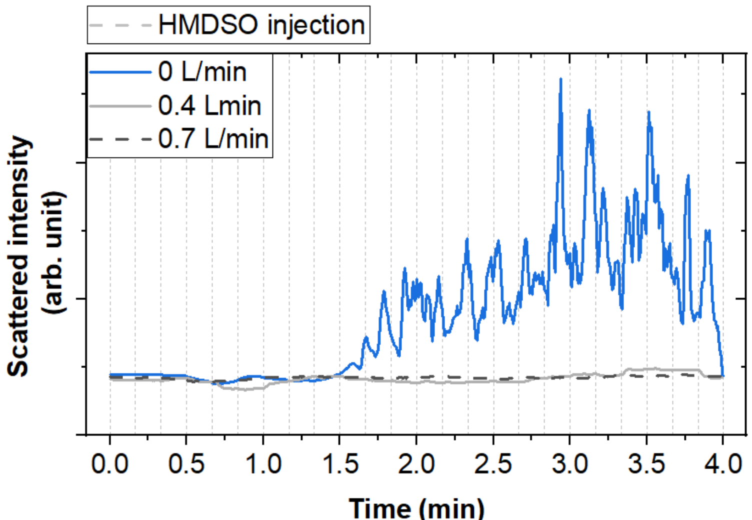

Figure 7: Temporal evolution of the intensity of light scattered at 90° with respect to the laser beam for experiments done without various continuous gas flow rate, from 0 to 0.7 L.min^{-1}.

As in the absence of continuous gas flow described in the previous section, FTIR measurements are also done for the various continuous neutral gas flow rates (Figure 8).

At higher continuous flow, an increase of the relative intensity of the $Si(CH_3)_2$ band can be noticed. As discussed above, this suggests an increase in the degree of plasma polymerization through a methyl group removal. A rise in the relative SiH band intensity at 2250 cm^{-1} can also be seen. In atmospheric-pressure plasma processes, this latter band is the image of the molecular fragmentation of $Si(CH_3)_3$ such that the SiH-to-$Si(CH_3)_3$ band ratio characterizes the molecular fragmentation of the $SiCH_3$ and CH bonds [76]. The variation with the continuous gas flow rate thus also reveals different degree of monomer fragmentation with the droplet residence time.

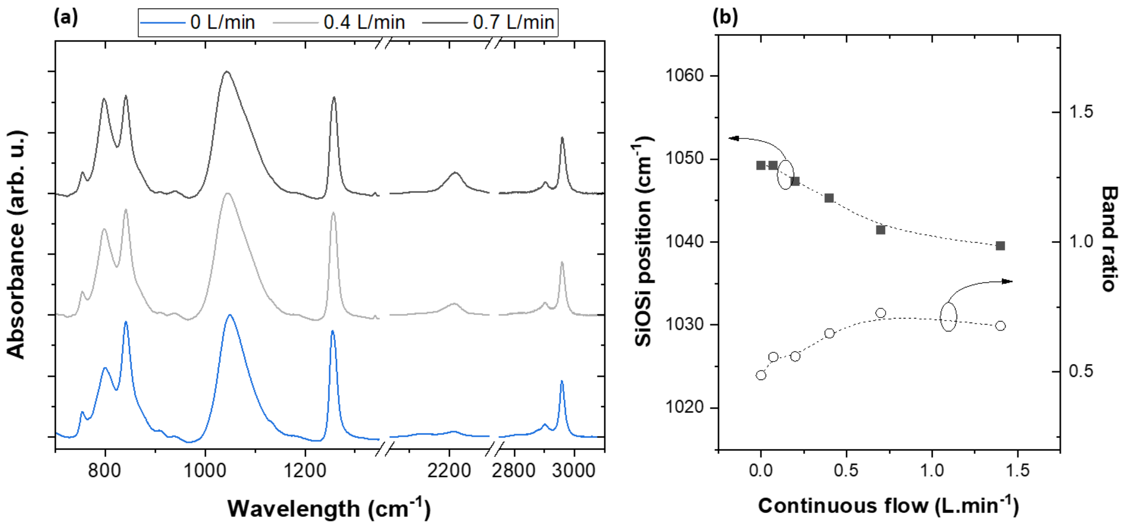

Figure 8: a) FTIR spectra taken in the middle of the sample for various continuous flow at 4 min b) on the left scale Si-O-Si peak position and on the right scale degree of polymerization (Si-$(CH_3)_2$-to- Si-$(CH_3)_3$ band ratio) as a function of continuous flow.

In line with the FTIR analysis done in Figure 5, Figure 8b displays the influence of the continuous gas flow rate on the Si-$(CH_3)_2$-to- Si-$(CH_3)_3$ band ratio and the position of the Si-O-Si band. Here, the degree of polymerization rises with the flow rate, while the Si-O-Si band position decreases from 1049 cm^{-1} to 1043 cm^{-1} between 0 and 1.4 $L.min^{-1}$. Soft polymerization assisted by plasma is thus modified by a continuous nitrogen gas flow, i.e. with the droplet residence times.

5. Discussion

At a given injection rate, i.e. with the same type and number of droplets injected in the aerosols, the results obtained in Figure 5 and Figure 8 show that the thin-film morphology and plasma polymerization of HMDSO in a DBD operated in a pulsed direct-liquid-injection mode strongly depends on the deposition parameters, including the deposition time and the droplet residence time. This latter aspect is examined in more details by plotting the degree of plasma polymerization linked to the $Si(CH_3)_2$-to-$Si(CH_3)_3$ band ratio and the Si-O-Si band position as a function of the energy parameter (also called by some authors Specific Energy Input (SEI) [16]) that can be defined as $E = P \times t_{residence}$, where P is the power determined from electrical analysis of the DBD and $t_{residence}$ is the average time during which the gas remains in the discharge (calculated based on the dimensions of the inter-dielectric space and the continuous N_2 gas flow rate).

The results of the correlation are shown in Figure 9. Here, the set of data (full squares) comes from the FTIR plots after 4 min of deposition as in Figure 8 (influence of continuous nitrogen gas flow rate). Data obtained in a previous study dealing with the effects of other process parameters, namely, duty cycle, delay between precursor injection and discharge ignition, and the amount of injected HMDSO microdroplets are also reported (open squares) for comparison [42]. Clearly, in every condition, a shift in the position of the Si-O-Si peak is observed, from 1020 cm^{-1} at low energy parameter values to 1050 cm^{-1} at higher energies, i.e. between the ones of plasma-polymerized organosilicon coatings with fully vaporized HMDSO (as obtained by *Kale et al.* [56]) to liquid HMDSO [57], respectively. While vapor-based deposition processes typically reveal significant precursor fragmentation and high degree of cross-linking [8,56,74], the use of pulsed direct liquid injections at high specific input energies thus offers soft polymerization assisted by plasma with minor fragmentation of the monomer [57,74], as typically reported in free-radical polymerization [77]. Such finding is contrary to the intuition as one would expect soft polymerization to occur at low and not at higher energy conditions.

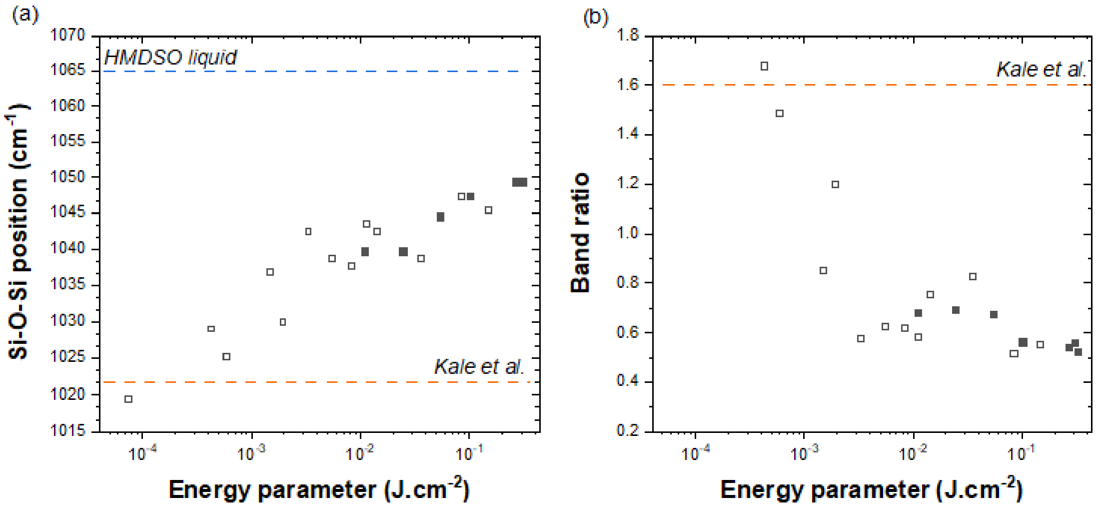

Figure 9: (a) Variation of the Si-O-Si peak position and (b) Si-$(CH_3)_2$-to- Si-$(CH_3)_3$ band ratio recorded for a total process time of 4 min. as a function of the energy parameter obtained for various plasma deposition times and continuous carrier gas flow rates (full squares). Pulsed injection time of 10 ms, pulsed injection frequency of 0.1 Hz. The results are also shown for various plasma-on times and delay times between precursor injection and plasma ignition with or without a continuous N_2 gas flow (empty square). Dark yellow and blue lines correspond to values for liquid HMDSO (without plasma polymerization) and plasma-polymerized organosilicon coatings with fully vaporized HMDSO (Kale et al. [56]*).*

In a previous paper, it was shown that thin-film deposition rates with direct-liquid injections coupled to a DBD are limited by the amount of energy provided to precursor droplets, and not by precursor insufficiency [42]. More specifically, the thickness of the deposited film for a total process duration of 4 min. (linked to the deposition rate) increased linearly with the specific energy input. By comparing these findings with the one displayed in Figure 9, it seems that low-energy conditions associated to low thin-film deposition rates are linked to high fragmentation of the monomer. On the other hand, high-energy conditions characterized by high deposition rates yield to soft polymerization assisted by plasma. This conclusion is in sharp contrast to typical vapor-phase plasma deposition for which higher specific energy inputs induce enhanced deposition rates, significant plasma polymerization, and high degrees of cross-linking [73]. With liquid injection, higher thin-film deposition rates are therefore matched with viscous matter.

In our case, the presence of the Si-$(CH_3)_2$ group, considered a chain propagator as in the polydimethylsiloxane, is indicative of the formation of long chains of organosilicon material. In contrast, in vapour-phase deposition as reported by many authors [8,56,74], the film does not consist of long and isolated Si-O-Si chains, but there is also interchain

connections appearing by Si-Si and Si-CH_x cross-linking. In this structure, as illustrated in Figure 10, the –Si-CH_2-Si– bond represents one of the cross-linking points of the long siloxane chains [78,79]. However, the identification of this group in the FTIR spectra is difficult due to the strong absorption in the same wavenumber related to siloxane [80]. Other possibilities of cross-linking occur by means of the formation of Si-Si and Si-O-Si bonds [78,79]. In all cases, the connection implies the loss of hydrogen atoms and/or methyl groups and hydrogen recombination (Si-H).

On the other hand, for droplet-mediated deposition, FTIR analysis shows that although HMDSO can be dissociated by a methyl group removal in all experimental conditions investigated, only those involving high-deposition rates and the formation of viscous organosilicon films yield to soft polymerization assisted by plasma (Figure 10). In such liquid-phase plasma polymerization conditions, the chemical pathways available for reaction seems much more tightly controlled. In particular, the next highest bond dissociation energy, the C-H bond, is not significantly disrupted by the plasma process (slight modifications of CH_x stretching bands and absence of SiH bands in Figure 5a). Hence, the specific set of plasma conditions appears to deliver sufficient energy to the HMDSO droplets and viscous films to break the weakest monomer bond, thereby enabling the molecule to react and polymerize in the droplet, but without providing the energy required to break higher energy bonds, in particular those leading to Si-CH2-Si, or any other kind of bridges [78,79]. In short, the monomer is not heavily fragmented, and the process leads to soft polymerization assisted by plasma in liquid droplets with very low cross-linking. At this stage of the study, it is however impossible to distinguish if polymerization occurs in the gas phase through filaments-droplets interactions and/or on the surface through plasma-coating interactions.

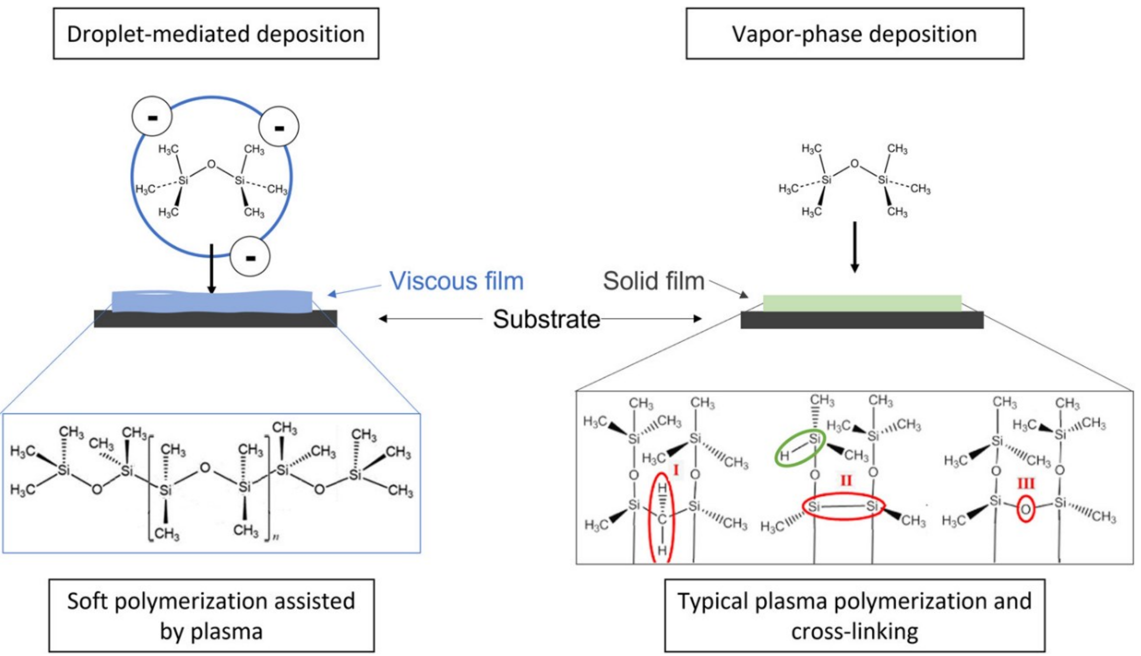

Figure 10: Comparison of droplet-mediated and vapor-phase deposition schemes. While droplet-mediated deposition can induce soft polymerization, vapor-phase deposition typically yields plasma polymers with significant cross-linking. In the latter scheme, the Si-CH_2-Si (I), Si-Si (II), and Si-O-Si (III) bonds are highlighted because they represent possible points of connection of adjacent chains in organosilicon thin films obtained by plasma polymerization.

6. Conclusion

This study investigates the process of plasma-assisted polymerization by pulsed DLI of HMDSO in a plane-to-plane DBD. The interaction of the plasma with the droplets injected into the interelectrode gap is analysed, and its effect on the deposition process is assessed. The effects of deposition time and droplet residence time on the characteristics of the deposited films are also examined. In the absence of a continuous carrier gas flow rate, it is shown that the morphology and the degree of precursor fragmentation evolve during the deposition process due to the confinement of charged droplets in the inter-dielectrics space. The plasma-droplet interactions and the nature of the plasma-deposited material can be further controlled by varying the carrier gas flow conditions. In general, the droplets injected into a DBD are subject to three main processes: droplet charging inside the plasma, deposition of small droplets by the low-frequency electrical field, and the escape of large droplets being confined in the gas gap and then being pushed out of the DBD cell by the neutral drag force. In contrast to typical vapor-phase deposition methods, the use of pulsed

DLI offers both enhanced thin-film deposition rates and original polymerization at high specific energy inputs. In such conditions, the plasma can deliver sufficient energy to the HMDSO droplets and viscous films to break the weakest monomer bond, thereby enabling the molecule to react and polymerize but without providing the energy required to break higher energy bonds. Judicious control of vapor and liquid phases injected in plasmas thus seems crucial for soft polymerization assisted by plasma and (multi)functional thin film deposition.

Acknowledgments

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Data availability statement

The data are available from the corresponding author upon request.

References

[1] Machala Z, Janda M, Hensel K, Jedlovský I, Leštinská L, Foltin V, Martišovitš V and Morvová M 2007 Emission spectroscopy of atmospheric pressure plasmas for bio-medical and environmental applications *J Mol Spectrosc* **243** 194–201

[2] Durán I R, Profili J, Stafford L and Laroche G 2020 Beyond microelectronics with 1,3,5,7-tetramethylcyclotetrasiloxane: A promising molecule for anti-fogging coatings *Mater Chem Phys* **242** 122508

[3] Vallade J, Pouliquen S, Lecouvreur P, Bazinette R, Hernandez E, Quoizola S and Massines F 2012 a-SiNx:H Antireflective And Passivation Layer Deposited By Atmospheric Pressure Plasma *Energy Procedia* **27** 365–71

[4] Profili J, Rousselot S, Tomassi E, Briqueleur E, Aymé-Perrot D, Stafford L and Dollé M 2020 Toward More Sustainable Rechargeable Aqueous Batteries Using Plasma-Treated Cellulose-Based Li-Ion Electrodes *ACS Sustain Chem Eng* **8** 4728–33

[5] Asadollahi S, Farzaneh M and Stafford L 2019 On the Icephobic Behavior of Organosilicon-Based Surface Structures Developed Through Atmospheric Pressure Plasma Deposition in Nitrogen Plasma *Coatings* **9** 679

[6] Jafari R, Momen G and Eslami E 2018 Surface Engineering Fabrication of icephobic aluminium surfaces by atmospheric plasma jet polymerisation Fabrication of icephobic aluminium surfaces by atmospheric plasma jet polymerisation *Surface Engineering* **35** 450–5

[7] Fanelli F, Mastrangelo A M, Caputo G and Fracassi F 2019 Tuning the structure and wetting properties of organic-inorganic nanocomposite coatings prepared by aerosol-assisted atmospheric pressure cold plasma deposition *Surf Coat Technol* **358** 67–75

[8] Bour J, Bardon J, Aubriet H, del Frari D, Verheyde B, Dams R, Vangeneugden D and Ruch D 2008 Different Ways to Plasma-Polymerize HMDSO in DBD

Configuration at Atmospheric Pressure for Corrosion Protection *Plasma Processes and Polymers* **5** 788–96

[9] Merche D, Vandencasteele N and Reniers F 2012 Atmospheric plasmas for thin film deposition: A critical review *Thin Solid Films* **520** 4219–36

[10] Massines F, Sarra-Bournet C, Fanelli F, Naudé N and Gherardi N 2012 Atmospheric pressure low temperature direct plasma technology: Status and challenges for thin film deposition *Plasma Processes and Polymers* **9** 1041–73

[11] Fanelli F 2010 Thin film deposition and surface modification with atmospheric pressure dielectric barrier discharges *Surf Coat Technol* **205** 1536–43

[12] Uricchio A and Fanelli F 2021 Low-Temperature Atmospheric Pressure Plasma Processes for the Deposition of Nanocomposite Coatings *Processes* **9** 2069

[13] Babaei S, Profili J, Asadollahi S, Sarkassian A, Dorris A, Beck S and Stafford L 2020 Analysis of transport phenomena during plasma deposition of hydrophobic coatings on porous cellulosic substrates in plane-to-plane dielectric barrier discharges at atmospheric pressure *Plasma Processes and Polymers* **17** 2000091

[14] Vinogradov I and Lunk A 2009 Film Deposition in the Dielectric Barrier Discharge at Atmospheric Pressure in He/O_2/HMDSO and He/N_2O/HMDSO mixtures *Plasma Processes and Polymers* **6** S514–8

[15] Nisol B, Ghesquière J and Reniers F 2016 Easy Synthesis of Ageing-Resistant Coatings with Tunable Wettability by Atmospheric Pressure Plasma *Plasma Chemistry and Plasma Processing* **36** 1239–52

[16] Hegemann D, Bülbül E, Hanselmann B, Schütz U, Amberg M and Gaiser S 2021 Plasma polymerization of hexamethyldisiloxane: Revisited *Plasma Processes and Polymers* **18** 2000176

[17] Choudhury A J, Chutia J, Kakati H, Barve S A, Pal A R, Sarma N sen, Chowdhury D and Patil D S 2010 Studies of radiofrequency plasma deposition of hexamethyldisiloxane films and their thermal stability and corrosion resistance behavior *Vacuum* **84** 1327–33

[18] Levasseur O, Stafford L, Gherardi N, Naudé N, Blanchard V, Blanchet P, Riedl B and Sarkissian A 2012 Deposition of Hydrophobic Functional Groups on Wood Surfaces Using Atmospheric-Pressure Dielectric Barrier Discharge in Helium-Hexamethyldisiloxane Gas Mixtures *Plasma Processes and Polymers* **9** 1168–75

[19] Loffhagen D, Becker M M, Hegemann D, Nisol B, Watson S, Wertheimer M R and Klages C P 2020 Large-area atmospheric pressure dielectric barrier discharges in Ar–HMDSO mixtures: Experiments and fluid modelling *Plasma Processes and Polymers* **17**

[20] Siliprandi R A, Zanini S, Grimoldi E, Fumagalli F S, Barni R and Riccardi C 2011 Atmospheric pressure plasma discharge for polysiloxane thin films deposition and comparison with low pressure process *Plasma Chemistry and Plasma Processing* **31** 353–72

[21] Lukaszkowicz K 2011 Review of Nanocomposite Thin Films and Coatings Deposited by PVD and CVD Technology *Nanomaterials* ed M Rahman pp 146–62

[22] Ogawa D, Saraf I, Sra A, Timmons R, Goeckner M and Overzet L 2009 The direct injection of liquid droplets into low pressure plasmas *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* **27** 342–51

[23] Chouteau S, Mitronika M, Goullet A, Richard-Plouet M, Stafford L and Granier A 2022 Kinetics driving nanocomposite thin film deposition in low-pressure misty plasma processes *J Phys D Appl Phys*

[24] Vasudev M C, Anderson K D, Bunning T J, Tsukruk V v. and Naik R R 2013 Exploration of Plasma-Enhanced Chemical Vapor Deposition as a Method for Thin-Film Fabrication with Biological Applications *ACS Appl Mater Interfaces* **5** 3983–94

[25] Beck A J, Short R D and Matthews A 2008 Deposition of functional coatings from acrylic acid and octamethylcyclotetrasiloxane onto steel using an atmospheric pressure dielectric barrier discharge *Surf Coat Technol* **203** 822–5

[26] Twomey B, Dowling D, Byrne G, O'Neill L and O'Hare L-A 2007 Properties of Siloxane Coatings Deposited in a Reel-to-Reel Atmospheric Pressure Plasma System *Plasma Processes and Polymers* **4** S450–4

[27] Tatoulian M, Arefi-Khonsari F and Borra J-P 2007 Deposition of Organic Coatings at Atmospheric Pressure from Liquid Precursors *Plasma Processes and Polymers* **4** 360–9

[28] Heyse P, Dams R, Paulussen S, Houthoofd K, Janssen K, Jacobs P A and Sels B F 2007 Dielectric Barrier Discharge at Atmospheric Pressure as a Tool to Deposit Versatile Organic Coatings at Moderate Power Input *Plasma Processes and Polymers* **4** 145–57

[29] Fanelli F, Lovascio S, d'Agostino R and Fracassi F 2012 Insights into the Atmospheric Pressure Plasma-Enhanced Chemical Vapor Deposition of Thin Films from Methyldisiloxane Precursors *Plasma Processes and Polymers* **9** 1132–43

[30] Brunet P, Rincón R, Martinez J-M, Matouk Z, Fanelli F, Chaker M and Massines F 2017 Control of composite thin film made in an Ar/isopropanol/TiO_2 nanoparticles dielectric barrier discharge by the excitation frequency *Plasma Processes and Polymers* **14** 1700049

[31] Mitronika M, Villeneuve-Faure C, Massol F, Boudou L, Ravisy W, Besland M P, Goullet A and Richard-Plouet M 2021 TiO2-SiO2 mixed oxide deposited by low pressure PECVD: Insights on optical and nanoscale electrical properties *Appl Surf Sci* **541** 148510

[32] Profili J, Levasseur O, Blaisot J-B, Koronai A, Stafford L and Gherardi N 2016 Nebulization of Nanocolloidal Suspensions for the Growth of Nanocomposite Coatings in Dielectric Barrier Discharges *Plasma Processes and Polymers* **13** 981–9

[33] Brunet P, Rincón R, Margot J, Massines F and Chaker M 2017 Deposition of homogeneous carbon-TiO2 composites by atmospheric pressure DBD *Plasma Processes and Polymers* **14** 1600075

[34] Uricchio A, Nadal E, Plujat B, Plantard G, Massines F and Fanelli F 2021 Low-temperature atmospheric pressure plasma deposition of TiO2-based nanocomposite coatings on open-cell polymer foams for photocatalytic water treatment *Appl Surf Sci* **561** 150014

[35] Herbert P A F, O'Neill L and Jaroszyńska-Wolińska J 2009 Soft Plasma Polymerization of Gas State Precursors from an Atmospheric Pressure Corona Plasma Discharge *Chemistry of Materials* **21** 4401–7

[36] Ward L J, Schofield W C E, Badyal J P S, Goodwin A J and Merlin P J 2003 Atmospheric Pressure Plasma Deposition of Structurally Well-Defined Polyacrylic Acid Films *Chemistry of Materials* **15** 1466–9

[37] O'Hare L-A, O'Neill L and Goodwin A J 2006 Anti-microbial coatings by agent entrapment in coatings deposited via atmospheric pressure plasma liquid deposition *Surface and Interface Analysis* **38** 1519–24

[38] Albaugh J, O'Sullivan C and O'Neill L 2008 Controlling deposition rates in an atmospheric pressure plasma system *Surf Coat Technol* **203** 844–7

[39] Heyse P, Dams R, Paulussen S, Houthoofd K, Janssen K, Jacobs P A and Sels B F 2007 Cover Picture: Plasma Process. Polym. 2/2007 *Plasma Processes and Polymers* **4** 105–105

[40] Hegemann D and Gaiser S 2022 Plasma surface engineering for manmade soft materials: a review *J Phys D Appl Phys* **55** 173002

[41] Jacobs T, Morent R, de Geyter N, Dubruel P and Leys C 2012 Plasma Surface Modification of Biomedical Polymers: Influence on Cell-Material Interaction *Plasma Chemistry and Plasma Processing* **32** 1039–73

[42] Cacot L, Carnide G, Kahn M L, Clergereaux R, Naudé N and Stafford L 2022 Kinetics driving thin-film deposition in dielectric barrier discharges using a direct liquid injector operated in a pulsed regime *J Phys D Appl Phys* **55** 475202

[43] Coppins M 2010 Electrostatic Breakup in a Misty Plasma *Phys Rev Lett* **104** 065003

[44] Profili J, Dap S, Levasseur O, Naude N, Belinger A, Stafford L and Gherardi N 2017 Interaction of atomized colloid with an ac electric field in a dielectric barrier discharge reactor used for deposition of nanocomposite coatings *J Phys D Appl Phys* **50** 075201

[45] Enache I, Caquineau H, Gherardi N, Paulmier T, Maechler L and Massines F 2007 Transport Phenomena in an Atmospheric-Pressure Townsend Discharge Fed by N2/N2O/HMDSO Mixtures *Plasma Processes and Polymers* **4** 806–14

[46] Bardon J, Dieden R, Grysan P, Mertz G, Martin A, Delmée M and Ruch D 2019 Mechanical properties of thin plasma polymer coatings from hexanediol dimethacrylate and relations with their chemical properties *Surf Coat Technol* **358** 320–30

[47] Shelemin A, Choukourov A, Kousal J, Slavínská D and Biederman H 2014 Nitrogen-doped TiO2 nanoparticles and their composites with plasma polymer as deposited by atmospheric pressure DBD *Steel Res Int* **11** 864–77

[48] Petersen J, Bardon J, Dinia A, Ruch D and Gherardi N 2012 Organosilicon Coatings Deposited in Atmospheric Pressure Townsend Discharge for Gas Barrier Purpose: Effect of Substrate Temperature on Structure and Properties *ACS Appl Mater Interfaces* **4** 5872–82

[49] M. Kahn, Y. Champouret, R. Clergereaux, C. Vahlas A F M 2016 Process for the preparation of nanoparticles *Office*

[50] Mejanes N de, Profili J, Babaei S, Naudé N and Stafford L 2021 Refined analysis of current–voltage characteristics in Townsend dielectric barrier discharges in nitrogen at atmospheric pressure *J Phys D Appl Phys* **54** 095204

[51] Profili J, Levasseur O, Naudé N, Chaneac C, Stafford L and Gherardi N 2016 Influence of the voltage waveform during nanocomposite layer deposition by aerosol-assisted atmospheric pressure Townsend discharge *J Appl Phys* **120** 053302

[52] Manley T C 1943 The Electric Characteristics of the Ozonator Discharge *Trans. Electochem. Soc.* **84** 83

[53] Zhao Z, Zheng Z, Roux C, Delmas C, Marty J-D, Kahn M L and Mingotaud C 2016 Importance of the Correlation between Width and Length in the Shape Analysis of Nanorods: Use of a 2D Size Plot To Probe Such a Correlation *Chemistry - A European Journal* **22** 12424–9

[54] Massines F, Gherardi N, Fornelli A and Martin S 2005 Atmospheric pressure plasma deposition of thin films by Townsend dielectric barrier discharge *Surf Coat Technol* **200** 1855–61

[55] Rodríguez Durán I, Durocher-Jean A, Profili J, Stafford L and Laroche G 2020 Atmospheric pressure Townsend discharges as a promising tool for the one-step deposition of antifogging coatings from N_2O/TMCTS mixtures *Plasma Processes and Polymers* **17** 1900186

[56] Kale K H and Palaskar S 2011 Atmospheric pressure plasma polymerization of hexamethyldisiloxane for imparting water repellency to cotton fabric *Textile Research Journal* **81** 608–20

[57] O'Neill L, Herbert P A F, Stallard C and Dowling D P 2010 Investigation of the Effects of Gas versus Liquid Deposition in an Aerosol-Assisted Corona Deposition Process *Plasma Processes and Polymers* **7** 43–50

[58] Morent R, de Geyter N, van Vlierberghe S, Dubruel P, Leys C, Gengembre L, Schacht E and Payen E 2009 Deposition of HMDSO-based coatings on PET substrates using an atmospheric pressure dielectric barrier discharge *Prog Org Coat* **64** 304–10

[59] Wavhal D S, Zhang J, Steen M L and Fisher E R 2006 Investigation of Gas Phase Species and Deposition of SiO2 Films from HMDSO/O2 Plasmas *Plasma Processes and Polymers* **3** 276–87

[60] Lin Y-C and Wang M-J 2019 Fabrication of hydrophobic/hydrophilic HMDSO films by atmospheric pressure plasma jet deposition *Japanese Journal of APllied Physics* **58** SAAC01

[61] Kogelschatz U 2002 Filamentary, patterned, and diffuse barrier discharges *IEEE Transactions on Plasma Science* **30** 1400–8

[62] Gherardi N, Gouda G, Gat E, Ricard A and Massines F 2000 Transition from glow silent discharge to micro-discharges in nitrogen gas *Plasma Sources Sci Technol* **9** 340–6

[63] Naudé N, Cambronne J-P, Gherardi N and Massines F 2005 Electrical model of an atmospheric pressure Townsend-like discharge (APTD) *The European Physical Journal Applied Physics* **29** 173–80

[64] Fortelný I, Jůza J and Dimzoski B 2012 Coalescence in quiescent polymer blends with a high content of the dispersed phase *Eur Polym J* **48** 1230–40

[65] Sheng Q, Sun J, Wang Q, Wang W and Wang H S 2016 On the onset of surface condensation: formation and transition mechanisms of condensation mode *Sci Rep* **6** 30764

[66] Naudé N, Cambronne J-P, Gherardi N and Massines F 2005 Electrical model and analysis of the transition from an atmospheric pressure Townsend discharge to a filamentary discharge *J Phys D Appl Phys* **38** 530–8

[67] Cacot L, Kahn M, Clergereaux R, Stafford L and Naude N 2023 Tuning plasma-droplet interactions in dielectric barrier discharge for thin-film deposition

[68] Bennet E D, Mahony C M O, Potts H E, Everest P, Rutherford D, Askari S, McDowell D A, Mariotti D, Kelsey C, Perez-Martin F, Hamilton N, Maguire P and Diver D A 2016 Precision charging of microparticles in plasma via the Rayleigh instability for evaporating charged liquid droplets *J Aerosol Sci* **100** 53–60

[69] Li K-Y, Tu H and Ray A K 2005 Charge Limits on Droplets during Evaporation *Langmuir* **21** 3786–94

[70] Seco-Gudiña R, Guadarrama-Cetina J and González-Viñas W 2017 Dynamics of water condensation over arrays of hydrophilic patches *Eur. Phys. J. Special Topics* **226** 1189–98

[71] Guadarrama-Cetina J and González-Viñas W 2013 Breath figures of two immiscible substances on a repellent surface *Phys Rev E* **87** 054401

[72] Ristenpart W D, McCalla P M, Roy R v. and Stone H A 2006 Coalescence of Spreading Droplets on a Wettable Substrate *Phys Rev Lett* **97** 064501

[73] Stallard C P, Iqbal M M, Turner M M and Dowling D P 2013 Investigation of the Formation Mechanism of Aligned Nano-Structured Siloxane Coatings Deposited Using an Atmospheric Plasma Jet *Plasma Processes and Polymers* **10** 888–903

[74] Morent R, de Geyter N, van Vlierberghe S, Dubruel P, Leys C and Schacht E 2009 Organic-inorganic behaviour of HMDSO films plasma-polymerized at atmospheric pressure *Surf Coat Technol* **203** 1366–72

[75] Bour J, Bardon J, Aubriet H, Frari D del, Verheyde B, Dams R, Vangeneugden D and Ruch D 2008 Different Ways to Plasma-Polymerize HMDSO in DBD Configuration at Atmospheric Pressure for Corrosion Protection *Plasma Processes and Polymers* **5** 788–96

[76] Ricci M, Dorier J, Hollenstein C and Fayet P 2011 Influence of Argon and Nitrogen Admixture in HMDSO / O 2 Plasmas onto Powder Formation *Plasma Processes and Polymers* **8** 108–17

[77] Elias H-G 1977 Principles of Polymerization *Macromolecules* (Boston, MA: Springer US) pp 535–93

[78] de Freitas A S M, Maciel C C, Rodrigues J S, Ribeiro R P, Delgado-Silva A O and Rangel E C 2021 Organosilicon films deposited in low-pressure plasma from hexamethyldisiloxane — A review *Vacuum* **194** 110556

[79] Ribeiro R P, Rangel R de C C, Fernandes F O, Cruz N C and Rangel E C 2021 Effect of Plasma Oxidation Treatment on Production of a SiOx/SiOxCyHz Bilayer to Protect Carbon Steel Against Corrosion *Materials Research* **24**

[80] Rau C and Kulisch W 1994 Mechanisms of plasma polymerization of various silico-organic monomers *Thin Solid Films* **249** 28–37

Chapitre IV. Influence des paramètres du procédé sur le dépôt de couches minces

Les travaux présentés jusqu'ici montrent que les procédés couplant aérosols et plasmas à la pression atmosphérique sont contrôlés par les interactions plasma-gouttelettes. En particulier, la partie précédente a montré le rôle du temps d'interaction entre le plasma et le liquide, celui-ci étant directement fonction de la durée du plasma (pulsé) et du temps de résidence des gouttelettes dans la décharge. Nous avons vu que les interactions plasma-gouttelettes et la nature du dépôt sont contrôlés par trois procédés physique principaux : le chargement de la goutte dans le plasma, le dépôt de goutte de petite taille (< 10 µm) par le champ électrique de basse fréquence, et le piégeage dans l'espace inter-diélectriques puis le transport des plus grosses gouttes vers la sortie de la décharge par la force d'entrainement des neutres.

En capitalisant sur ce nouveau savoir, nous proposons dans cette première partie de chapitre de modifier les paramètres électriques de la décharge à barrière diélectrique. En effet, il est bien connu que le taux de fragmentation du précurseur et la vitesse de dépôt sont directement fonction de ce paramètre [93]. Ainsi, nous allons étudier dans cette partie l'efficacité du dépôt, la morphologie et la composition chimique des couches minces obtenues en changeant deux paramètres de la décharge, à savoir, la fréquence d'excitation et l'amplitude de la tension appliquée. L'impact de ces paramètres sur la polymérisation des gouttelettes d'HMDSO et donc sur la morphologie du dépôt sont analysés. Les résultats sont reportés dans l'article intitulé « *Control of plasma-droplet interactions during thin-film deposition by pulsed direct-liquid injections into dielectric barrier discharge* ». Cet article reprend les conditions d'injection (t_{gaz}= 5 ms, t_{liq}= 10 ms et f= 0.1 Hz) d'HMDSO dans la DBD décrite dans le chapitre précédent. Les outils de diagnostics de la décharge et des couches minces déposées sont aussi les mêmes.

Par la suite, pour mieux comprendre l'effet de l'évaporation des gouttelettes produites par injection pulsée de liquide, la deuxième partie de ce chapitre se concentre sur un précurseur avec une température d'évaporation plus faible, à savoir, le pentane.

IV.1. Control of plasma-droplet interactions during thin-film deposition by pulsed direct-liquid injections into dielectric barrier discharge

Tuning plasma-droplet interactions during thin-film deposition by pulsed direct-liquid injections into dielectric barrier discharge

L. Cacot[1,3], M. L. Kahn[2], R. Clergereaux[1], L. Stafford[3,**]and N. Naudé[1,††]

[1]LAPLACE, CNRS, UPS, INPT, Université de Toulouse, 31062 Toulouse, France

[2]LCC, CNRS, Université de Toulouse, 31062 Toulouse, France

[3]Département de physique, Université de Montréal, 1375 ave Thérèse-Lavoie-Roux, Montréal, QC, H2V 0B3, Canada

Abstract

This work investigates the effects of discharge parameters on the deposition of organosilicon thin films by pulsed direct liquid injections of hexamethyldisiloxane (HMDSO) into a plane-to-plane dielectric barrier discharge generated in nitrogen at atmospheric pressure. At low frequency of the applied voltage, plasma-deposited thin films exhibit viscous and droplet-like morphologies. Such feature is linked to the charging of HMDSO droplets in the discharge and their transport towards the substrate by the low-frequency electric field. Comparatively, the thin films obtained at high frequencies present rough morphologies with dust formation. In such conditions, the deposition efficiency decreases due to confinement of charged HMDSO droplets in the inter-electrode space. In addition, enhanced plasma-droplet interactions linked to neutral gas heating induce precursor evaporation. This yields to solid particles formation due to the onset of gas-phase association of precursor fragments.

Keywords: Thin Films, Atmospheric Pressure Plasma Deposition, Dielectric Barrier Discharge, Pulsed Direct Liquid Injection, Aerosols, Organosilicon Coatings

[**] Electronic mail: luc.stafford@umontreal.ca

[††] Electronic mail: nicolas.naude@laplace.univ-tlse.fr

1. Introduction

The formation of silicon-based thin films by plasma-enhanced chemical vapor deposition (PECVD) is a well-established process that was initially developed in low-pressure plasmas. During the past decades, atmospheric-pressure PECVD processes have also been examined [1–6], and their expansion is of great interest for industries that make use of silicon-based deposits in optical, electrical, electrochemical, and medical applications [7–15]. In such PECVD processes, the properties of the plasma-deposited materials can be tailored by varying the power injected into the plasma [16,17], the precursor injection rate [18,19], the duty cycle in pulsed plasma conditions [20,21], or the process pressure [22]. For example, in Ar-NH_3-SiH_4 gas mixtures, *Bazinette et al.* showed that tuning the excitation frequency from kHz to MHz increases the growth rate of SiN films from 10 up to 80 nm.min^{-1} [23].

Because it is stable, is non-explosive, is non-toxic, and contains a polydimethylsiloxane subunit, hexamethyldisiloxane (HMDSO) is a precursor frequently used in PECVD of organosilicon plasma polymers. At atmospheric pressure, organosilicon thin films are mostly formed by vaporizing the liquid and the vapor is transported towards the discharge by a carrier gas [24–27]. In such conditions, significant precursor fragmentation occurs, and the films exhbit a high degree of cross-linking [3,28,29]. In a study conducted by *O'Neill et al*. [30], it was found that the mechanisms involved in organosilicon thin-film deposition in an atmospheric pressure plasma reactor reactor is strongly linked to the precursor flow rate. At low precursor flow rates, HMDSO is fully vaporized, and this results in a standard gas-phase PECVD process. As the precursor flow rate increases, liquid droplets can not be fully vaporized and are injected in the plasma. The change from gaseous to liquid precursor phase was further shown to modify the surface properties of the films, with a droplet-like morphology at high precursor flow rates [27,30].

Similar droplet-like morphologies were recently obtained using a pulsed direct-liquid injection of HMDSO in a plane-to-plane dielectric barrier discharge (DBD) operated in

nitrogen at atmospheric pressure [31]. In such aerosol-assisted plasma deposition conditions, the presence of liquid droplets affects the plasma process in several ways. First, the droplets act as a sink for charged and excited species. Since any factor leading to a significant loss of electrons and metastable $N_2(A)$ states in nitrogen DBDs no longer ensure conditions for homogeneous discharge formation [32], the Townsend breakdown becomes replaced by a streamer breakdown, and the discharge transits from homogeneous to filamentary regime [33,34]. Second, the droplets electrically charge as a floating dust in the plasma [35], and this affects their transport properties in the discharge cell. For low carrier gas flow rates, and thus for low neutral gas forces along the gas flow lines, it was recently found that thin-film deposition results from the charging of HMDSO droplets by the filamentary discharge and their transport towards the top and bottom electrodes by the low-frequency electric field [36]. In such conditions, plasma polymerization involves plasma-droplet interactions. In addition, the chemical pathways available for reaction in the liquid phase are much more tightly controlled than in standard gas-phase PECVD processes. In particular, the monomer is not heavily fragmented, and the process can deliver soft plasma polymerization with very low crosslinking levels [31].

Depending on the experimental conditions, droplets injected into atmospheric pressure plasmas can also evaporate, producing a region of high vapor density around the droplets that will affect plasma chemistry and thus thin-film deposition. Droplet evaporation models were proposed for low-pressure plasmas [37]. Five basic phenomena were included: evaporation (cooling), recondensation (heating), neutral gas heating, radiation heating/cooling, vapor heating, and recombination heating. In the case of ethanol droplets exposed to a warm plasma (neutral gas temperatures in the 1500 K range) at low pressure, 10 μm size droplets completely evaporate within 2-3 ms [37]. Obviously, much longer evaporation times are expected for droplets exposed to low-frequency dielectric barrier discharges at atmospheric pressure that are characterized by much lower neutral gas temperatures [38,39], even after their transition from the homogeneous to the filamentary regime [40]. Depending on the liquid vaporization rates and the droplet residence time in the plasma (linked to the carrier gas flow rate) [37], thin-film deposition can thus involve

plasma interactions with a gaseous and/or liquid droplet precursor [41]. However, in many cases, the factors driving mist-assisted plasma deposition processes (combination of gas, liquid, and plasma phases [42]) remain poorly understood [43,44].

In this study, we investigate the effects of the discharge power, modified by changing the frequency and the amplitude of the applied voltage, during thin-film deposition by pulsed direct-liquid injections of HMDSO into nitrogen DBD at atmospheric pressure. As will be seen, such parametric study can tailor plasma-droplet interactions for judicious control of the thin-film deposition kinetics and plasma polymerization dynamics.

2. Experimental setup and diagnostics

The experimental setup used in this study has been described previously [9], and is schematically presented in Figure 1. The planar DBD is initiated in a chamber filled with N_2 at atmospheric pressure (Alphagaz 1, Air Liquide). A self-regulating valve is used to maintain the pressure at 750 Torr, and N_2 gas (continuous flow of 0.4 slm) is introduced into the inter-dielectrics space via a gas diffuser. The discharge is ignited between two electrodes (3 cm × 6 cm) consisting of alumina plates coated with conductive silver paste. The silicon wafer substrate is placed on the bottom dielectric and fixed on the edges (outside the discharge area) by Kapton. Two glass spacers are placed on top of this substrate to maintain a constant gas gap distance of 1 mm. To ignite the discharge in the gas gap, a sinusoidal voltage signal with 750 Hz–6 kHz frequency and 13 or 15 kV_{pp} amplitude is applied. The sinusoidal signal is generated by a Tektronix AFG3021C power supply connected to a linear amplifier (Crest Audio CC4000) and step-up transformer to obtain the desired voltage range. The applied voltage is measured using a high-voltage probe (Tektronix P6015A) connected to the high-voltage electrode, and the current passing through a 100 Ω resistor connected to the discharge cell in series is deduced from the voltage value. To determine the charge, the shunt resistor is replaced with a 220 nF capacitor, and the voltage across is measured. All electrical signals are acquired using an

oscilloscope (TELEDYNE Lecroy HD06104A), and the surface power is calculated according to the Lissajous method [45].

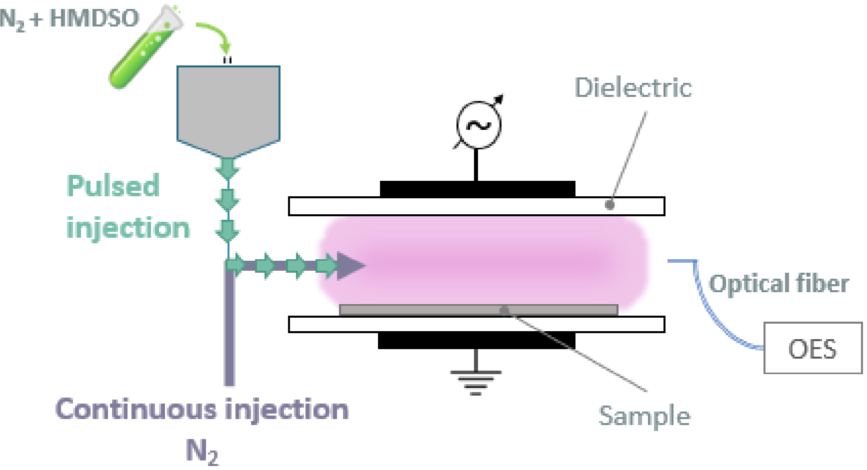

Figure 1:Scheme of the experimental setup used for thin-film deposition and process characterization.

HMDSO is injected into the discharge cell using a commercial direct liquid injector provided by Kemstream [46]. Direct-liquid injections are carried out in pulsed mode, and are controlled by an injection control unit, which may be used to adjust the liquid and exhaust injection time (t_{liq} and t_{out} are the durations of the pulse that direclty control the quantity of fluid injected) and pulse injection frequency (f). In this study, experiments are performed for t_{liq} = 5 ms with t_{out} = 10 ms pulse duration and f = 0.1 Hz pulse frequency. The injected liquid is introduced into the discharge cell through a pipe and a diffuser, the latter being placed at the entrance of the inter-electrode space to ensure a longitudinal flow. In all cases, a continuous nitrogen carrier gas flow of 0.4 L.min^{-1} is added to pulsed direct-liquid injections (Figure 1). As shown previously [36], such continuous nitrogen gas flow yields to a neutral drag force on the droplets and can be used to control their transport along the gas flow lines.

To analyze the discharge , optical emission spectroscopy (OES) is performed using an optical fiber positioned in front of the discharge. Photons are collected along an optical path parallel to the gas flow lines. Time-averaged discharge emission is monitored using a

high-resolution monochromator (Acton SP-2500) equipped with an intensified charged coupled device (iCCD) camera (Princeton Instruments PI-MAX3). The grating of the monochromator is centered at either 380 or 750 nm to record the second positive system (N_2-SPS) and the Herman Infrared system (N_2-HIR) of nitrogen, respectively.

Organosilicon deposits formed on the silicon substrate are observed after plasma treatment by optical microscopy (OMAX) in transmission mode. Selected samples are also analyzed by Scanning Electron Microscopy (SEM, 7600F JEOL). SEM observation is done with an acceleration voltage of 10 kV. Fourier Transform Infrared (FTIR) measurements in a transmission mode (Bruker, Vertex 70) for different positions along the gas flow lines are also done. The spectra are acquired in the range of 500–4000 cm^{-1} at the spectral resolution of 4 cm^{-1}, and each spectrum consists of 16 averaged scans.

3. Thin-film characterization

Figure 2 presents multi-scale optical images recorded under variable frequency conditions (750 Hz–6 kHz), at the voltage amplitude of 13 kV_{pp}. The images corresponding to the applied voltage conditions of 15 kV_{pp} and 1 kHz are also shown for comparison. On one hand, low-magnification images show that the thin films deposited at 750 Hz and 1 kHz are viscous with droplet-like morphologies [27,30,31,36]. In addition, different levels of iridescence, linked to thin-film thickness variations, can be seen. On the other hand, the coatings obtained at higher voltage amplitude (15 kV_{pp}) and at higher frequency (2 and 6 kHz) show no iridescence signature.

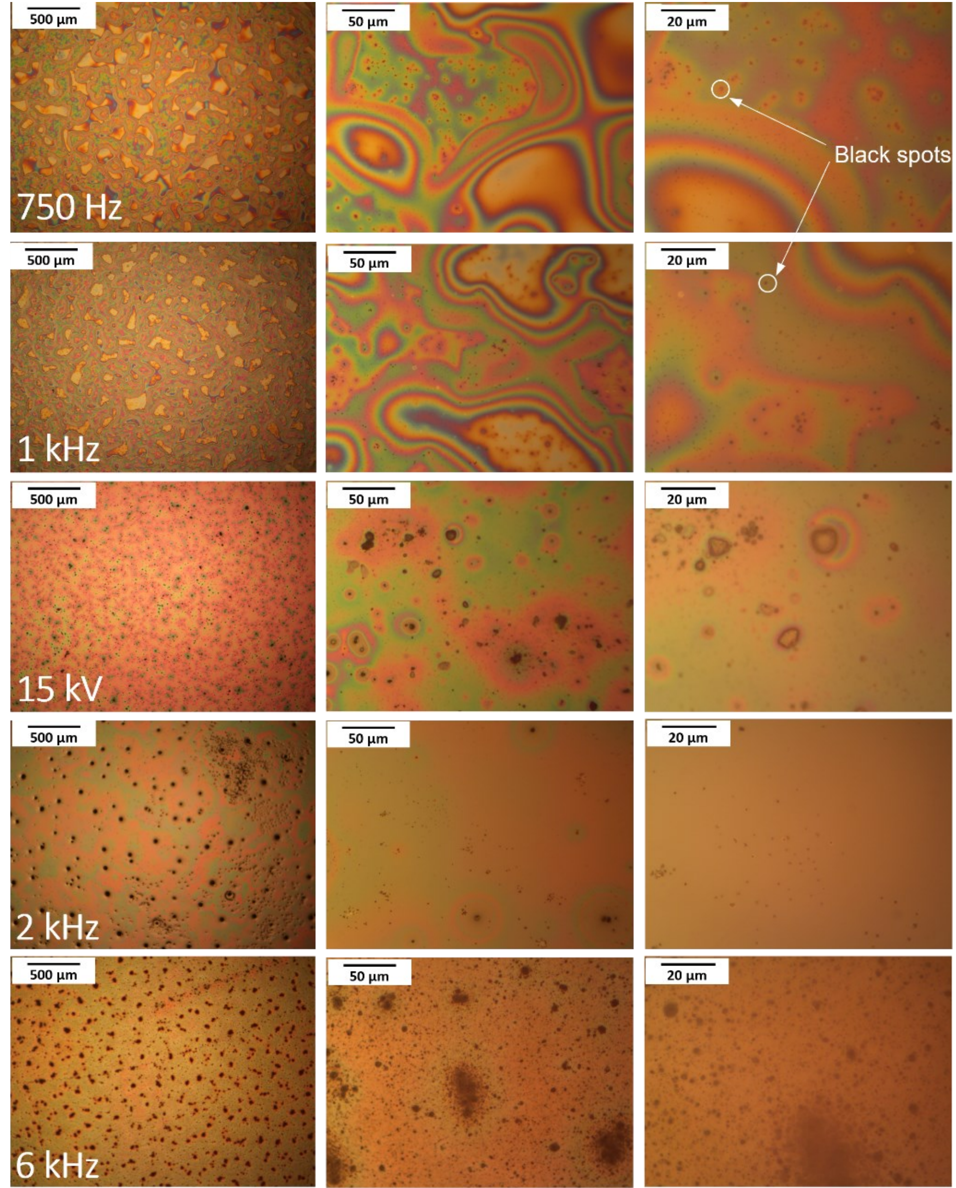

Figure 2: Optical images of the plasma-deposited organosilicon layer recorded under various conditions of frequency and amplitude of the applied voltage.

In high-magnification images, Figure 2 reveals that black spots with dimensions in the 1 µm range appear on the plasma-deposited layers. Such feature cannot be attributed to the impact of filaments on the surface, since their average diameter of about 200 µm [47,48] is much larger than 1 µm. This result rather underlines that thin-film deposition comes from ~1 µm droplet following their interaction with the discharge. As previously discussed, the interaction of ions and electrons from the filaments with the aerosol induces surface charging of HMDSO droplets over very short time scales (~5 ns with average ion and electron number densities of ~10^{12} cm^{-3} in filamentary discharges operated in nitrogen

[39]). While charged HMDSO droplets much smaller than 10 µm can easily be transported towards the substrate surface by the low-frequency electric field within half-period of the applied voltage, charged droplets much larger than 10 µm oscillate with an amplitude much lower than the gas gap and thus remain trapped between the two electrodes over multiple low-frequency cycles [36]. In such conditions, the film grows by deposition of ~1 µm droplet droplets on the film surface [31], as observed by other authors [49,50].

From the low- and high-magnification images presented in Figure 2, it can further be seen that much larger black features appear as the frequency increases from 750 Hz to 6 kHz. These features are analyzed by scanning electron microscopy. For the coating deposited at 6 kHz, Figure 3 reveals that they correspond to dust particles and clusters of particles deposited on the film surface. In addition, the film topmost surface is relatively rough, suggesting that particles are also embedded into the coating; similar morphologies were observed for TiO_2 particles embedded into silica and hydrocarbon films [51–53].

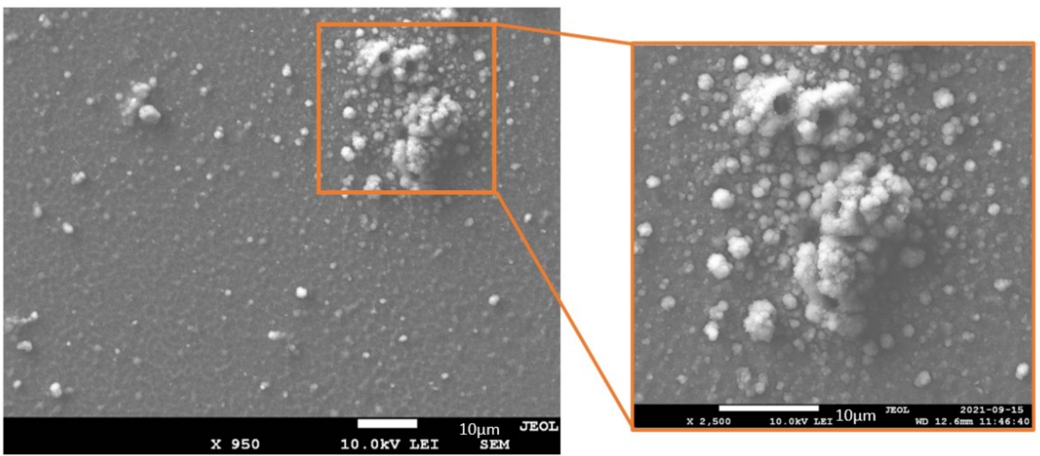

Figure 3: Scanning electron microscopy images of the coatings deposited at 6 kHz.

In HMDSO-based plasmas, dust particles result from gas-phase nucleation of radicals and dissociation products [54,55]. Such particles thus form with gaseous precursors when the total energy provided to gaseous precursor molecules allows decomposition, nucleation, and growth [56]. From literature, the energy per mass of HMDSO required for particle

production in DBD reactor is around 65 MJ kg^{-1} [57]. Over the range of experimental conditions investigated, HMDSO enters into the DBD cell as an aerosol. As underlined above, HMDSO droplets become charged and are then transported by the electric field towards the substrate where thin-film deposition occurs. At low frequency, the deposition of viscous films without particles reveals that the process is driven by plasma-droplet interactions with no significant precursor evaporation [36]. On the other hand, at high frequency, the presence of particles on the surface and in the coatings suggests that some droplets are partially vaporized and that some energy is provided to HMDSO vapors. Under the assumption that droplet evaporation is driven by heat transport through conduction between the droplet and the neutral plasma species, the change over time in the droplet surface area ($4\pi a^2$, where a is the droplet radius) can be written as [58]

$$\frac{da^2}{dt} = \left(\frac{2\lambda_{gV}}{h_{LV}\,\rho_L}\right)\left[T_L - T_g\right] \qquad (1)$$

where λ_{gV} is the thermal conductivity of the ambient gas-vapor mixture, h_{LV} is the enthalpy of evaporation of the droplet, ρ_L is the density of the liquid, and $T_L - T_g$ is the difference between the temperature of the droplet surface and the neutral gas species in the plasma, respectively. Based on Equation (1), precursor evaporation, and thus particle formation through gas-phase nucleation of radicals and dissociation products [54,55], could result from a rise in the neutral gas temperature with the frequency of the applied voltage; we will come back to this point in the next section.

The chemical composition of the plasma-deposited layers is analyzed by transmission FTIR. As shown in Figure 4, the absorbance spectra present the main features of the HMDSO monomer [59,60], including CH_3 rocking in Si-$(CH_3)_3$ at ~840 cm^{-1}, Si-CH_3 symmetric bending at ~1260 cm^{-1}, and asymmetric and symmetric CH_x bending at ~2900 cm^{-1}. With respect to the monomer, the intense Si-O-Si asymmetric stretching moves to lower wavenumbers [27]. Other bands reported for plasma-polymerized thin films using HMDSO are also detected. In particular, the CH_3 rocking in Si-$(CH_3)_2$ at ~800 cm^{-1} is the signature of a methyl group removal from the monomer and the deposition of polydimethylsiloxane-like coatings [27]. At higher frequencies, Si-H stretching at

~2200 cm^{-1} reveals an efficient mechanism of H atoms recombination on pending Si atoms. Such feature is typically seen in organosilicon plasma polymers with plasma-surface interactions and significant crosslinking [3,28,29].

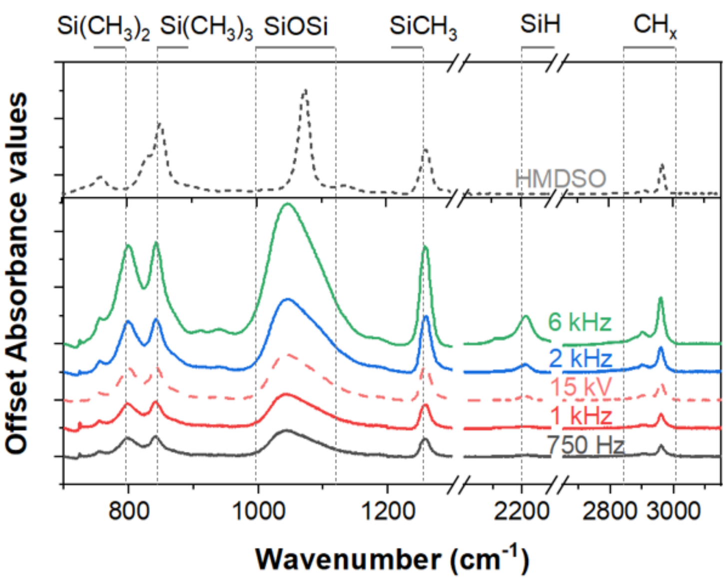

Figure 4: FTIR spectra from thin films obtained for different frequency and amplitude of the applied voltage. FTIR spectrum from liquid HMDSO is also shown for comparison.

Considering Beer-Lambert, a rise in the FTIR band absorbance highlights that the thickness of the plasma-deposited thin film increases. This phenomenon is well-documented for plasma deposition processes operated with fully vaporized HMDSO at low [61] and atmospheric pressure [62]. A rise in the film thickness for a specific precursor concentration fraction is generally attributed to a more prominent precursor dissociation, for example, through a rise in the electron population involved in electron-impact dissociation of HMDSO [63]. In nitrogen DBD operated in a homogeneous regime with fully vaporized HMDSO, a rise in the film thickness for a given precursor concentration is usually linked to an increase in the population of metastable $N_2(A)$, as the latter is the prominent species involved in HMDSO dissociation [62]. As shown in Figure 4, the intensities of all absorbance bands increase upon increasing the frequency or amplitude of the applied voltage. This suggests that the thin-film deposition rate increases with the power injected into the DBD [36].

To further assess the thin-film deposition kinetics and plasma polymerization dynamics, coatings are analyzed at several different positions along the gas flow lines (linked to the precursor residence time). Selected data are presented in Figure 5. As shown in Figure 5a, at low frequency of the applied voltage, the evolution of the Si-O-Si band area exhibits a maximum close to the outlet. As the frequency increases, the spatially-averaged thickness of the plasma-deposited film increases and the maximum thickness moves closer to the entrance. Similar results were reported by *Enache et al.*[62] for fully-vaporized HMDSO by increasing the injected power from 2 to 10 W.cm^3 in a nitrogen DBD operated in a homogeneous regime. In this case, the efficiency of HMDSO dissociation increases with power (due to the corresponding increase of the metastable $N_2(A)$ populations [64]), such that spatially-averaged deposition rates are higher. In addition, the precursor becomes consumed faster at the entrance of the discharge cell and the deposition rate reaches a maximum value in this region.

As shown in Figure 2, thin-film deposition with pulsed aerosol injection results from two mechanisms: (i) the first one is based on HMDSO droplet charging and their transport towards the substrate by the electric field [31,36], while (ii) the second one relies on particles produced by gas-phase nucleation of radicals and dissociation products [54,55]. In presence of particles in vapor-phase deposition processes, two maxima are typically observed along the gas flow lines [65]. While the first one is associated to a decrease in the number of radicals reaching the surface due to their consumption [63], the second one is due to particles that form when the total energy input provided to gaseous precursor molecules allows decomposition, nucleation, and growth [56]. Over the range of experimental conditions investigated, only one maximum is observed close to the entrance, suggesting that the contribution of particles and clusters of particles play a minor role in the total mass balance of the plasma-deposited organosilicon thin films.

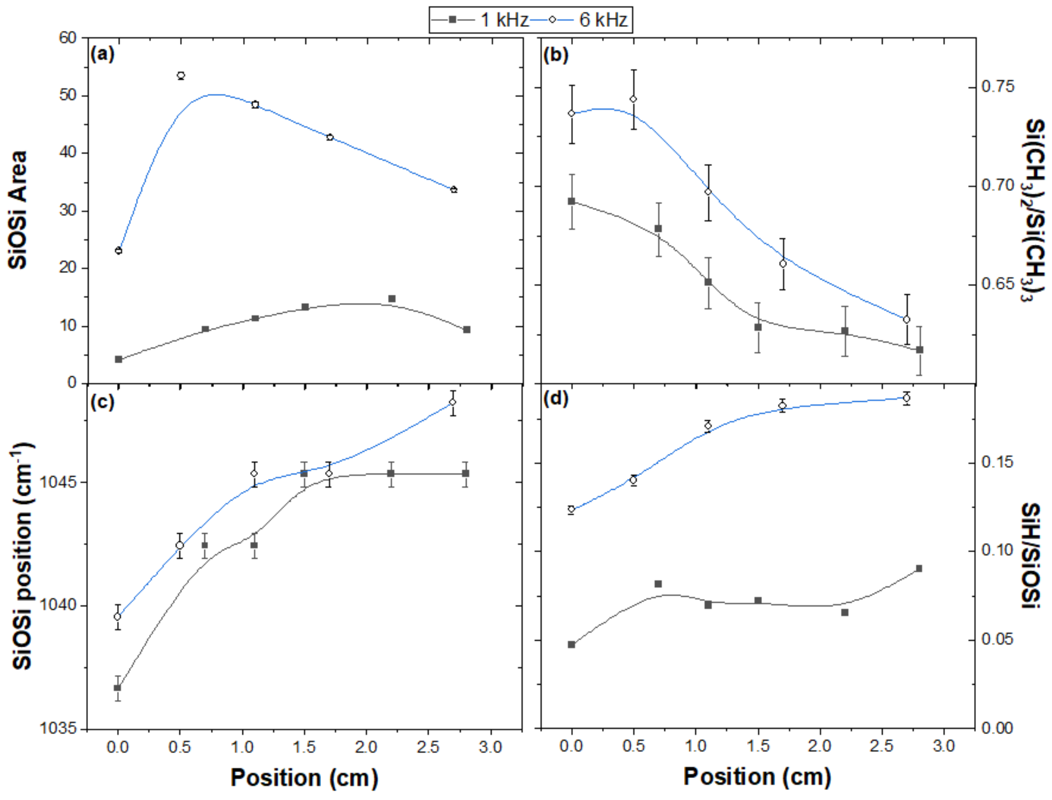

Figure 5: Influence of the position along the gas flow lines on (a) the thin-film deposition rate provided by the Si-O-Si absorbance, (b) the degree of polymerization provided by the Si-$(CH_3)_2$-to-Si-$(CH_3)_3$ band ratio, and (c) the position of the Si-O-Si band. The results are shown at two frequencies of the applied voltage.

To further investigate FTIR evolutions as a function of position along the gas flow lines (linked to the precursor residence time), the Si-$(CH_3)_2$-to-Si-$(CH_3)_3$ band ratio is calculated [31,60]. This band ratio is related to the degree of polymerization: in highly-fragmented deposits, Si-$(CH_3)_2$ relative absorbance increases, while in low-fragmented deposits, there is a high retention of Si-$(CH_3)_3$ and the Si-$(CH_3)_2$ relative absorbance decreases. Independently of the frequency, Figure 5b reveals that even if the thin-film deposition rate exhibits a maximum (as reported in Figure 5a), the degree of polymerization monotonously decreases from the entrance to the exit. Hence, for processes relying on direct-liquid injection of HMDSO in nitrogen DBDs, the degree of polymerization decreases with the droplet residence time in the plasma volume. Plasma polymerization can also be monitored by plotting the position of the Si-O-Si band observed by FTIR (from 1000 to 1100 cm^{-1}) [31]. As can be seen in Figure 5c, an important shift in the position of the Si-O-Si band is observed, from 1035-1040 cm^{-1} at the discharge entrance to 1045-1048 cm^{-1} at the

discharge outlet. Of note, the value for liquid HMDSO without plasma polymerization is 1065 cm^{-1} (see Figure 4). Hence, with the increase of position along the gas flow lines, or of the droplet residence time in the plasma volume, a large amount of matter probed by transmission FTIR tends towards soft plasma polymerization conditions [31].

The extent of plasma-surface interactions and cross-linking in plasma-deposited thin films can be described by the Si-H-to-Si-O-Si band ratio [3,28,29]. Weak values of this ratio express that plasma polymerization mostly occur in the liquid phase with minimal contributions of plasma-generated H atoms interaction with the droplets and/or the film surface; this yields to a low cross-linking level and a strong preservation of the precursor conformation in the solid. In contrast, high values of this ratio indicates significant interactions between the droplet and/or the film with plasma-generated H atoms; this convey a high cross-linking level and a strong loss of the precursor conformation. As can be seen in Figure 5d, a small rise in the band ratio is observed with positions along the gas flow lines, or with the droplet residence time in the plasma volume. In addition, much higher Si-H-to-Si-O-Si band ratios are observed at 1 than at 6 kHz. Hence, with the increase of power injected in the discharge, the extent of H-surface interactions increases and the cross-linking levels rise [66]. This conclusion seems consistent with precursor evaporation at high frequency and thus a more important concentration of gaseous H atoms available for plasma-droplet and/or plasma-film interactions.

4. Discharge characterization

The effects of frequency and amplitude of the applied voltage on the plasma deposition process is further assessed by characterizing the discharge using electrical diagnostics (current-voltage and charge-voltage) and optical emission spectroscopy. Over the range of experimental conditions investigated, the discharge rapidly transits from homogeneous to filamentary following pulsed, direct-liquid injection of HMDSO droplets [31,36]. As underlined above, this is because droplets act as a sink for charged and excited species [32] such that the Townsend breakdown becomes replaced by a streamer breakdown [33,34]. Figure 6 depicts a typical time-averaged optical emission spectrum of filamentary nitrogen

discharges in presence of HMDSO droplets. The emissions of the N_2 Second Positive System (SPS) and N_2 Herman InfraRed (HIR) system are clearly observed. Over the range of experimental conditions investigated, the emitting N_2(C) and N_2(C'') states are mainly produced by electron-impact excitation on ground state N_2(X), $N_2(X) + e^- \rightarrow N_2(C) + e^-$, and pooling reaction involving metastable N_2(A) states, $N_2(A) + N_2(A) \rightarrow N_2(C'') + N_2(X)$, respectively [67]. The emission intensities of these bands are thus used to probe the electron and metastable N_2(A) populations, respectively. Spectrally-resolved emission bands can also be used to estimate the rotational temperature, or neutral gas temperature assuming efficient rotation-translation equilibrium [33,68]. Here, the rotational structure of some SPS bands are fitted with a theoretical spectrum using the rotational temperature as the only adjustable parameter. The inset shown in Figure 6 presents an example of the rotational temperature fit corresponding to the Δν = 2 band of N_2 SPS at 380 nm.

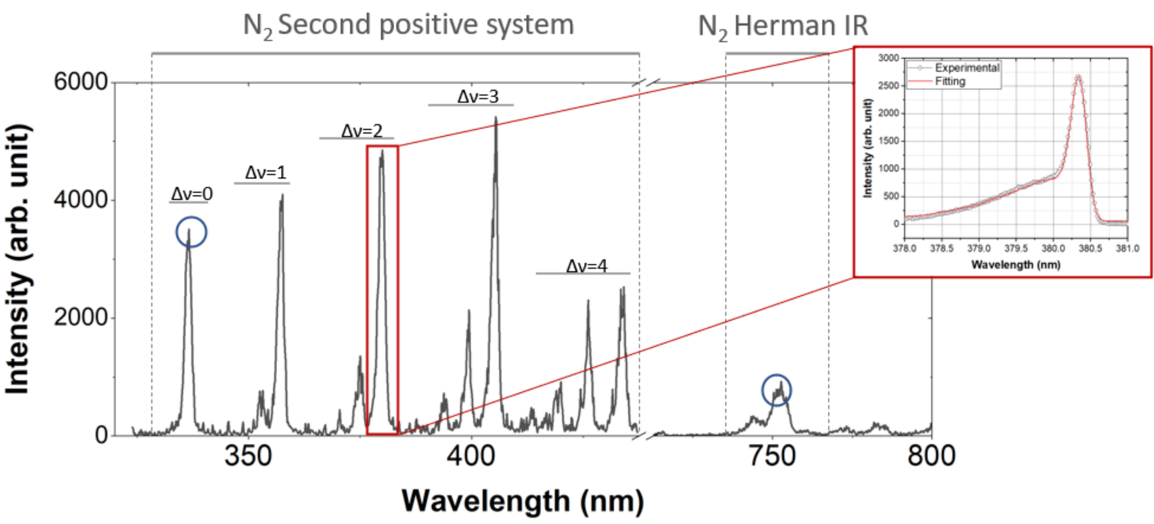

Figure 6: Typical optical emission spectrum of the nitrogen Townsend discharge. The insert shows the N_2 SPS fitting at 380 nm, which was used to determine the rotational temperature.

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The effects of frequency and amplitude of the applied voltage on the neutral gas temperature, the time-averaged emission intensities of the N_2 SPS and N_2 HIR, and the power density injected into the discharge obtained from Lissajou plots [69], are shown in Figure 7. Clearly, the neutral gas temperature rises from about 300 K at 750 Hz to about 375 K at 6 kHz (Figure 7a). Such increase is consistent with the corresponding rise of the

power injected into the discharge, going from 0.1 to 1.4 $W.cm^{-2}$ between 1 and 6 kHz (see Figure 7b). As shown in Figure 7c, the emission intensities of the SPS and HIR systems both increase with increasing discharge power. Considering that the chamber pressure is constant, the rise of the SPS signifies an increase in electron density and/or electron temperature. Since the N_2 HIR emission is related to the density of $N_2(A)$ metastables, the results indicate that the production of both charged and metastable species increases at higher frequency, which agrees well with the available literature [70,71].

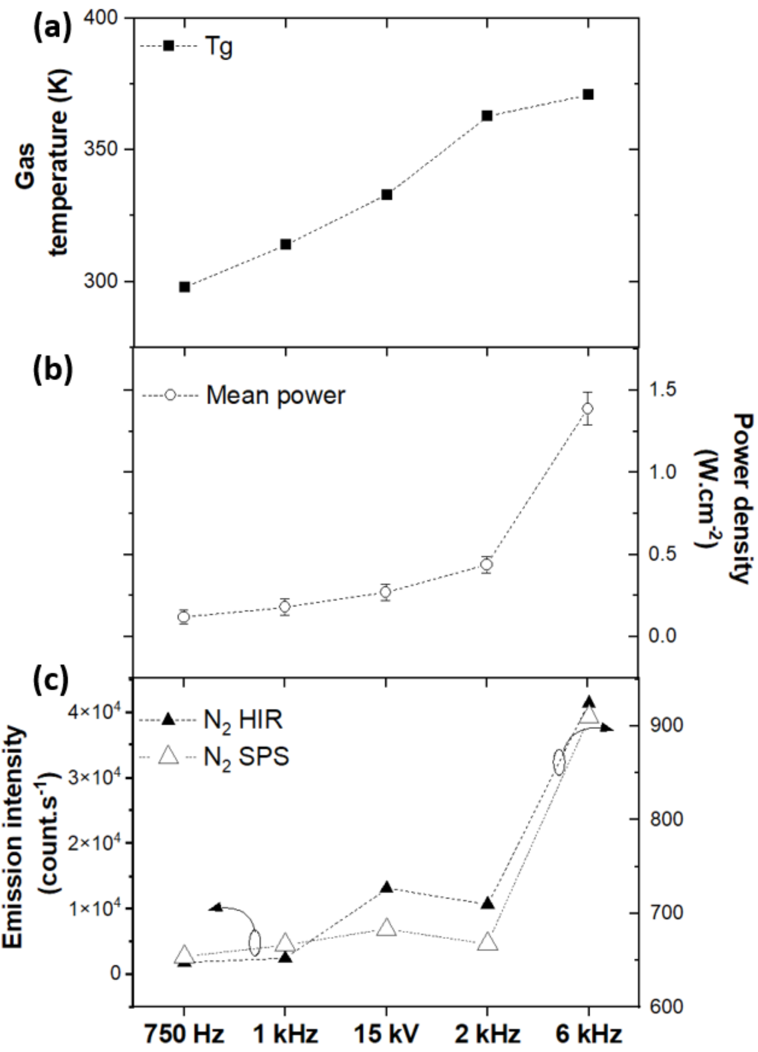

Figure 7: (a) Neutral gas temperature, (b) Power density, and (c) Time-averaged emission intensity from N_2 SPS and N_2 HIR for discharges generated at 13 kV_{pp} (750 Hz to 6 kHz) and 15 kV_{pp} (1 kHz).

5. Discussion

In a previous paper [36], the effects of selected process parameters, namely, duty cycle, delay between precursor injection and discharge ignition, and the amount of injected HMDSO microdroplets on the plasma-assisted deposition rate of organosilicon thin films in DBDs operated in nitrogen and sustained at 1 kHz was assessed. It was found that the deposition rate is directly proportional to an energy parameter E (also called the Specific Energy Input [72]) defined as $E=P\times t_{residence}\times Duty\ Cycle$, where P is the power density determined from electrical analysis of the DBD, $t_{residence}$ is the average time during which the droplet remains in the discharge (calculated based on the dimensions of the inter-dielectric space and the continuous N_2 gas flow rate), and Duty Cycle is the ratio between the plasma-on time and the liquid injection time [36]. Such linear trend revealed that the thin-film deposition rate is limited by the amount of energy provided to precursor droplets, and not by precursor insufficiency [73–75]. To examine if this trend holds for the set of experimental conditions examined in this work, the thin-film thickness is divided by the energy parameter. Such ratio can be defined as a process efficiency and the results are plotted in Figure 8 for the various process conditions.

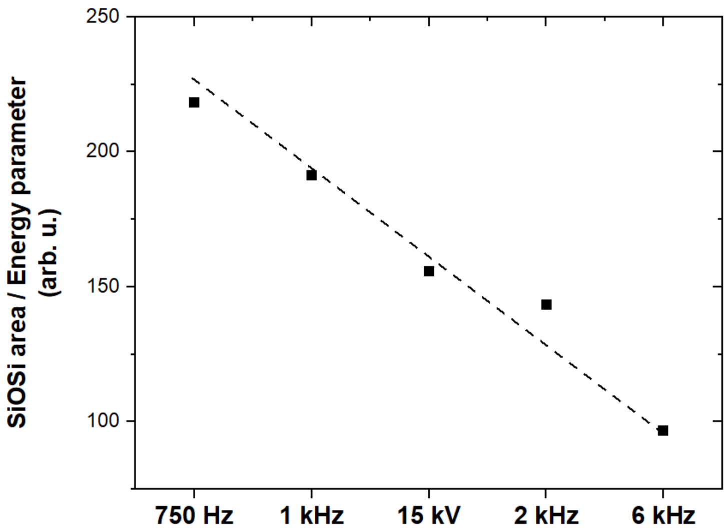

Figure 8: Values of the SiOSi absorbance obtained by FTIR averaged over all positions along the gas flow lines (linked to the spatially-averaged thin-film deposition rate) over the energy injected into the system obtained from electrical diagnostics. The results are for discharges generated at 13 kV_{pp} (750 Hz to 6 kHz) and 15 kV_{pp} (1 kHz).

As can be seen in Figure 8, the thin-film deposition efficiency decreases by about a factor of 3 between 750 Hz and 6 kHz. Over the range of experimental conditions investigated, since the contribution of particles and clusters of particles play a minor role in the total mass balance of the films (see Figure 5), thin-film deposition mostly results from the charging of HMDSO droplets and their transport towards the substrate by the electric field [31,36]. However, the latter strongly depends on the operating conditions. For example, at 1 kHz, only droplets much smaller than 10 mm can be efficiently transported to the substrate since larger ones remain trapped in the gas gap over multiple low-frequency cycles [36]. Assuming a similar steady-state charge on HMDSO droplets for all conditions, their amplitude of oscillations in the electric field, and thus their collection efficiency on the substrate surface, is expected to decrease with increasing frequency, as seen in the experiments. However, the decay observed in Figure 8 (factor of 3) is lower than the one expected from the simple trajectory model of charged droplets in the oscillating electric field (factor of 6 between 1 and 6 kHz). This indicates that the charge on HMDSO droplets most likely rise with increasing power injected into the DBD [76,77].

In the literature, a critical value of the energy per mass of precursor has been established to highlight the regime for particle production in DBD with organosilicon precursors [57]. For HMDSO, this critical value is 65 MJ kg^{-1} [57]. If the energy per mass of precursor is above 65 MJ kg^{-1}, dust particles are formed by from gas-phase nucleation of radicals and dissociation products [54,55]. On the other hand, if the energy per mass of precursor is below 65 MJ kg^{-1}, the films are homogeneous with no dust particles. This value is calculated for a number of studies reported in scientific literature. The results are shown in Figure 9, along with the corresponding film morphology (with or without particles). This set of data includes thin film deposition experiments based on both plasma-gas and plasma-liquid precursor interactions.

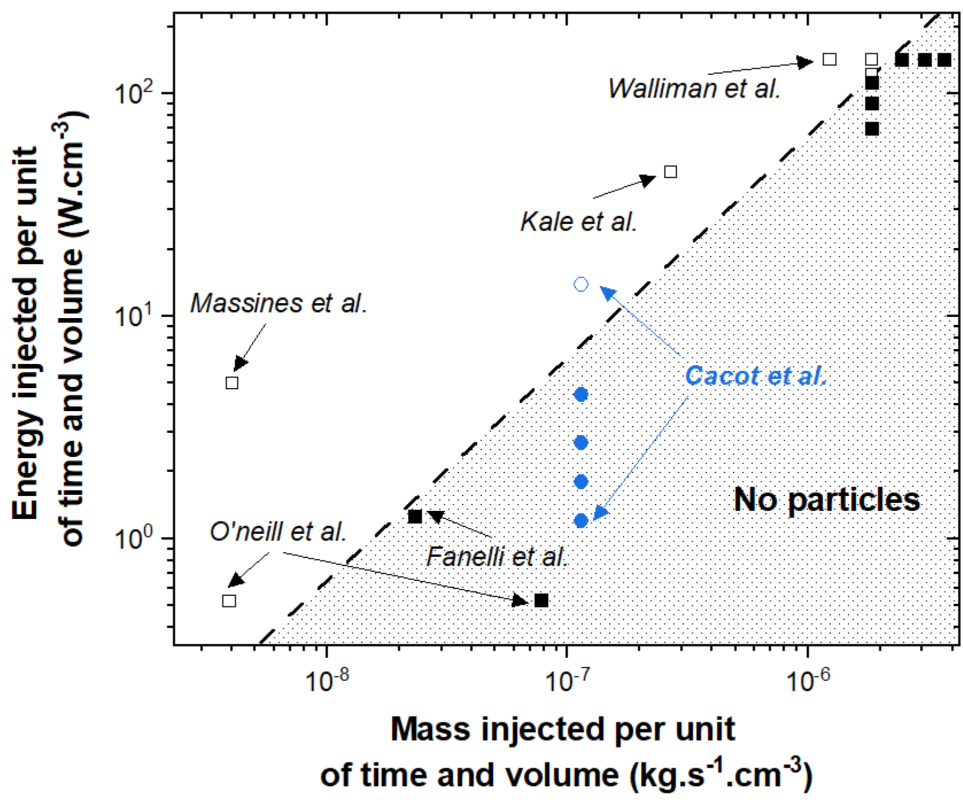

Figure 9: Comparison between the energy injected in the plasma per unit of time and volume and the the mass of HMDSO precursor injected in the system per unit of time and volume. The dashed line corresponds to the critical value of 65 MJ kg^{-1} for dust particle formation in HMDSO-based plasmas[57]. *Data points orginate from Massines et al.* [78], *O'Neil et al.* [30], *Fanelli et al.* [27], *Kale and al.* [29], *Walliman et al.*[57]. *Open symbols correspond to rough films with dust particles while full symbols relate to smooth films without particles. The results obtained in this study (Cacot et al.) for direct liquid injections of HMDSO are also shown.*

Clearly, only studies involving energy per mass of HMDSO superior to 65 MJ kg^{-1} yields to particles and/or rough film surfaces (open symbols in Figure 9). For the pulsed, direct-liquid injections examined in this study, this criterion also holds (blue symbols in Figure 9): while droplet-like morphologies without particles are observed at 1 kHz (18 MJ.kg^{-1}), rough surfaces with significant particles are seen at 6 kHz (115 MJ.kg^{-1}). Therefore, the critical value of 65 MJ kg^{-1} for particle formation in HMDSO-based plasmas holds for both gaseous and liquid precursor systems.

After a discussion on thin film deposition efficiency and dust particle formation conditions, it is also worth examining the role of plasma-droplet interactions on plasma polymerization. The results obtained Figure 5 show that the degree of plasma polymerization of HMDSO in a DBD operated in a pulsed direct-liquid-injection mode

strongly depends on the discharge parameters, including the frequency and amplitude of the applied voltage. Inspired by our previous work [31], this aspect is examined in more details by plotting the Si-O-Si band position and the degree of plasma polymerization linked to the $Si(CH_3)_2$-to-$Si(CH_3)_3$ band ratio as a function of the specific energy input [72]. For spatially-resolved measurements along the gas flow lines, this energy is calculated as $E=P\times t_{residence}\times(x / L)$, where x is the position along the gas flow lines and L is the total discharge length. The results are shown in Figure 10. Clearly, the complete set of data follow the same trend. On one hand, Figure 10 reveals a shift in the position of the Si-O-Si peak, from 1020 cm^{-1} at low energy parameter values to 1050 cm^{-1} at higher energies, i.e. between the ones of plasma-polymerized organosilicon coatings with fully vaporized HMDSO (as obtained by *Kale et al.* [29]) and liquid HMDSO [30], respectively. On the other hand, Figure 10 shows a decrease in the degree of plasma polymerization with the specicic energy input. The values go from the ones seen in vapor-based deposition processes characterized by significant precursor fragmentation and high degree of cross-linking [28,29,79], to the ones recently observed in liquid-based deposition characterized by by low precursor fragmentation and soft polymerization [3,30]. Based on these results, low power-low neutral gas temperatures (low frequency) and high-power-high neutral gas temperatures (high frequency) yield to similar polymerization. Thus, even if some droplet evaporation occurs at high frequency, similar precursor fragmentation can be seen. However, as highlighted in the decription of Figure 5d, plasma-generated H atoms play a more important role with droplet evaporation at high frequency. Such rise in the interaction of H atoms with the droplets and/or the film surface yields to higher SiH-SiOSi band ratios and more cross-linked coatings [66].

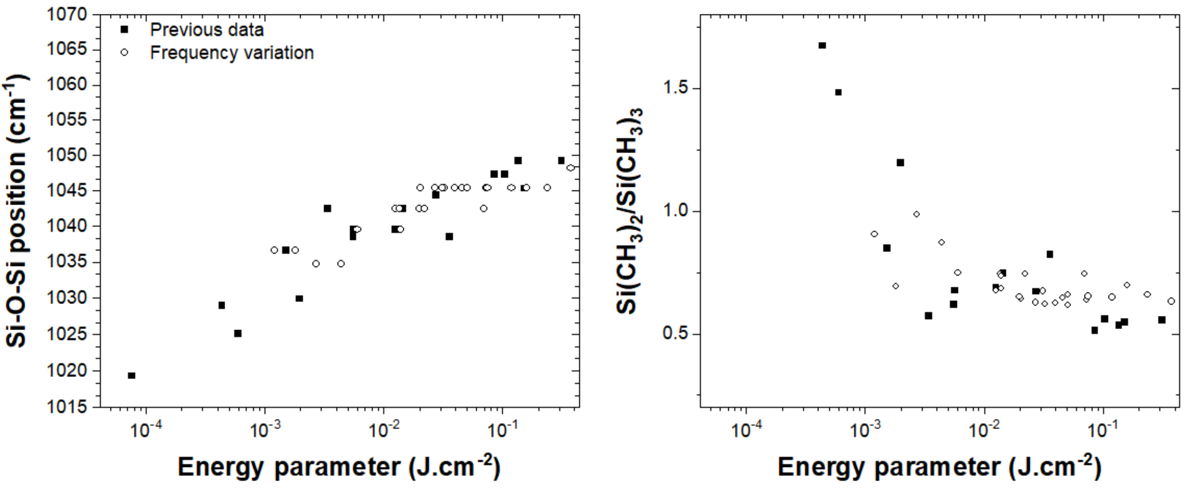

Figure 10: (left) Variation of the Si-O-Si peak position and (right) Si-$(CH_3)_2$-to- Si-$(CH_3)_3$ band ratio as a function of the energy parameter obtained for various operating conditions.

6. Conclusion

This study investigates the influence of discharge power on the morphology of the organosilicon coating deposited by direct liquid injection of HMDSO into a filamentary dielectric barrier discharge operated in nitrogen. The results show that when the frequency or amplitude of the applied voltage are adjusted to increase the plasma power, the chemical properties of the coating is altered, and its morphology is changed from droplet-like to rough surfaces with dust particles. In addition, the deposition efficiency decreases due to confinement of charged HMDSO droplets in the inter-electrode space. Discharge characterization analyses reveal that the rotational temperature and the emission intensities from N_2 SPS and HIR also increase with plasma power, indicating that the neutral gas temperature, electron population, and number density of $N_2(A)$ metastable species rise. The change in coating morphology and the formation of dust particles is linked to the onset of droplet evaporation through gas-phase nucleation of radicals and dissociation products. Through a judicious control of the energy injected to the precursor, soft plasma polymerization with low crosslinking can be achieved. Overall, the results presented herein show that tuning plasma-droplet interactions, droplet transport, and droplet evaporation play a crucial role on the thin-film deposition kinetics and plasma polymerization dynamics in aerosol-assisted processes.

Acknowledgments

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References

[1] Premkumar P A, Starostin S A, Creatore M, de Vries H, Paffen R M J, Koenraad P M and van de Sanden M C M 2010 Smooth and Self-Similar SiO2-like Films on Polymers Synthesized in Roll-to-Roll Atmospheric Pressure-PECVD for Gas Diffusion Barrier Applications *Plasma Processes and Polymers* **7** 635–9

[2] Gherardi N, Maechler L, Naudé N and Massines F 2009 APGD and APTD for the deposition of silicon based thin films from N 2 O / HMDSO mixtures : application to gas-barrier layers *Ispc 19* pp 1–4

[3] Morent R, de Geyter N, van Vlierberghe S, Dubruel P, Leys C and Schacht E 2009 Organic-inorganic behaviour of HMDSO films plasma-polymerized at atmospheric pressure *Surf Coat Technol* **203** 1366–72

[4] Trunec D, Navrátil Z, Sťahel P, Zajíčková L, Buršíková V and Ćech J 2004 Deposition of thin organosilicon polymer films in atmospheric pressure glow discharge *J Phys D Appl Phys* **37** 2112–20

[5] Sinha Ray S and Okamoto M 2003 Polymer/layered silicate nanocomposites: a review from preparation to processing *Prog Polym Sci* **28** 1539–641

[6] Savin de Larclause I, Paulmier T, Enache I, Caquineau H, Raynaud P, Massines F and Gherardi N 2009 Conformity of Silica-like Thin Films Deposited by Atmospheric Pressure Townsend Discharge and Transport Mechanisms *IEEE Transactions on Plasma Science* **37** 970–8

[7] Gilman J W, Jackson C L, Morgan A B, Harris R, Manias E, Giannelis E P, Wuthenow M, Hilton D and Phillips S H 2000 Flammability properties of polymer

- Layered-silicate nanocomposites. Polypropylene and polystyrene nanocomposites *Chemistry of Materials* **12** 1866–73

[8] Manca M, Cannavale A, de Marco L, Aricò A S, Cingolani R and Gigli G 2009 Durable superhydrophobic and antireflective surfaces by trimethylsilanized silica nanoparticles-based sol-gel processing *Langmuir* **25** 6357–62

[9] Babaei S, Profili J, Asadollahi S, Sarkassian A, Dorris A, Beck S and Stafford L 2020 Analysis of transport phenomena during plasma deposition of hydrophobic coatings on porous cellulosic substrates in plane-to-plane dielectric barrier discharges at atmospheric pressure *Plasma Processes and Polymers* **17** 2000091

[10] Levasseur O, Vlad M, Profili J, Gherardi N, Sarkissian A and Stafford L 2017 Deposition of fluorocarbon groups on wood surfaces using the jet of an atmospheric-pressure dielectric barrier discharge *Wood Sci Technol* **51** 1339–52

[11] Shah A v., Schade H, Vanecek M, Meier J, Vallat-Sauvain E, Wyrsch N, Kroll U, Droz C and Bailat J 2004 Thin-film silicon solar cell technology *Progress in Photovoltaics: Research and Applications* **12** 113–42

[12] Ma C, Wang L, Nikiforov A, Onyshchenko Y, Cools P, Ostrikov K (Ken), de Geyter N and Morent R 2021 Atmospheric-pressure plasma assisted engineering of polymer surfaces: From high hydrophobicity to superhydrophilicity *Appl Surf Sci* **535**

[13] Dimitrakellis P and Gogolides E 2018 Hydrophobic and superhydrophobic surfaces fabricated using atmospheric pressure cold plasma technology: A review *Adv Colloid Interface Sci* **254** 1–21

[14] Nagasawa H, Yasunari R, Kawasaki M, Kanezashi M and Tsuru T 2021 Facile low-temperature route toward the development of polymer-supported silica-based membranes for gas separation via atmospheric-pressure plasma-enhanced chemical vapor deposition *J Memb Sci* **638**

[15] Profili J, Rousselot S, Tomassi E, Briqueleur E, Aymé-Perrot D, Stafford L and Dollé M 2020 Toward More Sustainable Rechargeable Aqueous Batteries Using

Plasma-Treated Cellulose-Based Li-Ion Electrodes *ACS Sustain Chem Eng* **8** 4728–33

[16] Choukourov A, Gordeev I, Polonskyi O, Artemenko A, Krakovsky I, Slavı D and Hanykova L 2010 Poly (ethylene oxide) -like Plasma Polymers Produced by Plasma-Assisted Vacuum Evaporation 445–58

[17] Michelmore A, Steele D A, Robinson D E, Whittle J D and Short R D 2013 The link betwenn mechanisms of deposition and the physico-chemical properties of plasma polymer films *Soft Matter* **9** 6167

[18] Mansilla R M, Teixidó J M, Kan C W and Jovančić P 2015 Plasma assisted polymerization of fluorinated monomer in ethanol P-I-3-18 1–4

[19] Premkumar P A, Starostin S A, Premkumar P A, Creatore M, van de Sanden M C M, Starostin S A, de Vries H and Koenraad M 2013 Morphological Description of Ultra-Smooth Organo-Silicone Layers Synthesized Using Atmospheric Pressure Dielectric Barrier Discharge Assisted PECVD *Plasma Process. Polym* **10** 313–9

[20] Manakhov A, Moreno-Couranjou M, Boscher N D, Rogé V, Choquet P and Pireaux J-J 2012 Atmospheric Pressure Pulsed Plasma Copolymerisation of Maleic Anhydride and Vinyltrimethoxysilane: Influence of Electrical Parameters on Chemistry, Morphology and Deposition Rate of the Coatings *Plasma Processes and Polymers* **9** 435–45

[21] Moreno-Couranjou M, Mauchauffé R, Bonot S, Detrembleur C and Choquet P 2018 Anti-biofouling and antibacterial surfaces: Via a multicomponent coating deposited from an up-scalable atmospheric-pressure plasma-assisted CVD process *J Mater Chem B* **6** 614–23

[22] Shirtcliffe N, Thiemann P, Stratmann M and Grundmeier G 2001 Chemical structure and morphology of thin, organo-silicon plasma-polymer films as a function of process parameters *Surf Coat Technol* **142–144** 1121–8

[23] Bazinette R, Lelièvre J-F, Gaudy L and Massines F 2016 Influence of the Discharge Mode on the Optical and Passivation Properties of SiNx:H Deposited by PECVD at Atmospheric Pressure *Energy Procedia* **92** 309–16

[24] Morent R, de Geyter N, van Vlierberghe S, Dubruel P, Leys C, Gengembre L, Schacht E and Payen E 2009 Deposition of HMDSO-based coatings on PET substrates using an atmospheric pressure dielectric barrier discharge *Prog Org Coat* **64** 304–10

[25] Vautrin-Ul C, Boisse-Laporte C, Benissad N, Chausse A, Leprince P and Messina R 2000 Plasma-polymerized coatings using HMDSO precursor for iron protection *Prog Org Coat* **38** 9–15

[26] Lin Y-C and Wang M-J 2019 Fabrication of hydrophobic/hydrophilic HMDSO films by atmospheric pressure plasma jet deposition *Japanese Journal of APllied Physics* **58** SAAC01

[27] Fanelli F, Lovascio S, d’Agostino R, Arefi-Khonsari F and Fracassi F 2010 Ar/HMDSO/O2 Fed Atmospheric Pressure DBDs: Thin Film Deposition and GC-MS Investigation of By-Products *Plasma Processes and Polymers* **7** 535–43

[28] Bour J, Bardon J, Aubriet H, del Frari D, Verheyde B, Dams R, Vangeneugden D and Ruch D 2008 Different Ways to Plasma-Polymerize HMDSO in DBD Configuration at Atmospheric Pressure for Corrosion Protection *Plasma Processes and Polymers* **5** 788–96

[29] Kale K H and Palaskar S 2011 Atmospheric pressure plasma polymerization of hexamethyldisiloxane for imparting water repellency to cotton fabric *Textile Research Journal* **81** 608–20

[30] O’Neill L, Herbert P A F, Stallard C and Dowling D P 2010 Investigation of the Effects of Gas versus Liquid Deposition in an Aerosol-Assisted Corona Deposition Process *Plasma Processes and Polymers* **7** 43–50

[31] Cacot L, Carnide G, Kahn M, Naude N, Stafford L and Cleregereaux R 2022 Soft plasma polymerization of HMDSO droplets by coupling pulsed direct-liquid injections with dielectric barrier discharge *Plasma Processes and Polymers*

[32] Massines F, Gherardi N, Naudé N and Ségur P 2009 Recent advances in the understanding of homogeneous dielectric barrier discharges *The European Physical Journal Applied Physics* **47** 22805

[33] Naudé N, Cambronne J-P, Gherardi N and Massines F 2005 Electrical model and analysis of the transition from an atmospheric pressure Townsend discharge to a filamentary discharge *J Phys D Appl Phys* **38** 530–8

[34] Naudé N, Cambronne J-P, Gherardi N and Massines F 2005 Electrical model of an atmospheric pressure Townsend-like discharge (APTD) *The European Physical Journal Applied Physics* **29** 173–80

[35] Bennet E D, Mahony C M O, Potts H E, Everest P, Rutherford D, Askari S, McDowell D A, Mariotti D, Kelsey C, Perez-Martin F, Hamilton N, Maguire P and Diver D A 2016 Precision charging of microparticles in plasma via the Rayleigh instability for evaporating charged liquid droplets *J Aerosol Sci* **100** 53–60

[36] Cacot L, Carnide G, Kahn M L, Clegereaux R, Naude N and Stafford L 2022 Kinetics driving thin-film deposition in dielectric barrier discharges using a direct liquid injector operated in a pulsed regime *J Phys D Appl Phys*

[37] Takenaka K and Setsuhara Y 2019 Droplet-vaporization behavior during plasma-assisted mist chemical vapor deposition of zinc oxide films *Plasma Sources Sci Technol* **28** 065015

[38] Wang Li-Ming, Liang Zhuo, Guan Zhi-Cheng, Luo Hai-Yun and Wang Xin-Xin 2010 Influences of gas flow on gas temperature and discharge mode in dielectric barrier discharge of nitrogen at atmospheric pressure *Acta Physica Sinica* **59** 8739

[39] Massines F, Sarra-Bournet C, Fanelli F, Naudé N and Gherardi N 2012 Atmospheric pressure low temperature direct plasma technology: Status and challenges for thin film deposition *Plasma Processes and Polymers* **9** 1041–73

[40] Prégent J, Vandsburger L, Blanchard V, Blanchet P, Riedl B, Sarkissian A and Stafford L 2015 Modification of hardwood samples in the flowing afterglow of N2–O2 dielectric barrier discharges open to ambient air *Cellulose* **22** 3397–408

[41] Iqbal M M and Turner M M 2015 Investigations of Droplet-Plasma Interaction using Multi-Dimensional Coupled Model *Contributions to Plasma Physics* **55** 627–42

[42] Coppins M 2010 Electrostatic Breakup in a Misty Plasma *Phys Rev Lett* **104** 065003

[43] Stancampiano A, Gallingani T, Gherardi M, Machala Z, Maguire P, Colombo V, Pouvesle J-M and Robert E 2019 Plasma and Aerosols: Challenges, Opportunities and Perspectives *Applied Sciences* **9** 3861

[44] Fanelli F 2010 Thin film deposition and surface modification with atmospheric pressure dielectric barrier discharges *Surf Coat Technol* **205** 1536–43

[45] Manley T C 1943 The Electric Characteristics of the Ozonator Discharge *Trans. Electochem. Soc.* **84** 83

[46] M. Kahn, Y. Champouret, R. Clergereaux, C. Vahlas A F M 2016 Process for the preparation of nanoparticles *Office*

[47] Tatoulian M, Arefi-Khonsari F and Borra J-P 2007 Deposition of Organic Coatings at Atmospheric Pressure from Liquid Precursors *Plasma Processes and Polymers* **4** 360–9

[48] Heyse P, Dams R, Paulussen S, Houthoofd K, Janssen K, Jacobs P A and Sels B F 2007 Dielectric Barrier Discharge at Atmospheric Pressure as a Tool to Deposit Versatile Organic Coatings at Moderate Power Input *Plasma Processes and Polymers* **4** 145–57

[49] Fortelný I, Jůza J and Dimzoski B 2012 Coalescence in quiescent polymer blends with a high content of the dispersed phase *Eur Polym J* **48** 1230–40

[50] Sheng Q, Sun J, Wang Q, Wang W and Wang H S 2016 On the onset of surface condensation: formation and transition mechanisms of condensation mode *Sci Rep* **6** 30764

[51] Profili J, Levasseur O, Blaisot J-B, Koronai A, Stafford L and Gherardi N 2016 Nebulization of Nanocolloidal Suspensions for the Growth of Nanocomposite Coatings in Dielectric Barrier Discharges *Plasma Processes and Polymers* **13** 981–9

[52] Brunet P, Rincón R, Margot J, Massines F and Chaker M 2017 Deposition of homogeneous carbon-TiO2 composites by atmospheric pressure DBD *Plasma Processes and Polymers* **14** 1600075

[53] Brunet P, Rincón R, Martinez J-M, Matouk Z, Fanelli F, Chaker M and Massines F 2017 Control of composite thin film made in an Ar/isopropanol/TiO_2 nanoparticles dielectric barrier discharge by the excitation frequency *Plasma Processes and Polymers* **14** 1700049

[54] Roth C, Oberbossel G, Buitrago E, Heuberger R and Rudolf von Rohr P 2012 Nanoparticle Synthesis and Growth in a Continuous Plasma Reactor from Organosilicon Precursors *Plasma Processes and Polymers* **9** 119–34

[55] Ussenov Y A, Hansen L, Krüger T, Ramazanov T S and Kersten H 2020 Particle formation during deposition of SiO_x nanostructured thin films by atmospheric pressure plasma jet *Jpn J Appl Phys* **59** SHHE06

[56] Krueger T, Hansen L and Kersten H 2020 Deposition of SiO_x thin films using hexamethyldisiloxane in atmospheric pressure plasma enhanced chemical vapor deposition *J Phys Conf Ser* **1492** 012023

[57] Wallimann R, Roth C and Rudolf von Rohr P 2018 Nanoparticle production from HMDSO in atmospheric pressure argon-oxygen plasma *Plasma Processes and Polymers* **15** 1700202

[58] Jakubczyk D, Kolwas M, Derkachov G, Kolwas K and Zientara M 2012 Evaporation of Micro-Droplets: the "Radius-Square-Law" Revisited *Acta Phys Pol A* **122** 709–16

[59] Tran T H, Au D B, Diawara B, Fatyeyeva K, Marais S, Ortiz J, Debarnot D and Poncin-Epaillard F 2019 How the chemical structure of the plasma-deposited SiOx film modifies its stability and barrier properties: FTIR study *Prog Org Coat* **137** 105332

[60] Siliprandi R A, Zanini S, Grimoldi E, Fumagalli F S, Barni R and Riccardi C 2011 Atmospheric pressure plasma discharge for polysiloxane thin films deposition and comparison with low pressure process *Plasma Chemistry and Plasma Processing* **31** 353–72

[61] Raynaud P, Despax B, Segui Y and Caquineau H 2005 FTIR Plasma Phase Analysis of Hexamethyldisiloxane Discharge in Microwave Multipolar Plasma at Different Electrical Powers *Plasma Processes and Polymers* **2** 45–52

[62] Enache I, Caquineau H, Gherardi N, Paulmier T, Maechler L and Massines F 2007 Transport Phenomena in an Atmospheric-Pressure Townsend Discharge Fed by N2/N2O/HMDSO Mixtures *Plasma Processes and Polymers* **4** 806–14

[63] Despax B, Gaboriau F, Caquineau H and Makasheva K 2016 Influence of the temporal variations of plasma composition on the cyclic formation of dust in hexamethyldisiloxane-argon radiofrequency discharges: Analysis by time-resolved mass spectrometry ARTICLES YOU MAY BE INTERESTED IN *AIP Adv* **6** 105111

[64] Choi Y H, Kim J H and Hwang Y S 2006 One-dimensional discharge simulation of nitrogen DBD atmospheric pressure plasma *Thin Solid Films* vol 506–507 pp 389–95

[65] Martin S, Massines F, Gherardi N and Jimenez C 2004 Atmospheric pressure PE-CVD of silicon based coatings using a glow dielectric barrier discharge *Surf Coat Technol* **177–178** 693–8

[66] Borella M, Plissonnier M and Belmonte T 2007 PECVD Synthesis of Polysiloxane-Like Thin Films with Very Low Contact Angle Hysteresis *Plasma Processes and Polymers* **4** S771–5

[67] Cejas E, Mancinelli B R and Prevosto L 2019 Glow Discharge in a High-Velocity Air Flow: The Role of the Associative Ionization Reactions Involving Excited Atoms *Materials* **12** 2524

[68] Naudé N 2005 *Etude électrique de la physique d ' une décharge de Townsend à la pression atmosphérique et de son interaction avec un générateur : Modèle et Expérience To cite this version : HAL Id : tel-00601053*

[69] Pipa A and Brandenburg R 2019 The Equivalent Circuit Approach for the Electrical Diagnostics of Dielectric Barrier Discharges: The Classical Theory and Recent Developments *Atoms* **7** 14

[70] Naudé N, Belinger A, Dap S and Gherardi N 2015 Memory effects in Atmospheric Pressure Townsend Discharges in N 2 and air *32 ICPIG*

[71] Annušová A, Cermák P, Rakovský J, Martišovitš V and Veis P 2017 Monitoring active species in an atmospheric pressure dielectric-barrier discharge: Observation of the Herman-infrared system *Contrib. Plasma Phys* **57** 67–75

[72] Hegemann D, Bülbül E, Hanselmann B, Schütz U, Amberg M and Gaiser S 2021 Plasma polymerization of hexamethyldisiloxane: Revisited *Plasma Processes and Polymers* **18** 2000176

[73] Petersen J, Bardon J, Dinia A, Ruch D and Gherardi N 2012 Organosilicon Coatings Deposited in Atmospheric Pressure Townsend Discharge for Gas Barrier Purpose: Effect of Substrate Temperature on Structure and Properties *ACS Appl Mater Interfaces* **4** 5872–82

[74] Bardon J, Dieden R, Grysan P, Mertz G, Martin A, Delmée M and Ruch D 2019 Mechanical properties of thin plasma polymer coatings from hexanediol dimethacrylate and relations with their chemical properties *Surf Coat Technol* **358** 320–30

[75] Shelemin A, Choukourov A, Kousal J, Slavínská D and Biederman H 2014 Nitrogen-doped TiO2 nanoparticles and their composites with plasma polymer as deposited by atmospheric pressure DBD *Steel Res Int* **11** 864–77

[76] Zhang Y, Cheng H, Gao H, Liu D and Lu X 2021 On the charged aerosols generated by atmospheric pressure non-equilibrium plasma *High Voltage* **6** 408–25

[77] Borra J P 2008 Charging of aerosol and nucleation in atmospheric pressure electrical discharges *Plasma Phys Control Fusion* **50**

[78] Massines F, Gherardi N, Fornelli A and Martin S 2005 Atmospheric pressure plasma deposition of thin films by Townsend dielectric barrier discharge *Surf Coat Technol* **200** 1855–61

[79] Morent R, de Geyter N, Jacobs T, van Vlierberghe S, Dubruel P, Leys C and Schacht E 2009 Plasma-Polymerization of HMDSO Using an Atmospheric Pressure Dielectric Barrier Discharge *Plasma Processes and Polymers* **6** S537–42

IV.2. Influence du précurseur : étude du procédé de dépôt en pentane

Nous avons vu précédemment le rôle de la décharge sur le chauffage et l'évaporation de gouttes d'HMDSO. Ceci conduit au dépôt de couches organosiliciées variées. Afin de compléter cette étude, un second précurseur, le pentane, est étudié. Le pentane est un alcane linéaire couramment utilisé en chimie organique comme solvant. C'est un liquide incolore, très inflammable mais de même classe de santé et de sécurité au travail que l'HMDSO.

Les données physico-chimiques de ces deux précurseurs, HMDSO et pentane, sont reportées dans le Tableau 3. En comparaison avec l'HMDSO, le pentane a une pression de vapeur saturante plus élevée et une viscosité plus faible. Si la première peut fortement modifier la taille des gouttes et l'interaction plasma-gouttelettes, le second peut agir sur l'injection liquide.

Tableau 3: Comparaison des propriétés chimique de l'HMDSO et du pentane

Précurseur	HMDSO Hexaméthyldisiloxane	Pentane
Formule brute	$C_6H_{18}OSi_2$	C_5H_{12}
	$(H_3C)_3Si–O–Si(CH_3)_3$	$CH_3–CH_2–CH_2–CH_2–CH_3$
C	6	5
H	18	12
O	1	0
Si	2	0
Masse molaire (g/mol)	162	72
T° d'évaporation (°C)	101	36
Masse volumique (g/cm³)	0,76	0,621
Viscosité (mm²/s)	0,65	0,36
Pression de vapeur saturante (Pa)	2000-3266	53300

Dans les paragraphes suivants, nous allons reprendre les différentes méthodes utilisées en HMDSO pour discuter le rôle du précurseur sur les mécanismes de dépôt avec une injection pulsée de liquide. Cette partie concernera les caractéristiques de l'aérosol, la caractérisation des couches minces obtenues ainsi que les analyses de la décharge pour différentes conditions d'injection.

IV.2.1 Caractéristiques de l'aérosol de pentane

Figure 32 présente une image typique de la lumière diffusée par un aérosol de pentane produit dans des conditions t_{liq}=5 ms et t_{gaz}=10 ms. Comme pour l'HMDSO, celui-ci est sous la forme d'un nuage de gouttelettes, la vitesse de l'aérosol étant estimée à 6 m.s^{-1}.

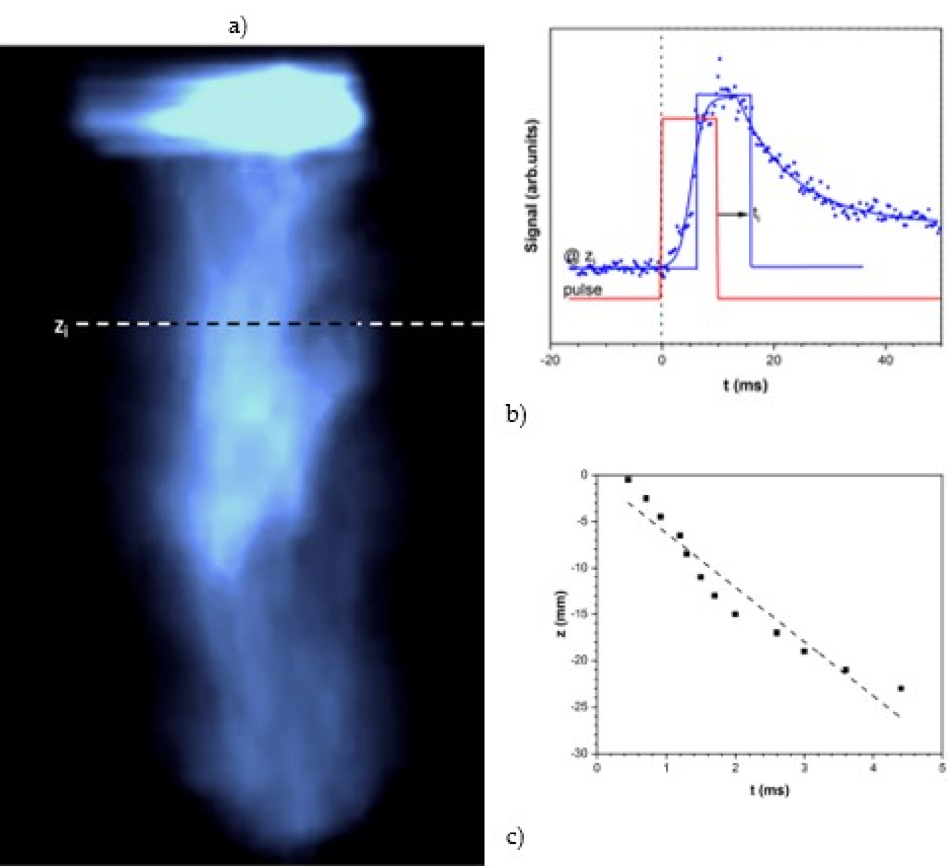


Figure 32: Caractérisation des aérosols formés à la sortie de l'Atokit avec un DLI de pentane. Ici, le spray a été éclairé par une lumière bleue et observé à 45° à l'aide d'une caméra FastCAM (APX RS Photron, 1500 fps). (a) Images typiques enregistrées par l'imagerie rapide. Comme on peut le voir, l'aérosol est composé de microgouttelettes qui s'étendent à la sortie de l'injecteur (z=0). (b) L'évolution temporelle de l'intensité de la lumière diffusée enregistrée à différentes positions (zi) permet de déterminer le transport de l'aérosol, c'est-à-dire le délai (ti) entre l'injection pulsée de l'aérosol (courbe rouge en b) et la variation de l'intensité lumineuse (courbe bleue en b). (c) Position de l'aérosol (zi) en fonction du délai (ti). La pente de la ligne en (c) correspond à la vitesse moyenne de la gouttelette.

Il est malheureusement impossible de discuter de différence de taille entre les gouttes formées en pentane et en HMDSO, l'imagerie rapide ne permettant pas d'observer des gouttes individuelles. Toutefois, la nébulisation étant contrôlée par le différentiel de pression, la pression de vapeur saturante et la température d'évaporation du pentane, on peut émettre l'hypothèse que, dans les mêmes conditions d'injection, les gouttes de pentane transportées jusque dans la cellule de décharge sont plus petites que celles d'HMDSO.

D'autre part, le débit liquide de pentane est de l'ordre de 6,0 µL par pulse en comparaison avec l'HMDSO (2,6 µL par pulse). Cette différence en quantité d'injection peut s'expliquer par la différence de viscosité entre les deux précurseurs. Ainsi, en modifiant le débit d'injection liquide, le bilan de matière entre le pentane et l'HMDSO devrait être différent. Néanmoins, une quantité de liquide supérieure peut également avoir un impact sur la décharge différent.

IV.2.2 Caractéristiques de la couche mince

La Figure 33 présente des images des dépôts avec injection de pentane (en bas), en comparaison, avec HMDSO (en haut) pour différents débits de gaz continu. Les conditions d'injection du DLI sont les mêmes dans les différentes conditions, soit t_{liq}=5 ms, t_{gaz}=10 ms et f=0.1Hz. Les dépôts sont collectés pour 4 min de plasma pour l'HMDSO et 10 min en pentane qui nécessite un temps de dépôt plus long pour obtenir un dépôt d'épaisseur appropriée aux analyses.

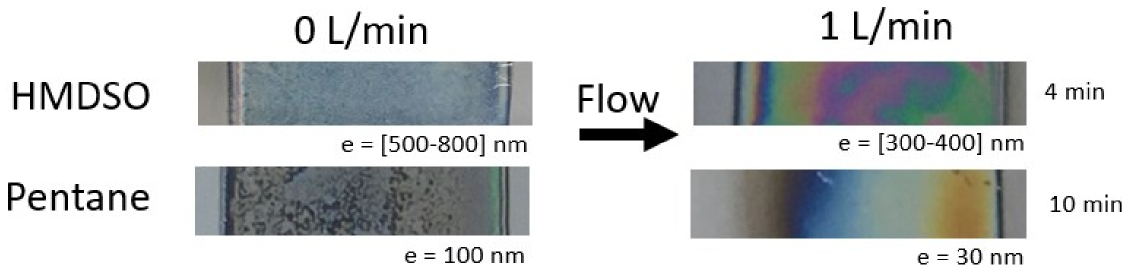


Figure 33: Image des dépôts pour l'HMDSO et le pentane pour différents débits

De même qu'en HMDSO, le dépôt avec pentane se produit uniquement dans l'espace inter-diélectriques en bon accord avec un dépôt contrôlé par les interactions plasma-gouttelettes, à

savoir le chargement et le transport par le champ électrique. Les dépôts obtenus sans gaz porteur sont relativement homogènes. Néanmoins, le dépôt peut présenter un fort gradient d'épaisseur (irisation sur le dépôt) lié au transport des gouttes par la force d'entrainement des neutres en présence d'un flux de gaz continu comme dans le cas des dépôts obtenus avec un flux de gaz porteur de 1 L/min.

Nous avons précédemment montré que les mécanismes de dépôt sont plus favorables pour des gouttes de petite dimension. En effet, en considérant une goutte de 10 µm avec un rapport masse-sur-charge de ~10^2 kg/C, l'excursion calculée est comparable à la distance inter-diélectriques (~1mm). Une goutte de taille supérieur sera quant à elle confinée dans le gap à une fréquence plasma de 1 kHz.

Ainsi, en accord avec l'hypothèse de gouttes de plus petite taille, on devrait s'attendre à ce que la vitesse de dépôt et ainsi le rendement de dépôt soient plus important en pentane qu'en HMDSO. Néanmoins, comme noté sur les images de la Figure 33, l'épaisseur de la couche déposée en pentane est toujours inférieure à celle obtenue en HMDSO. Une différence similaire est observée à basse pression. Ce phénomène est généralement expliqué par des différences de coefficients de collage des espèces hydrocarbonées (de 2.5 10^{-2} pour CH_2 à 10^{-4} pour CH_3 [128,129]) et des espèces siliciées (1 en SiH_4 et en HMDSO [93]). Néanmoins, il peut être aussi re lié aux processus d'érosion induite par l'hydrogène [130] ou encore à l'évaporation plus importante du pentane. En effet, nous avons montré que le dépôt se produisait à partir des gouttes de liquides. Celles-ci sont confinées électrostatiquement dans la décharge et s'accumulent dans la décharge. Contrairement aux gouttes de liquides, les vapeurs ne peuvent pas être confinées. Ainsi, l'évaporation des gouttes liquides conduit à un procédé de dépôt moins efficace.

Ce phénomène apparaît sur les spectres FTIR (Figure 34). Si on focalise sur les bandes de stretching des hydrocarbures, on voit que l'absorption de la couche déposée en HMDSO est très supérieure à celle de la couche déposée en pentane. Néanmoins, de même que la couche déposée à partir d'HMDSO présente des bandes caractéristiques du précurseur, à savoir les bandes de stretching du CH_3 (2875 et 2960 cm^{-1}), la couche déposée à partir de pentane présente

des caractéristiques de ce précurseur, à savoir les bandes de stretching de CH_2 (2855 et 2925 cm^{-1}) et du CH_3. Ainsi, les deux couches seraient formées principalement par les gouttes de l'aérosol, l'efficacité du procédé diminuant lorsque l'évaporation des gouttes est favorisée (c'est à dire en chauffant le gaz ou en utilisant des liquides plus volatil).

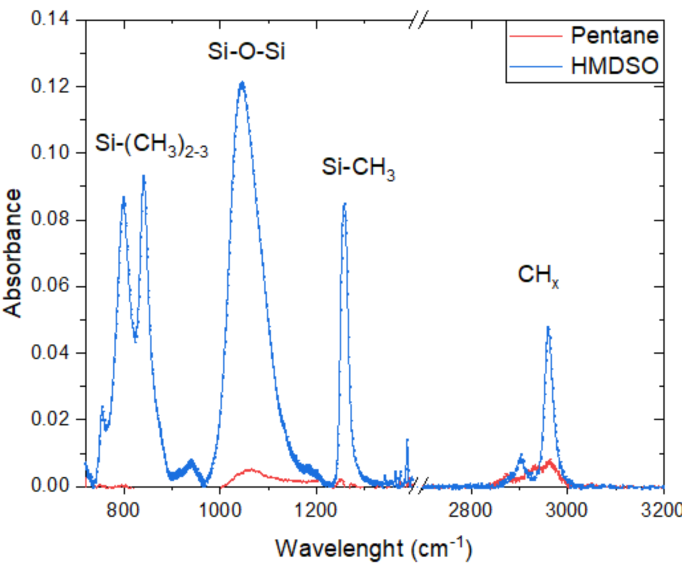


Figure 34: Spectre FTIR en transmission d'une couche mince de pentane et d'HMDSO à 0L/min.

En bon accord avec cette observation, la Figure 35 montre l'aspect des couches obtenues à 1, 2 et 4 min de dépôt sans débit continu. À 1 min les dépôts observés avec les deux précurseurs semblent identiques, soit une matrice plutôt homogène avec l'observation de points noirs de taille micrométrique attribués au dépôt de gouttes d'aérosol. Pour les deux aérosols, les points noirs observés sont de taille similaire, cela est cohérent avec les résultats obtenus précédemment où une taille de goutte minimale est nécessaire pour avoir une excursion suffisante pour se rendre jusqu'au substrat. Au-delà de 2 min, la morphologie droplet-like commence à apparaitre pour les deux précurseurs. Néanmoins, contrairement au dépôt coalescé à 4 min en HMDSO, le dépôt en pentane présente des microstructures d'environ 4 mm de diamètre en bon accord avec la présence de gouttes de taille plus petites avec ce précurseur. Ce phénomène plus lent de coalescence conduit une vitesse de dépôt plus faible avec l'aérosol de pentane.

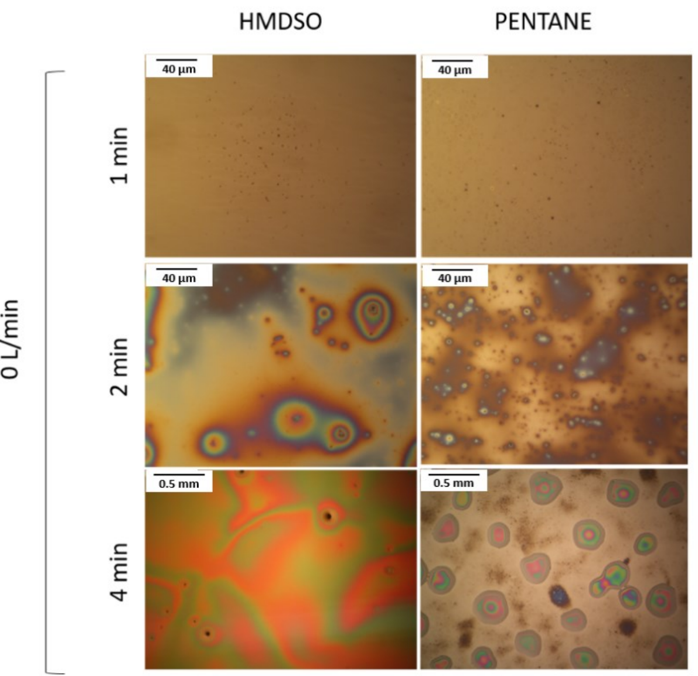


Figure 35: Imagerie des dépôts en HMDSO et en pentane pour différents temps 1, 2 et 4 min à 0L/min

Ainsi, les changements de morphologie et de vitesse de dépôt montrent que les aérosols d'HMDSO et de pentane transporté dans la décharge sont différents. Nous allons maintenant étudier leur impact sur la décharge.

IV.2.3 Analyse de la décharge

La dernière étape concerne l'étude de la décharge en présence de l'aérosol de pentane. Dans les chapitres précédents, nous avons discuté le régime de décharge avec injection pulsée d'azote et d'HMDSO. Contrairement au cas de l'injection pulsée d'azote qui peut, selon le système d'injection, fonctionner en régime homogène (Figure 36.a), la décharge en présence d'aérosols d'HMDSO mais aussi de pentane, présente un comportement électrique typique d'une décharge filamentaire (Figure 36.b et c.). En effet, on observe la présence d'impulsions de courte durée sur la mesure du courant dues à la présence de micro-décharges dans l'espace inter-diélectriques. Il est intéressant de remarquer que la valeur moyenne de la puissance reste identique en pentane et en HMDSO. Ainsi, malgré des caractéristiques (vitesse, forme, taille) des gouttelettes, les caractéristiques électriques de la décharge sont inchangées.

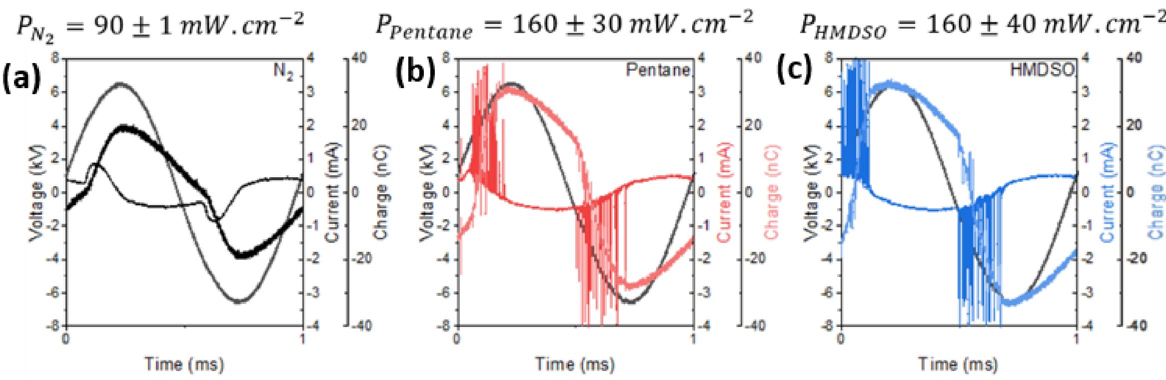


Figure 36: Comparaison des caractéristiques électriques avec injection a) d'azote, b) de pentane et c) d'HMDSO

Comme montré précédemment (Figure 36),), le passage en régime filamentaire se traduit par la présence d'une multitude d'impulsions de courant de faible durée (10-100 ns) et d'amplitude importante (~ 4 mA). Afin d'illustrer la dynamique de transition d'un régime à l'autre, nous avons défini le paramètre I_{area} (Equation $I_{area}(t) = \int_{t_0}^{t_0+T} |I_{mes}| dt$ (6) qui renseigne sur la valeur du courant lissée sur une période de la tension appliquée.

$$I_{area}(t) = \int_{t_0}^{t_0+T} |I_{mes}| dt \qquad (6)$$

Ce paramètre permet de s'affranchir des fortes variations des valeurs du courant mesurées en régime filamentaire en donnant une valeur moyenne sur une période.

Des mesures ont été réalisées dans les conditions t_{liq}=5 ms, t_{gaz}=10 ms et f=0.1Hz sur une période complète d'injection (10 s) pour le pentane et l'HMDSO ainsi que pour deux débits différents. La Figure 37.a montre en grisé le courant brut superposé avec le calcul fait pour obtenir la variation de courant sur l'échelle de gauche. Dans un premier temps, le courant augmente d'un facteur 1,5 après le premier pulse d'aérosol. Néanmoins, 3 s après l'injection pulsée, celui-ci redescend vers la valeur initiale. Il est également intéressant de remarquer que ces comportements apparaissent d'abord en entrée de décharge avant de se propager sur les deux autres zones. Enfin, ce comportement (perturbation time) est d'autant plus rapide que le débit de gaz porteur est important (Figure 37.a et b). Ainsi, ce comportement de la valeur moyenne du courant sur une période est une signature de l'aérosol et, surtout de la présence de gouttes dans l'aérosol. En effet, des mesures similaires réalisées en HMDSO (Figure 37.c et d) montre des comportements similaires.

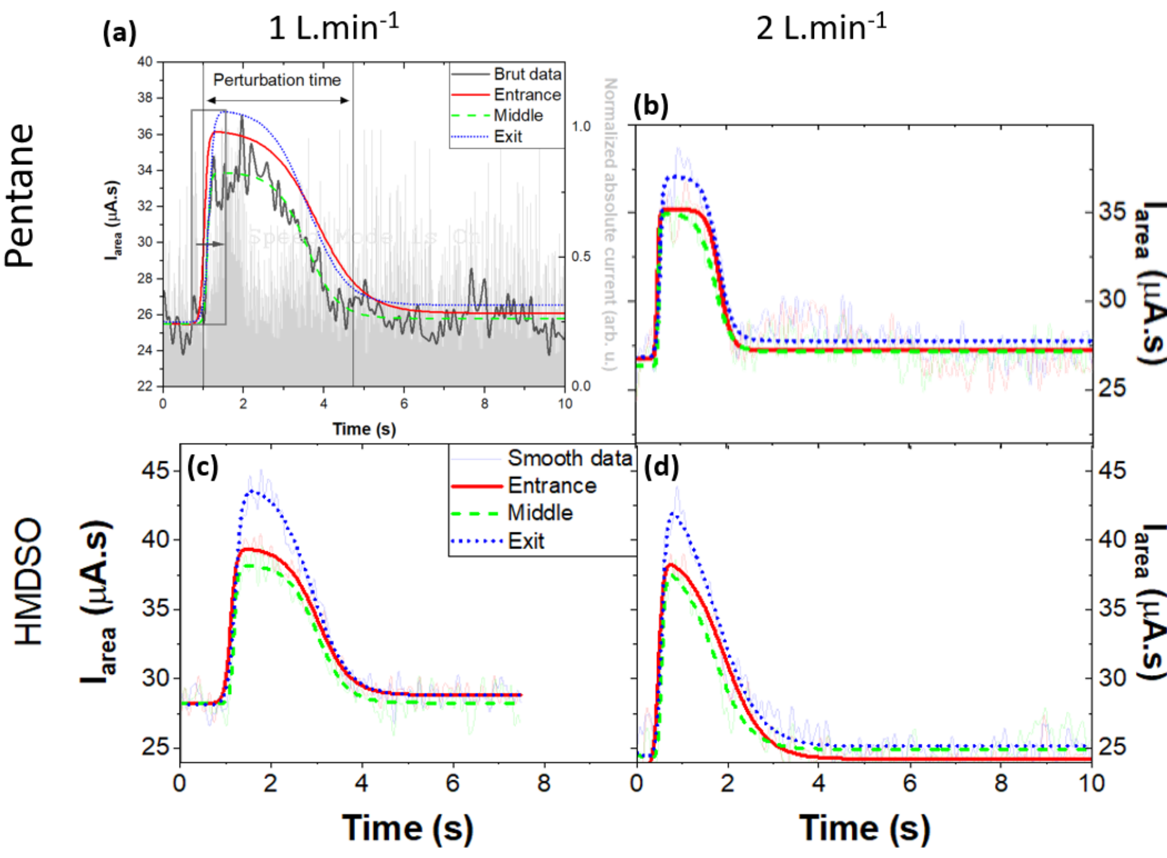


Figure 37: Aire du courant en entrée, milieu et sortie de décharge en pentane avec un débit continu de a) 1L/min et b) 2L/min et en HMDSO à c) 1L/min et d) 2L/min.

Néanmoins, il est difficile de discuter plus en détail aujourd'hui ce comportement qui peut également être lié à la taille des gouttes mais également à une modification du comportement de la décharge filamentaire.

Il est cependant possible de confirmer que la perturbation de la décharge est due à la présence de gouttelettes. En effet en augmentant la fréquence d'injection à 1Hz (Figure 38), et donc la quantité de précurseur la valeur d'intensité du courant ne redescend pas vers une valeur initiale mais oscille autour du maximum.

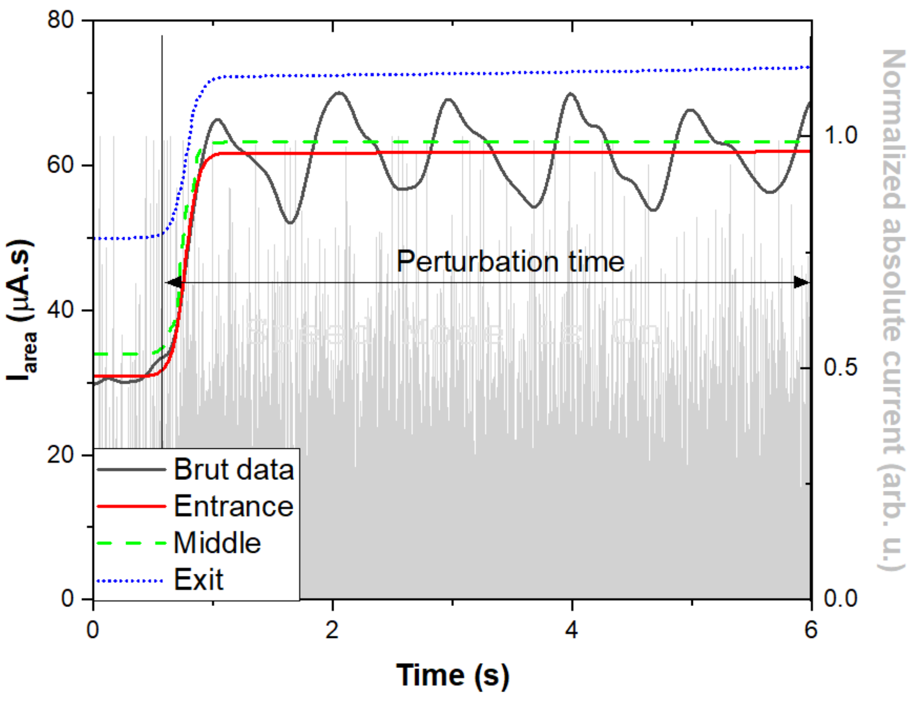


Figure 38: Aire du courant en entrée, milieu et sortie de décharge avec une fréquence d'injection du pentane de 1 Hz

Chapitre V. Synthèse de couches minces nanocomposites assistée par plasma

Dans le dernier chapitre, nous avons montré que les conditions opératoires de la décharge à barrière diélectrique pouvaient être utilisées pour contrôler les interactions plasmas-gouttelettes et donc les propriétés des films déposées. Nous avons aussi pu démontrer que le procédé couplant aérosols et DBD est utilisable avec différents précurseurs liquides, cette versatilité permettant de viser un plus large éventail d'applications.

Dans ce contexte, nous capitalisons dans ce chapitre sur l'ensemble des savoirs obtenus pour réaliser une étape préliminaire à l'utilisation, comme en plasma à basse pression, d'un réacteur-injecteur de nanoparticules à pression atmosphérique. Ici, le réacteur-injecteur permet non seulement une injection pulsée du précurseur pour le dépôt de la matrice, mais aussi une injection pulsée de nanoparticules pour la production de couches minces nanocomposites. Les données sont présentées sous la forme d'un article intitulé : « Direct Liquid Reactor Injector of Nanoparticles : an aerosol injection method adapted to various plasma processes of nanocomposite thin-film deposition ». Ce dernier sera prochainement soumis à la revue Coatings.

V.1. (Article) Direct Liquid Reactor Injector of Nanoparticles: an aerosol injection method adapted to various plasma processes of nanocomposite thin-film deposition

Direct Liquid Reactor-Injector of Nanoparticles: a safer-by-design aerosol injection for nanocomposite thin-film deposition adapted to various plasma-assisted processes

Guillaume Carnide[1,2,4,+], Laura Cacot[1,3,+], Yohan Champouret[1,2,+], Vincent Pozsgay[1], Thomas Verdier[1], Adèle Girardeau[1,2,4], Marjorie Cavarroc[4], Andranik Sarkissian[5], Anne-Françoise Mingotaud[6], Constantin Vahlas[7], Myrtil L. Kahn[2], Nicolas Naudé[1], Luc Stafford[3], Richard Clergereaux[1]*

[1] LAPLACE, UMR5213, CNRS, UPS, INPT, Université de Toulouse, 1; e-mail@e-mail.com

[2] LCC, CNRS UPR8241, Université de Toulouse, 205 route de Narbonne, 31077 Toulouse, France 2

[3] Département de physique, Université de Montréal, 1375 av. Thérèse-Lavoie-Roux, Montréal, QC, H2V 0B3, Canada

[4] Safran Tech, Materials and Processes, Rue des Jeunes Bois, Châteaufort, 78114 Magny-Les-Hameaux, France

[5] Plasmionique Inc., 1650 boul. Lionel Boulet, Varennes, QC J3X 1S2, Canada

[6] Laboratoire des IMRCP, Université de Toulouse, CNRS UMR 5623, Université Toulouse III - Paul Sabatier, 118 route de Narbonne, 31062, Toulouse, France. 4

[7] CIRIMAT, Université de Toulouse, CNRS, INPT, Toulouse, France

* Correspondance: richard.clergereaux@laplace.univ-tlse.fr

+ These authors contributed equally

Abstract

The properties of nanocomposite multifunctional thin films are controlled by the characteristics of the matrix, of the nanoparticles, including their concentration, size, shape, and distribution and, consequently, of the interfaces between the nanoparticles and the matrix. Aerosol-assisted plasma processes used to prepare these coatings usually involve the direct spray of colloidal solutions into the plasma phase. However, this technique does not necessarily meet the specifications of the plasma process (i.e. the flow rates and the pressure), the requirements of nanocomposite thin films (i.e. small nanoparticles, homogeneously-dispersed and non-aggregated), and implies environmental and safety risks. Most of these limitations can be overcome by using a Direct Liquid Reactor-Injector (DLRI) of nanoparticles. This method allows in-situ synthesis of nanoparticles by mixing liquid and gas phases prior to their injection in the downstream plasma process. As this pulsed injection does not require handling of the nanoparticles, it is thus safer for manufacturers and users, as well as environmentally friendly. In addition, DLRI is fully compatible with various dry processes, including those based on plasmas. In this study, it is il-lustrated in an asymmetric low-pressure RF plasma and in a plane-to-plane atmospheric pres-sure Dielectric Barrier Discharge. The effects of the plasmas on the deposited nanocomposite thin films are assessed. The results show that in both cases, the deposited material consists of small ZnO nanoparticles (< 10 nm) in a diamond-like carbon matrix and that this method overcomes the drawbacks of the injection of preprepared nanoparticle solutions. Nevertheless, the nano-composite thin film composition varies with the plasma process. It is attributed to different mechanisms of transport of the aerosols in the plasma volume. Overall, this study proposes the DLRI as a generic technology for the preparation of nanocomposite thin films by plasma deposition and highlights some of the scientific mechanisms.

Keywords: Nanocomposite thin films, Nanoparticles, Aerosols, Pulsed Direct Liquid Reactor Injector, Plasma Deposition, Low-pressure discharges, Dielectric Barrier Discharges, Safer-by-design.

1. Introduction

Nanocomposite thin films are coatings of matrix-embedded nanoparticles targeted for their multifunctional properties. These functions can vary depending on the concentration, size, shape, and distribution of the nanoparticles, as well as on the characteristics of the matrix and the interfaces, especially in the case of really small nanoparticles [1]. Usually, the methods for the preparation of nanocomposite materials are complex and should be designed for each process [1], [2].

If we focus on plasma-assisted approaches, different processes have been developed. The injection of complex molecular precursor(s) in plasma processes is the simplest method. For example, organometallic molecules, *i.e.* molecular species containing metal atoms (including silicon) bonded with organic compounds, are widely used as precursors for Plasma Enhanced Chemical Vapor Deposition (PE-CVD). In specific conditions, it enables to form nanocomposite materials with nanoparticles embedded in an organic matrix [3], [4]. However, the precursors must be compatible with the experimental conditions (*e.g.* volatile at the working pressure), as well as stable during storage, manipulation, and use, which limits the range of materials that can be prepared.

Multifunctional nanocomposite thin films may also be prepared in multi-step processes. For example, few-nanometer silicon nano-crystals can be produced by post-growth heating sub-stoichiometric silicon nitrides deposited by PE-CVD [5]. It can also be obtained by coupling different physical and chemical processes. The techniques commonly used include evaporation [6], sputtering [7]–[9], and nucleation [10]. However, all of these techniques are tricky, as they require specific experimental conditions (*e.g.* working pressure, gas mixture, and plasma operating mode). Recently, new attractive methods based on aerosols have been proposed [11], [12]. Such approach deals with liquid solutions of pre-prepared nanoparticles directly injected into the plasma in the form of liquid droplets. The aerosols can be produced by bubbling [13], [14], nebulization [15]–[17], or Direct Liquid Injection (DLI) [18], as applied in Chemical Vapor Deposition (CVD) and Atomic Layer Deposition (ALD) processes [19].

However, the nanoparticles in nanocomposite thin films deposited by aerosol-assisted plasma processes are usually highly aggregated [12]. Aggregation can start in the liquid solution. Hence, colloidal solutions instead of liquid dispersions of nanoparticles [20], *i.e.* highly stable suspensions of non-aggregated nanoparticles, must be used. To prepare colloidal solutions, it is necessary to

functionalize the nanoobjects, for example, by using ligands. However, this critical step often requires large quantities of stabilizing agents with heteroatoms (*e.g.* amines with nitrogen or thiols with sulfur) [21]. Therefore, the processes of colloidal solution preparation are not always green and can pose serious environmental hazards [22]. In addition, in conflict with the principle of atom economy [23], they introduce new species in the final process, affect the downstream process and consequently contaminate the final coatings with heteroatoms from the ligands.

Aggregation may also arise in the aerosol upon the evaporation of the liquid droplets [16]. According to the balance between nanoparticle diffusion in the liquid phase and the solvent evaporation rate, it can form compact aggregates [24]. Injected in plasmas, the liquid evaporation in the droplet can be enhanced due to plasma-droplet interactions [25]. Besides aggregation, the interactions of plasma species with droplets can induce additional phenomena including droplets charging [26] as well as electrostatic droplet breakup [27], [28]. For example, the charging of droplets in plasmas promotes their electrical confinement enhancing their residence time in the plasma volume [29]. Consequently, plasma-droplet interactions can have a significant effect not only on the plasma behavior (*e.g.* electron temperatures, plasma densities, and transport properties [30]–[33]), but also on the plasma-deposition process (*e.g.* precursor fragmentation [34], thin-film deposition rates [18], [35], and degree of plasma polymerization [36], [37]).

Finally, although aerosol-assisted processes are simpler and more versatile than all other processes used to prepare nanocomposite thin films, they require the handling of nanoparticles, at least during the preparation of the colloidal solution [38], which can adversely impact the human health and the environment.

Therefore, it is of paramount importance to develop safer-by-design processing methods for the formation of nanocomposite thin films with small (< 10 nm) and highly dispersed nanoparticles. Recently, we proposed a safer-by-design method to form small nanoparticles (<10 nm) prior to their injection as an aerosol in a downstream process. Called Direct Liquid Reactor-Injector (DLRI) [39], it relies on the use of a two-stage pulsed DLI that enables the synthesis of nanoparticles from liquid organometallic compounds mixed with gaseous reactive species prior to the injection of the as-prepared nanoparticles as aerosols. This study aims to apply DLRI for nanocomposite thin film deposition using two plasma processes namely, a low-pressure RF discharge and an atmospheric-pressure Dielectric Barrier Discharge (DBD). In both cases, coatings are obtained with ZnO nanoparticles synthesized in the DLRI by the hydrolysis of zinc dicyclohexyl complex ($Zn(Cy)_2$)

diluted in pentane, the latter acting both as the solvent of the aerosol and the precursor of the Diamond-like Carbon (DLC) matrix formed by PE-CVD. The obtained results demonstrate that DLRI coupled with plasma processes provides a simple, economic, and environmentally friendly method for the preparation of nanocomposite thin films that overcomes the drawbacks of the injection of pre-prepared nanoparticle solutions. The crucial mechanisms controlling thin-film deposition with DLRI coupled with these two plasma processes are highlighted.

2. Materials and Methods

The DLRI set-up used herein consists of an Atokit injection-atomizer purchased from Kemstream®. As shown in Figure 1, this injection-atomizer operates in two-stage: (1) the pulsed injection of a liquid solution containing the organometallic precursors into a mixing chamber fed with a reactive gas leading to the formation of the targeted nanoparticles, and (2) the pulsed injection downstream of the as-synthesized nanoparticles as an aerosol. DLRI can thus be considered as a safer-by-design method for the preparation of nanoparticles containing aerosols.

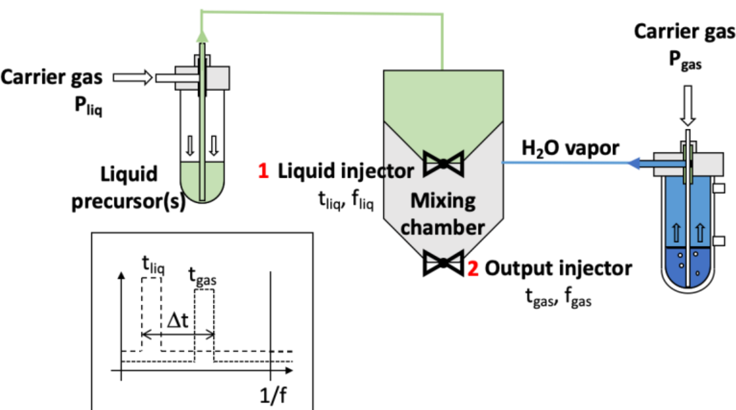


Figure 1: Scheme of the DLRI with various operating parameters and the temporal definition of each injection parameters (in the box below).

In this study, ZnO nanoparticles were synthesized by the hydrolysis of $Zn(Cy)_2$ (from Nanomeps) shown in Scheme 1 [24]. The liquid phase consisted of a liquid solution of the organometallic precursor (0.025 mol.L^{-1}) dissolved in dried pentane, with dodecylamine (DDA) used as stabilizing agent (0.1 eq.). It was introduced (t_{liq} = 5 ms and f_{liq} = 1 Hz) by the liquid injector (1 in Figure 1)

in the mixing chamber used as a chemical reaction chamber. Water vapor was produced and transported to the latter by bubbling a neutral gas flow in water. The ZnO nanoparticles produced herein were sprayed downstream (t_{gas} = 10 ms, Δt = 2 ms, f_{gas} = 1 Hz) by the output injector (2 in Figure 1) [39] .

$$[Zn(Cy)_2] + H_2O \xrightarrow[\text{DDA, solvent}]{\text{Room temperature}} ZnO + 2HCy$$

Scheme 1. Chemical equation of the hydrolysis reaction of dicyclohexyl zinc leading to ZnO nanoparticles.

To confirm the advantages of DLRI over other conventional aerosol-assisted methods, a colloidal solution of pre-prepared ZnO nanoparticles was prepared and injected in the plasma processes to form nanocomposite thin films in the so-called Direct Liquid Injection (DLI) mode. Of note, the colloidal solution was prepared in pentane with the same concentration of ZnO nanoparticles (0.025 mol.L^{-1}, 15 mL). However, to obtain a stable ZnO colloidal solution in pentane, 150 more time of DDA was required [40].

DLRI (and DLI) was coupled with either an asymmetric capacitively-coupled radiofrequency (RF - 13.56 MHz) plasma reactor at low pressure (0.1 mbar) or a low-frequency (1 kHz) plane-to-plane Dielectric Barrier Discharge (DBD) at atmospheric pressure [41].

At low-pressure plasma, DLRI was connected to the shower electrode system positioned at 5 cm above the lower polarized electrode (30 cm of diameter). Argon (Alphagaz 1) was used as the carrier gas, as well as to ignite and sustain the plasma. Different parameters were measured during the deposition process, including working pressure and the injected RF power (set to 100 W) from a Cesar Power Supply coupled with an impedance matchbox (in automatic mode).

In the atmospheric-pressure plasma, DLRI was connected to a diffuser, which was supplied with a continuous flow of nitrogen gas between the two plane-to-plane electrodes (3 cm x 3 cm) separated by a 0.1 cm gas gap. Nitrogen (Alphagaz 1) was used as the carrier gas, as well as to work in Townsend discharge mode [42]. Current-voltage characteristics were measured throughout the

deposition process. For all conditions, the amplitude of the applied sinusoidal voltage was set to 13 kV peak-to-peak.

The nanocomposite thin films were deposited on silicon samples, and their thickness was determined using spectroscopic ellipsometry (Semilab – SE 2000): considering a uniform multilayer structure with the thin film described by a Forouhi-Bloomer dispersion law [43] sandwiched between a native silica substrate (2.7 nm thick oxide) and void, the measured Ψ-Δ angles were compared to the theoretical ones. The optical indexes (refractive index and extinction coefficient) and the thickness were then obtained by regression through a minimization of the ki^2.

Silicon samples with plasma-deposited thin films were also *ex-situ* analyzed by transmission infrared spectroscopy (Burker – Vertex 70).

For Transmission Electron Microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) analyses (JEOL - JEM1011 at 100 kV, JEM 2100F at 200 kV, and JEM-ARM200F at 200 kV from 'Centre de microcaractérisation Raimond Castaing'), copper grids were also coated. Of note, this type of sample was only collected in low-pressure processes as the presence of metallic grids induce parasitic effects (arcing, contamination, nucleation) in the DBD. The recorded TEM images were magnified by two perpendicular sizes (denoted as d_1 and d_2) to characterize the sizes of the nanoparticles using the ImageJ software [free software: https://imagej.nih.gov/ij/]. Further processing of these images was conducted according to the 2D size plot method developed by Zhao *et al.* [16].

3. Results

3.1. DLRI in a low-pressure plasma process

3.1.1. Thin film characteristics

Figure 2.a shows a typical TEM image of the nanocomposite thin films obtained by coupling the DLRI with a low-pressure RF discharge. Nanoparticles are evidenced and, clearly, are

homogeneously dispersed in the matrix. The 2D size plot shown in Figure 2.b demonstrates that it consists of a single population of isotropic nanoparticles, with an average diameter of 6 ± 2 nm. Notably, the nanoparticles in the film are crystalline: the distances determined by Fourier transformation of the HRTEM images (Figure 2.c) correspond to the (100), (002), (101), and (201) interplanar distances anticipated for wurtzite ZnO (0.281, 0.260, 0.247, and 0.136 nm, respectively).

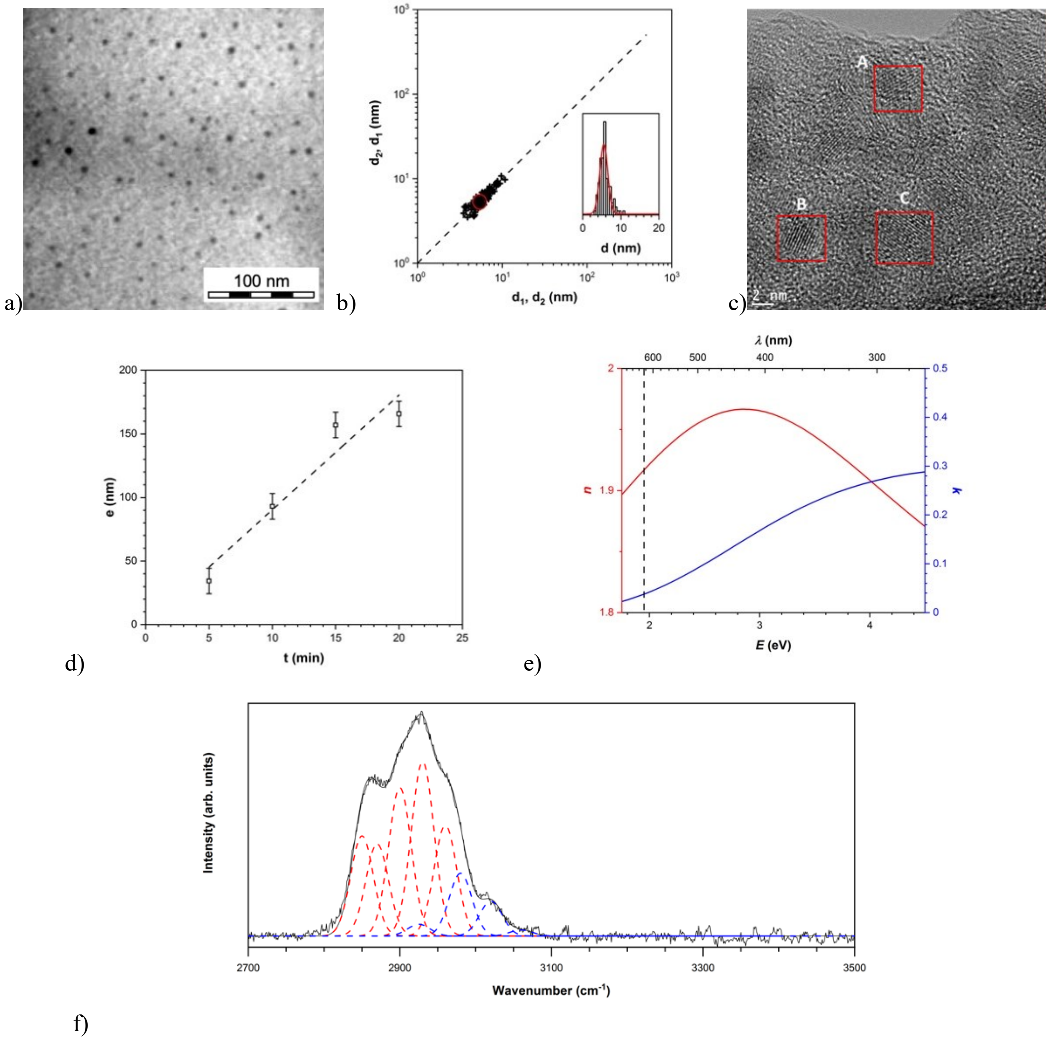


Figure 2: Characteristics of the coatings obtained with DLRI into an asymmetric low-pressure RF discharge with t_{liq} = 5 ms, t_{gas} = 10 ms, Δt = 2 ms, f = 1 Hz and a deposition time of 10 min. a) Typical TEM image of the ZnO/DLC nanocomposite thin film. b) 2D size plot of ZnO nanoparticles determined from TEM images – the red curve highlight the size distributions [16]. c) HRTEM image of the ZnO nanoparticles in the film. d) Evolution of the nanocomposite thin film thickness determined by spectroscopic ellipsometry as a function of plasma deposition time. e) Refractive index and extinction coefficient spectra in the UV-visible

range. f) Typical IR spectrum in the range of 2700–3500 cm^{-1}. The deconvolution considers 9 Gaussian peaks corresponding to the different stretching bands of sp^3 (red curves) and sp^2 (blue curves) CH_x bands.

Along the process, Figure 2.d highlights that the film thickness increases linearly with the deposition time, yielding a thin-film deposition rate of 9.2 ± 1.8 nm.min^{-1}. Coupled with the set of TEM images, it enables to estimate the ZnO nanoparticles volume fraction of ~5 vol%. With such load of ZnO nanoparticles, neither the optical indexes obtained by spectroscopic ellipsometry (Figure 2.e) nor the IR spectra can be used to further investigate the presence of ZnO nanoparticles. However, both can be used to characterize the matrix structure. The optical indexes within (1.92 + 0.04 i) at 1.96 eV (Figure 2.e) are characteristics of Diamond-like Carbon (DLC) with a high concentration of hydrogen and a rich sp^3 carbon composition [43], [44]. This is in good agreement with the IR spectrum on the 2700-3500 cm^{-1} range (Figure 2.f) and its deconvolution that shows a more abundant contribution of sp^3 CH_x (in red with the stretching bands corresponding to CH_3 / ~2870 (symmetrical) and ~2960 cm^{-1} (asymmetrical), CH_2 / ~2850 (sym.) and ~2930 cm^{-1} (asym.) and CH / ~2900 cm^{-1}) than of sp^2 CH_x (in blue) whether in olefinic (CH_2 / ~2925 (sym.) and ~2980 cm^{-1} (asym.) and CH / ~3020 cm^{-1}) or aromatic (CH / ~3060 cm^{-1}) compounds [45].

Hence, DLRI coupled with a low-pressure plasma enable to form ZnO/DLC nanocomposite thin films with small (6 nm in diameter) and spatially dispersed nanoparticles.

3.1.2. Balance of matter

To further characterize the plasma deposition process, the balance of matter was estimated. The first point deals with the yield of conversion of pentane into DLC thin film defined as the ratio of the plasma-deposited thin film volume to the precursor injection rate [46]. Considering a liquid injection rate of 360 µL.min^{-1} at f = 1 Hz, and the deposition rate constant on the whole electrode of 300 mm in diameter, the yield is 0.3 vol%. This value is several orders of magnitude higher than the ones reported for PE-CVD processes in hydrocarbon gases estimated in the 10^{-4} to 10^{-2} vol% range [47], [48].

For the nanocomposite thin film composition, the theoretical volume fraction of ZnO nanoparticles is estimated. Since the stoichiometry of the reaction in Scheme 1 is 1:1 [49] (*i.e.* one mole of ZnO is produced per mole of [$Zn(Cy)_2$]), the theoretical number of ZnO nanoparticles produced and injected per pulse depends directly on the injection parameters, especially the liquid flow rate and the concentration of nanoparticles in the initial solution. Theoretically, the number of 6 nm ZnO nanoparticles produced per pulse at the $Zn(Cy)_2$ concentration of 0.025 mol.L^{-1} and liquid flow rate of ~6 µL per pulse is $1.1 \cdot 10^{15}$. Considering that the nanocomposite thin film composition is uniform on the whole electrode surface, the DLRI process yields a theoretical volume fraction of nanoparticles of ~16 vol%, which is about three times greater than the experimentally determined value. Such discrepancy indicates that the transport of nanoparticles to the substrate is incomplete. In other words, the plasma affects the ballistic transport of the ZnO nanoparticles from the output of the DLRI to the bottom electrode.

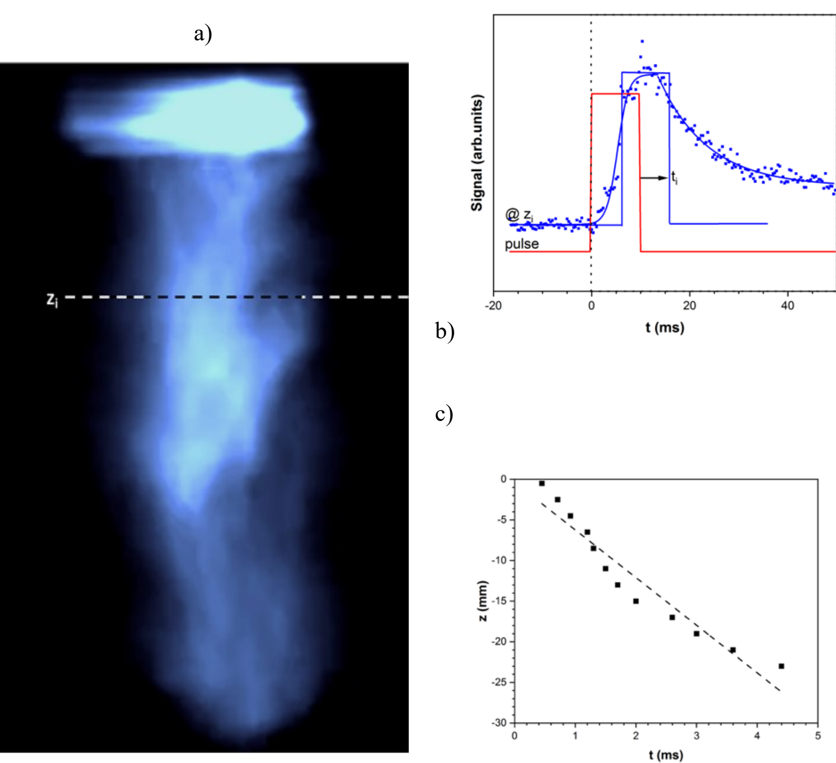


Figure 3: *(a) Typical image of the aerosol formed at the Atokit outlet with a DLI of pentane (t_{liq} = 5 ms, t_{gas} = 10 ms, Δt = 2 ms, and f = 1 Hz). Here, the spray, illuminated with a blue light and observed at 45° using a FastCAM camera (APX RS Photron, 1500 fps), is typical of an aerosol composed of micrometer droplets expanding at the outlet of the injector (z = 0). (b) Temporal*

evolution of scattered light intensity recorded at different positions (z_i). The delay t_i between pulsed aerosol injection (red curve in b) and the variation of light intensity (blue curve in b) enables to characterize the transport of the aerosol. (c) Position z_i versus delay t_i. The slope of the line in (c) corresponds to the droplet's average velocity: here ~6 m.s^{-1}.

As underlined in dusty plasmas [50], a nanoparticle injected into a plasma collect electrons and ions on its surface, and the balance of both currents on the floating surface leads to a negative charge. The time needed to charge this nanoparticle may be estimated by: $\tau_{ch} = \frac{\lambda_D}{r_{NP} \cdot \omega_p}$, where λ_D is the Debye length, ω_p the ion plasma frequency, and r_{NP} the nanoparticle size [51]. For instance, in a low-pressure argon plasma with $T_e = 1$ eV, T_i = 300 K, and $n_e = n_i = 10^{15}$ m^{-3} [50], a nanoparticle of $r_{NP} \approx 6$ nm will be charged within $\tau_{ch} \approx 2$ ms. If this charging time is less than the residence time of the ZnO nanoparticles in the plasma, then the nanoparticles will be efficiently confined in the plasma volume.

As a first assumption, considering that the residence time is comparable for all species in the aerosol, i.e. from small nanoparticles (diameter < 10 nm) to micrometric droplets, it can be defined as the time to reach the bottom electrode from the head electrode at a given velocity. The backscattered light intensity of pentane aerosol is recorded by fast imaging (Figure 3.a): considering the delay between the pulse injection and the maximum of intensity for different positions (Figure 3.b), the velocity of pentane droplets at low pressure (0.1 mbar) is ~6 m.s−1 (Figure 3) leading to a residence time of ~10 ms. As the charging time of nanoparticles is slightly below the residence time, most of the ZnO nanoparticles can efficiently be charged. Consequently, a few will be deposited on the substrate, while others will undoubtedly remain electrostatically confined in the plasma volume until the next injection pulse (the pulsed flow is evacuating the nanoparticles from the discharge). This explains why the experimentally measured volume fraction of nanoparticles in the final coating is less than the theoretically calculated value.

3.1.3. Plasma behavior

To confirm that the nanoparticles are being charged and electrostatically confined in the plasma, the electrical parameters of the discharge were measured. Figure 4.a depicts the temporal evolution

profile of the power injected in the discharge during a single DLRI pulse (red curve). Over the range of experimental conditions investigated in this work, the injected power decreases down to 30 W within 200–300 ms, until it reaches the set value of 100 W just before the injection of the subsequent pulse. Part of this temporal variation is linked to the sudden pressure rise due to the pulsed operation of the DLRI (Figure 4.b). Of note, even if the pulse duration is only 10 ms (t_{gas}), the use of a showerhead induces pressure variations over much longer time scales. However, this temporal variation also implies a temporal response of the plasma to the aerosol injection [52].

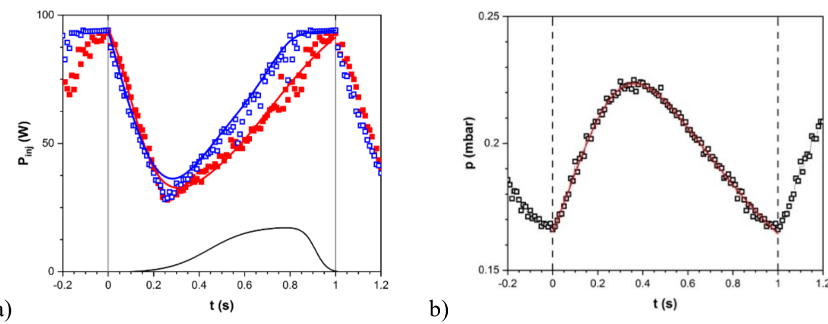


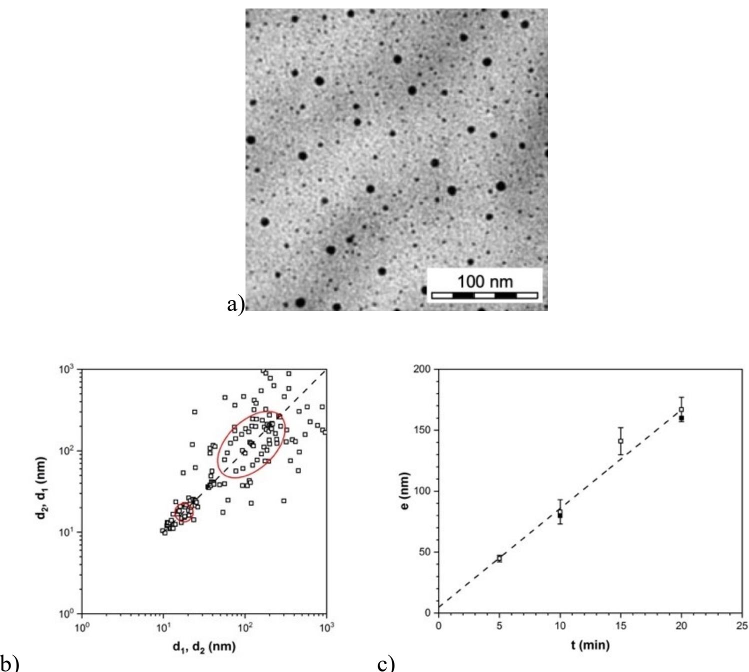
Figure 4: *Temporal evolution profiles of the process parameters with t_{liq} = 5 ms, t_{gas} = 10 ms, Δt = 2 ms, and f = 1 Hz. a) Power injected in an asymmetric low-pressure RF discharge coupled with either a DLRI (red) or a DLI (blue) and b) the pressure with a DLRI (similar values are measured for the DLI). In a), the red and blue curves correspond to the power injected with DLRI of nanoparticles and with DLI of pentane aerosols, respectively. As for the black curve, it represents the difference between the red and blue curves.*

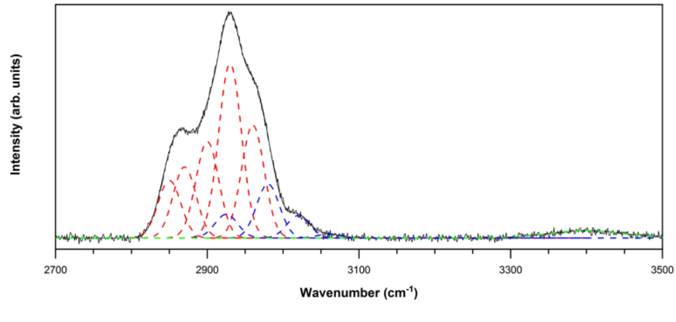
To investigate plasma-aerosol interactions, the temporal evolution profile of the power injected during a pulsed injection is compared to the one of pure pentane injection (Figure 4.a). Unlike the profile obtained with the DLRI (red curve), the injected power profile corresponding to the DLI (blue curve) attains the set power value faster (~800 ms after pulse injection) and remains constant until the next pulse is injected. This suggests that the injection of the set power is more difficult in the presence of nanoparticles (DLRI) than without (DLI), as underlined by the black curve in Figure 4.a corresponding to the difference between the two profiles. ZnO nanoparticles, confined in the plasma volume (as previously discussed), are introducing additional electron losses [50] that further affect the plasma impedance, and thus the injection of power. Hence, the plasma behavior results are consistent with the balance of matter: both reveal that the process of nanocomposite thin

film deposition by coupling DLRI with a low-pressure plasma is controlled by the plasma through its role on the charging and electrostatic confinement of nanoparticles.3.1.4. DLRI vs DLI of colloidal solutions

To highlight the advantages of DLRI to form nanocomposite thin films, coatings are deposited by injecting a colloidal solution in DLI mode into the low-pressure plasma.

Figure 5.a presents a typical TEM image of the nanocomposite thin film produced. Again, it shows ZnO nanoparticles homogeneously dispersed in the matrix. However, the 2D size plot, shown in Figure 5.b, exhibits two populations of nanoparticles with average sizes of 17 ± 1 nm and 118 ± 26 nm, respectively. Considering the initial diameter of nanoparticles in the solution of 8 ± 2 nm [39], this result highlights that aggregation occurs in this process.





d)

Figure 5: *Characteristics of the coatings obtained with DLI a colloidal solution into an asymmetric low-pressure RF discharge with t_{liq} = 5 ms, t_{gas} = 10 ms, Δt = 2 ms, f = 1 Hz and a deposition time of 10 min. a) Typical TEM image of the ZnO/DLC nanocomposite thin film. b) 2D plot of ZnO nanoparticles as determined from TEM images – the red curves highlight the size distributions [16]. c) Evolution of the nanocomposite thin film thickness as a function of plasma deposition time. d) Typical IR spectrum in the range of 2700–3500 cm^{-1}. The deconvolution considers 9 Gaussian peaks corresponding to the different stretching bands of sp^3 (red curves) or sp^2 (blue curves) CH_x and a Gaussian peak corresponding to amines (green curve).*

However, neither the deposition rate and the volume fraction of nanoparticles really change. Indeed, the film thickness variation as a function of deposition time, reported in Figure 5.c, reveals a deposition rate of 8.1 ± 0.5 $nm.min^{-1}$ and the set of TEM images highlights a volume fraction of ~5 vol%. Finally, the IR spectrum on the 2700-3500 cm^{-1} range reported in Figure 5.c exhibits the same characteristics of Diamond-like Carbon (DLC), the spectrum deconvolution highlighting really slight differences of the matrix composition. In addition, a small quantity of amines is detected (Figure 5.d; absorption band near 3400 cm^{-1}). These groups originate from the DDA ligand whose concentration in the colloidal solution injected by DLI (15.0 eq.) is much greater than that with the DLRI (0.1 eq.). Therefore, the ligands (DDA) injected in abundance in the DLI mode in the plasma can significantly contaminate the final coating which may impact its final properties.

To summarize, not only DLRI limits the aggregation of nanoparticles during the coating' preparation but also DLRI leads to unmodified-pure-DLC matrix process in contrast with the coatings obtained with DLI of colloidal solution.

The aggregation of nanoparticles in liquid droplets depends on the solvent, as well as on the concentration of the nanoparticles in the droplet [24]. To have a rough estimation of such mechanism, we consider that the aerosol is a distribution of droplets with a diameter D_d and that

each droplet dries and forms an aggregate of diameter D_{AG}. The volume of aggregated ZnO nanoparticles in the volume of injected solution is then only a function of the concentration, the molar mass and the mass density of ZnO. Hence, the theoretical average size of the aggregates formed upon the complete evaporation of the solvent in the liquid droplet is:

$$D_{AG} = \left(\frac{c_{ZnO\ NP} \cdot M_{ZnO}}{\rho_{ZnO}}\right)^{1/3} \cdot D_d$$

Under the experimental conditions used herein, the factor relating D_{AG} and D_d is 0.03. Considering that the aggregated ZnO nanoparticles size D_{AG} is of the order of a few hundred nm (Figure 5.a), one thus expects that the droplet size D_d at the exhaust of the DLI and DLRI is of a few micrometers.

Nevertheless, since DLI and DLRI are injecting the same concentration of ZnO nanoparticles, it is expected that aggregation occurs in both cases. However, no aggregation is observed with DLRI. In addition, size distributions of nanoparticles obtained with DLRI (Figure 5.b) are comparable to the ones obtained in batch synthesis [53]. This suggests that the droplets produced with DLRI are smaller than those injected with DLI. Indeed, while a fog of droplets is easily observed by light scattering with DLI, there is no backscattered light detected with DLRI. Based on the Mie scattering model, it reveals that the size of droplets in the DLRI-produced aerosols are much less than those obtained with DLI. Therefore, pentane evaporation occurs sooner in the DLRI than in the DLI, as discussed by Carnide *et al.* [40]. This result can be ascribed to an exothermic hydrolysis of the organometallic precursor [53]. This means that chemical reaction has also a significant effect on aerosol characteristics, on the plasma process and then on nanocomposite thin film deposition with non-aggregated small nanoparticles.

Overall, nanocomposite thin films with small (< 10 nm) and highly dispersed nanoparticles can be produced by coupling DLRI with a low-pressure plasma. In such DLRI system, the film structure

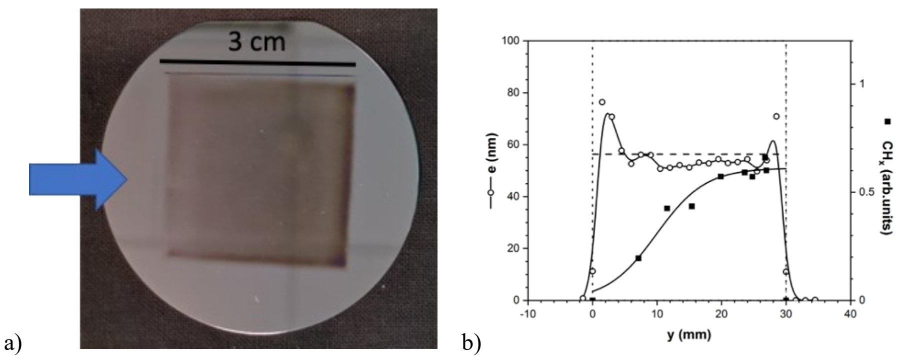
is controlled by the chemical reaction, the aerosol type, and the balance of forces on droplets and nanoparticles in the plasma.

3.2. DLRI in an atmospheric-pressure plasma process

3.2.1. Thin film characteristics

The DLRI system was also used to inject ZnO nanoparticles with pentane into a plane-to-plane DBD at atmospheric pressure. As shown in Figure 6.a, the coating deposited on a 4” silicon wafer is limited to the electrode region (3 cm x 3 cm) [18]. Since no significant deposit is observed outside the discharge region, this reveals that thin-film deposition results from charged species. Here, the aerosols (droplets and nanoparticles) are charged following their interactions with charged species in the plasma and are transported towards the top and bottom electrodes by the low-frequency electric field [18].

Considering a slight contribution of ZnO nanoparticles on the optical indexes as in low-pressure coatings, an ellipsometric model of the plasma-deposited layer is determined for different positions along the gas flow lines in the discharge cell. As shown in Figure 6.b, the film thickness is quite homogeneous along the discharge-struck area of ~60 nm corresponding to a deposition rate of ~15 nm.min^{-1}, with slightly thicker coatings at the entrance and exit of the electrodes. However, compared to Figure 6.a, the thin-film composition seems different along the gas flow lines (from left to right).



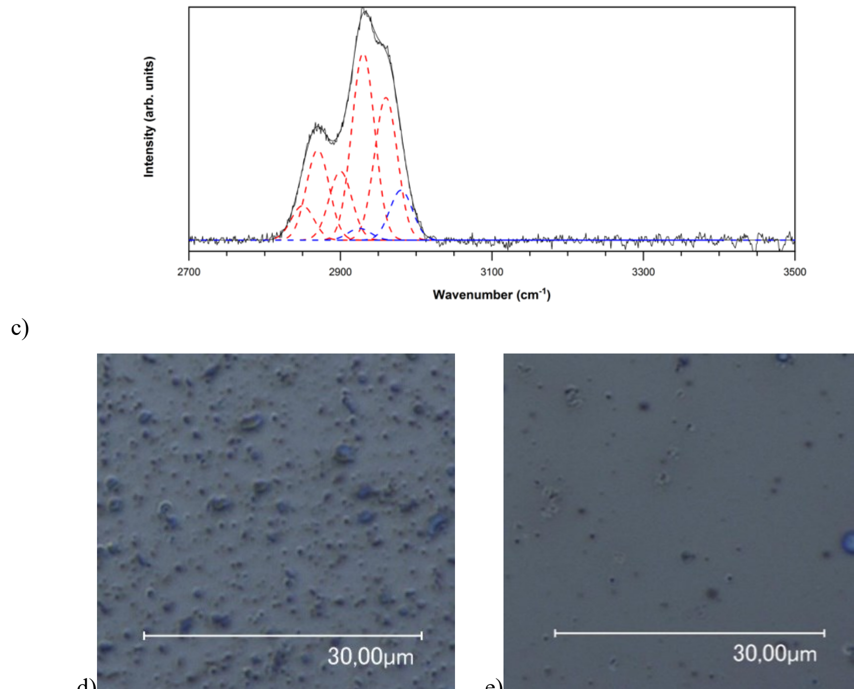


Figure 6: Characteristics of the coatings obtained with DLRI into a plane-to-plane DBD with t_{liq} = 5 ms, t_{gas} = 10 ms, Δt = 2 ms, f = 1 Hz and a deposition time of 4 min. a) Typical image of the nanocomposite thin film. b) Spatial evolution of the nanocomposite thin film thickness obtained by ellipsometry and of the carbonaceous matrix relative thickness determined from the IR spectra. c) Typical IR spectrum in the range of 2700–3500 cm^{-1}. The deconvolution considers 9 Gaussian peaks corresponding to the different stretching bands of sp^3 (red curves) or sp^2 (blue curves) CH_x. Optical microscope images collected d) at the entrance and e) close to the exit of the deposit area.

To investigate the matrix composition, IR spectra were recorded at different points along the gas flow lines. As shown in Figure 6.c, the matrix of the plasma-deposited film is still a DLC. CH_x bands between 2800 and 3000 cm^{-1} are integrated and reported as a function of position to plot a relative matrix thickness. In contrast with the thickness obtained from spectroscopic ellipsometry, the thickness of the matrix grows along the sample and is homogeneous only over the last 20 mm of the discharge-struck area (Figure 6.b). This means, first, that matrix deposition does not take place homogeneously along the discharge zone [18]. Droplets of pentane are efficiently confined in the discharge, leading to a matrix gradient along the gas flow lines, with a more prominent deposition near the exit. Secondly, it suggests a more prominent volume fraction of ZnO nanoparticles close to the entrance of the discharge than at the exit. Unlike pentane, the results presented in Figure 6 indicate that nanoparticles are not transported in liquid droplets and,

consequently, are deposited sooner on the substrate. To confirm such features, optical microscope images were collected. The results are shown in Figure 6.d and e. At the entrance, Figure 6.d reveals the presence of numerous submicron structures without an evident matrix coating between these structures. In contrast, close to the exit, Figure 6.e shows that the number of features strongly decreases. Hence, it seems that ZnO nanoparticles are mostly deposited at the entrance, while the matrix deposition takes place progressively towards the exit of the DBD.

To confirm such difference of transport between ZnO nanoparticles and the precursors of the matrix, optical measurements were performed. First, ellipsometric data were recorded as a function of position along the discharge cell. The refractive indexes at 350 nm are determined and reported in Figure 7.a. Both *n* and *k* present high gradients from the entrance to the exit of the deposit area. For *n*, the variation from 1.25 to 1.6 agrees very well with the porous aspect of the plasma-deposited coating observed from Figure 6.d and e and discussed by Martin *et al.* [54]. As for *k*, the behavior is in good agreement with an evolution of the film composition, *i.e.* of small ZnO nanoparticles more abundant at the entrance of the discharge cell than at the exit. Indeed, at small scale (< 10 nm), these nanoparticles are highly absorbent at 350 nm [55].

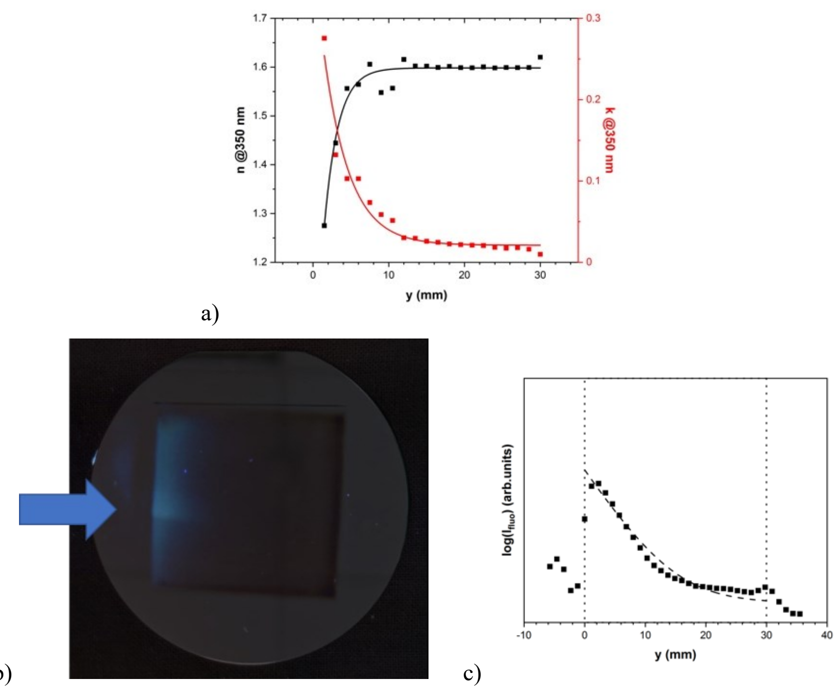


Figure 7: Optical properties of the coatings obtained with DLRI into a plane-to-plane DBD with t_{liq} = 5 ms, t_{gas} = 10 ms, Δt = 2 ms, f = 1 Hz and a deposition time of 4 min. a) Spatial distribution of the optical indexes obtained by spectroscopic ellipsometry. b) Same typical image of the nanocomposite thin film as in Figure 6.a recorded under UV light illumination. c) Spatial profile of the fluorescence intensity along the gas flow lines.

The sample is finally exposed to UV illumination (350 nm) for further investigate the location of ZnO nanoparticles in the nanocomposite thin films. As can be seen in Figure 7b, the plasma-deposited film exhibit typical fluorescence of ultrafine (< 10 nm) ZnO wurzite nanoparticles (fluorescence at 580 nm) [55]. The plot of the integrated fluorescence signal as a function of position along the gas flow lines (Figure 7.c) confirms that nanoparticles are mostly deposited at the entrance of the discharge cell.

Hence, DLRI coupled with atmospheric pressure discharges enable to form ZnO/DLC nanocomposite thin films. But in contrast with the low-pressure plasma processes, the deposition of the nanoparticles and their spatial dispersion are more evidently controlled by the process conditions (gas flow and electric field amplitude, with both driving the balance of forces on droplets and nanoparticles in the plasma).

3.2.2. Balance of matter

Considering a liquid injection rate of 360 µL.min^{-1} at f = 1 Hz, and a deposition rate of 15 nm.min^{-1}, the yield of pentane conversion into thin film is lower than at low-pressure of ~0.004 vol% but similar to data reported for hydrocarbon thin film deposition. For example, Sarra Bournet *et al.* [56] obtained a deposition rate up to 60 nm.min^{-1} in discharge produced with 400 ppm of C_2H_4 in N_2 and a gas flow rate of 1 L.min^{-1}. This corresponds to a conversion yield up to 0.015 vol%. Over the range of experimental conditions investigated, the low yield indicates that many droplets remain trapped in the gas gap over multiple low-frequency cycles until they are pushed out of the DBD cell by the gas flow [18]. Indeed, at T_e = 1 eV, T_i = 300 K, and $n_e = n_i \sim 10^{12}$ cm^{-3} in filamentary discharges operated in nitrogen [57], a steady-state charge of ~10^4 electrons per 10 µm pentane droplet (and thus a mass-to-charge ratio ~10^2 kg/C) can be estimated [16], [58]. Consequently, the

amplitude of oscillations of the charged droplet in a 4 $kV.mm^{-1}$ electric field (recall that the electric field is linked to the amplitude of the gas voltage after discharge breakdown and not to the externally applied voltage [59]) at 1 kHz becomes comparable to the gas gap (~1 mm). Therefore, droplets much smaller than 10 µm are easily collected within half-period of the electric field whereas droplets much larger than 10 µm can escape the DBD cell without being deposited [18].

In contrast, the transport and deposition of nanoparticles sprayed with the DLRI are independent of the matrix deposition leading to a more efficient deposition at the entrance of the discharge. Indeed, a 5 nm nanoparticle will be charged within 5 ns. Since this charging time is much shorter than (i) the period of the applied electric field (1 ms at 1 kHz), and (ii) the gas residence times linked to pulsed (> 3 ms) and continuous carrier gas injections (> 50 ms), one can safely assume that all nanoparticles become charged [36]. For a steady-state charge of ~5 electrons per 5 nm ZnO nanoparticles (and thus a mass-to-charge ratio ~10^{-4} kg/C), the amplitude of oscillations of charged nanoparticles in a 4 $kV.mm^{-1}$ electric field at 1 kHz becomes largely superior to the gas gap (~1 mm). Hence, all nanoparticles would rapidly be transported towards the substrate by the low-frequency electric field as discussed by other authors during nebulization of colloidal solutions in low-frequency DBDs [15], [16]. Hence, DLRI yields a theoretical volume fraction ranging from 100 to 0 vol% from the entrance to the exit of the discharge cell. Charging in low-frequency DBD thus enables to maximize the deposition of ZnO nanoparticles. Of note, though this process is limited to the discharge entrance, the volume fraction of nanoparticles could be smoothened out by using a substrate displacement method as underlined by Massines *et al.* [57] for typical PE-CVD processes at atmospheric pressure.

3.2.3. Plasma behavior

Electrical measurements were conducted to assess the plasma behavior and to obtained temporal evolution of current-voltage characteristics with the DLRI operating at 1 Hz. Over the range of experimental conditions investigated, discharges operated in nominally pure nitrogen are

representative of a homogeneous Townsend discharge with a single peak per half-cycle of the applied voltage [59]. However, as soon as the first pulse of precursor is injected, the onset of **Figure 8** shows that the discharge becomes filamentary, *i.e.* that micro-discharge channels perpendicular to the electrodes are formed [42]. Such feature is typically accompanied by a significant rise in the power injected into the DBD, as confirmed in **Figure 8**. This transition from homogeneous to filamentary regime is attributed to the presence of nanoparticles and droplets in the discharge [18].

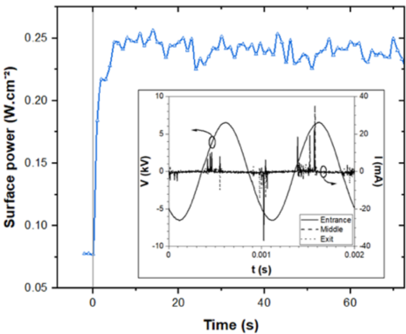


Figure 8: *Temporal evolution profiles of the electrical characteristics of the atmospheric-pressure DBD after injection of ZnO containing pentane aerosol by the DLRI with* t_{liq} *= 5 ms,* t_{gas} *= 10 ms,* Δt *= 2 ms, and f = 1 Hz. The time evolution of the power injected into the DBD cell along the plasma treatment time is also shown.*

In addition, once the discharge has transited to filamentary regime (*t* = 0 on Figure 8), the surface power converges to a constant, here, around 0.25 $W.cm^{-2}$. Hence, in such conditions, variations in discharge properties appear very fast after injection of the ZnO-containing pentane aerosol and then reaches steady-state after a small number of cycles. Of note, the time resolution is too small to discuss the mechanisms arising at the pulse scale and the possible temporal variations from one pulse to another.

3.2.4. DLRI vs DLI of colloidal solution

Nanocomposite thin films were finally deposited by DLI of a colloidal solution into the plane-to-plane DBD. As observed in Figure 9.a, the coating deposited on a 4” silicon wafer remains limited to the electrode region (3 cm x 3 cm) but seems more homogeneous along the gas flow. Considering that thin-film deposition results from the charging of the droplets in the aerosol and

their transport towards the top and bottom electrodes by the low-frequency electric field [18], it suggests that the aerosol, *i.e.* the liquid droplets size, is more homogeneous in that case. In addition, as shown in Figure 9.b, the film thickness is constant along the discharge-struck area. In contrast with DLRI, it is 2 times higher with the colloidal solution. Considering the same liquid injection rate, this suggests that the conversion yield is at least 2 times higher with the colloidal solution.

However, as reported in Figure 9.c and d, the gradients of n and k and, consequently, the fluorescence previously attributed to ZnO nanoparticles, are smaller in this case. This reveals that the volume fraction is lower than in the DLRI mode. Indeed, trapped in the liquid droplets, ZnO nanoparticles transport and deposition are directly controlled by the droplet transport and deposition [36], *i.e.* the transport of charged liquid droplets and their evacuation by the carrier gas. The balance of matter thus leads to a smaller volume fraction of ZnO nanoparticles [36].

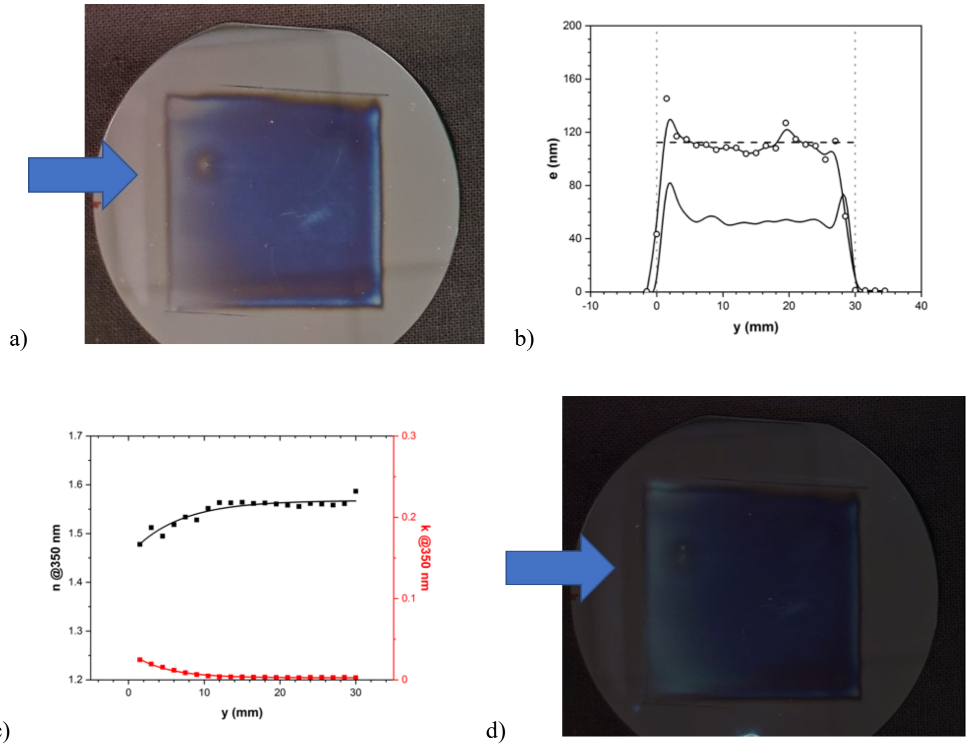


Figure 9: *Characteristics of the coatings obtained with DLI of a colloidal solution into a plane-to-plane DBD with* t_{liq} *= 5 ms,* t_{gas} *= 10 ms, Δt = 2 ms, f = 1 Hz and a deposition time of 4 min. a) Typical image of the nanocomposite thin film. b) Spatial evolution of the nanocomposite thin film thickness obtained by ellipsometry and compared to the NC thin film produced by DLRI. c) Spatial*

distribution of the optical indexes obtained by ellipsometry. d) Same typical image of the nanocomposite thin film as in a) recorded under UV light illumination.

In summary, nanocomposite thin films with ultrafine nanoparticles (< 10 nm) may be prepared by coupling a DLRI system with atmospheric-pressure plasmas. The structure of the deposited film is controlled by the balance of forces (controlling) acting on the droplets and the nanoparticles.

4. Conclusions

By coupling the DLRI system with plasmas, multifunctional nanocomposite thin films can be prepared. This robust and fast approach promotes the implementation of nanocomposite thin films in innovative materials and devices to meet current and future societal needs. DLRI is a simple, economic, and environmentally friendly method of nanoparticle injection that enables the control and monitoring of nanoparticle size and morphology. It is also robust and reproducible and, consequently, can be easily scaled-up and adapted to various plasma processes. Herein, we showed that the nanocomposite thin films prepared by DLRI with low-pressure RF discharge or atmospheric-pressure dielectric barrier discharge exhibit a uniform distribution of ultrafine ZnO nanoparticles (< 10 nm). The nanoparticles are formed via one-pot reaction of [$Zn(Cy)_2$] with water in presence of DDA. Pentane is used as precursor to form the carbonaceous matrix, which has characteristics of diamond-like carbon. In addition to minimizing nanoparticle handing and suppressing the aggregation of nanoparticles, the processes proposed in this study reduce the emission of the nanoparticle synthesis byproduct by involving this compound in the plasma deposition of the carbonaceous matrix. Considering the broad array of organometallic compounds that can be used in DLRI/plasma deposition processes, a wide variety of nanocomposite thin film materials may be prepared using this pulsed injection aerosol method.

5. Patents

DLRI application to dry processes was patented in EP 3275839 / WO 2018019862.

Supplementary Materials:

Author Contributions: The experiments were performed by GC, LC, YC, and AG. VP and TV developed the high-speed camera experiments. CV, AFM, MLK, NN, LS, and RC provided their expertise on DLI, soft matter, organometallic chemistry, nanocomposites, and plasma processes. All authors participated in the discussion and interpretation of data and contributed to the final manuscript.

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Conflicts of Interest:

References

[1] T. Hanemann and D. V. Szabó, "Polymer-nanoparticle composites: from synthesis to modern applications," *Materials*, vol. 3, no. 6, pp. 3468–3517, 2010.

[2] C. Sanchez, B. Julián, P. Belleville, and M. Popall, "Applications of hybrid organic–inorganic nanocomposites," *Journal of Materials Chemistry*, vol. 15, no. 35–36, pp. 3559–3592, 2005.

[3] Y.-M. Jeong, J.-K. Lee, S.-C. Ha, and S. H. Kim, "Fabrication of cobalt-organic composite thin film via plasma-enhanced chemical vapor deposition for antibacterial applications," *Thin Solid Films*, vol. 517, no. 9, pp. 2855–2858, 2009.

[4] X. Jiang and C.-P. Klages, "Synthesis of diamond/β-SiC composite films by microwave plasma assisted chemical vapor deposition," *Applied physics letters*, vol. 61, no. 14, pp. 1629–1631, 1992.

[5] J. Barbé *et al.*, "Silicon nanocrystals on amorphous silicon carbide alloy thin films: Control of film properties and nanocrystals growth," *Thin Solid Films*, vol. 522, pp. 136–144, 2012.

[6] K. Sattler, J. Mühlbach, and E. Recknagel, "Generation of metal clusters containing from 2 to 500 atoms," *Physical Review Letters*, vol. 45, no. 10, p. 821, 1980.

[7] L. Millière, K. Makasheva, C. Laurent, B. Despax, L. Boudou, and G. Teyssedre, "Silver nanoparticles as a key feature of a plasma polymer composite layer in mitigation of charge injection

into polyethylene under dc stress," *Journal of Physics D: Applied Physics*, vol. 49, no. 1, p. 015304, 2015.

[8] M. Drabik *et al.*, "Composite TiOx/hydrocarbon plasma polymer films prepared by magnetron sputtering of TiO2 and poly (propylene)," *Plasma Processes and Polymers*, vol. 4, no. 6, pp. 654–663, 2007.

[9] J. Drewes, A. Vahl, N. Carstens, T. Strunskus, O. Polonskyi, and F. Faupel, "Enhancing composition control of alloy nanoparticles from gas aggregation source by in operando optical emission spectroscopy," *Plasma Processes and Polymers*, vol. 18, no. 3, p. 2000208, 2021.

[10] M. Calafat, P. Yuryev, A. Drenik, A. Slim, and R. Clergereaux, "Carbon Nanoparticle/Hydrogenated Amorphous Carbon Composite Thin Films Formed in ECR Plasma," *Plasma Processes and Polymers*, vol. 8, no. 5, pp. 401–408, May 2011, doi: 10.1002/ppap.201000151.

[11] F. Palumbo, C. Lo Porto, F. Fracassi, and P. Favia, "Recent advancements in the use of aerosol-assisted atmospheric pressure plasma deposition," *Coatings*, vol. 10, no. 5, p. 440, 2020.

[12] M. Mitronika, A. Granier, A. Goullet, and M. Richard-Plouet, "Hybrid approaches coupling sol–gel and plasma for the deposition of oxide-based nanocomposite thin films: a review," *SN Applied Sciences*, vol. 3, no. 6, pp. 1–23, 2021.

[13] S. Collette *et al.*, "Photocatalytic TiO2 thin films synthesized by the post-discharge of an RF atmospheric plasma torch," *Surface and Coatings Technology*, vol. 289, pp. 172–178, 2016.

[14] M. Borella, M. Plissonnier, and T. Belmonte, "PECVD Synthesis of Polysiloxane-Like Thin Films with Very Low Contact Angle Hysteresis," *Plasma Processes and Polymers*, vol. 4, no. S1, pp. S771–S775, 2007.

[15] P. Brunet, R. Rincón, J. Margot, F. Massines, and M. Chaker, "Deposition of homogeneous carbon-TiO2 composites by atmospheric pressure DBD," *Plasma Processes and Polymers*, vol. 14, no. 7, p. 1600075, 2017.

[16] J. Profili, O. Levasseur, J.-B. Blaisot, A. Koronai, L. Stafford, and N. Gherardi, "Nebulization of nanocolloidal suspensions for the growth of nanocomposite coatings in dielectric barrier discharges," *Plasma Processes and Polymers*, vol. 13, no. 10, pp. 981–989, 2016.

[17] R. MAGNAN *et al.*, "Aerosol assisted atmospheric pressure plasma jet for a high deposition rate of silica-like thin films".

[18] L. Cacot, G. Carnide, M. L. Kahn, R. Clergereaux, and N. Naudé and L. Stafford, "Kinetics driving thin-film deposition in dielectric barrier discharges using a direct liquid injector operated in a pulsed regime," *Journal of Physics D-Applied Physics*, accepted for publication 2022.

[19] R. G. Palgrave and I. P. Parkin, “Aerosol assisted chemical vapor deposition using nanoparticle precursors: a route to nanocomposite thin films,” *Journal of the American Chemical Society*, vol. 128, no. 5, pp. 1587–1597, 2006.

[20] J. Rubio-Garcia *et al.*, “One-step synthesis of metallic and metal oxide nanoparticles using amino-PEG oligomers as multi-purpose ligands: size and shape control, and quasi-universal solvent dispersibility,” *Chemical Communications*, vol. 47, no. 3, pp. 988–990, 2011.

[21] E. Ramirez *et al.*, “Influence of organic ligands on the stabilization of palladium nanoparticles,” *Journal of Organometallic Chemistry*, vol. 689, no. 24, pp. 4601–4610, 2004.

[22] P. Anastas and N. Eghbali, “Green chemistry: principles and practice,” *Chemical Society Reviews*, vol. 39, no. 1, pp. 301–312, 2010.

[23] B. M. Trost, “Atom economy—a challenge for organic synthesis: homogeneous catalysis leads the way,” *Angewandte Chemie International Edition in English*, vol. 34, no. 3, pp. 259–281, 1995.

[24] J. Archer, J. S. Walker, F. K. Gregson, D. A. Hardy, and J. P. Reid, “Drying kinetics and particle formation from dilute colloidal suspensions in aerosol droplets,” *Langmuir*, vol. 36, no. 42, pp. 12481–12493, 2020.

[25] D. Ogawa, I. Saraf, A. Sra, R. Timmons, M. Goeckner, and L. Overzet, “The direct injection of liquid droplets into low pressure plasmas,” *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, vol. 27, no. 2, pp. 342–351, 2009.

[26] J.-P. Borra, “Review on water electro-sprays and applications of charged drops with focus on the corona-assisted cone-jet mode for High Efficiency Air Filtration by wet electro-scrubbing of aerosols,” *Journal of Aerosol Science*, vol. 125, pp. 208–236, 2018.

[27] L. Potočňáková, P. Synek, and T. Hoder, “Viscous droplet in nonthermal plasma: Instability, fingering process, and droplet fragmentation,” *Physical Review E*, vol. 101, no. 6, p. 063201, 2020.

[28] M. Coppins, “Electrostatic breakup in a misty plasma,” *Physical review letters*, vol. 104, no. 6, p. 065003, 2010.

[29] M. Rojo, X. Glad, J. Margot, S. Dap, and R. Clergereaux, “Charging and heating processes of dust particles in an electron cyclotron resonance plasma,” *Plasma Sources Science and Technology*, vol. 28, no. 8, p. 085004, Aug. 2019, doi: 10.1088/1361-6595/ab1cac.

[30] P. Tardiveau and E. Marode, “Point-to-plane discharge dynamics in the presence of dielectric droplets,” *Journal of Physics D: Applied Physics*, vol. 36, no. 10, p. 1204, 2003.

[31] V. Garofano, R. Berard, S. Boivin, C. Joblin, K. Makasheva, and L. Stafford, “Multi-scale investigation in the frequency domain of Ar/HMDSO dusty plasma with pulsed injection of

HMDSO,” *PLASMA SOURCES SCIENCE & TECHNOLOGY*, vol. 28, no. 5, May 2019, doi: 10.1088/1361-6595/ab07cc.

[32] Chouteau S, Mitronika M, Goullet A, Richard-Plouet M, Granier A and Stafford L, “Kinetics driving nanocomposite thin film deposition in misty plasma processes,” *Journal of Physics D-Applied Physics*, 2022.

[33] A. Stancampiano *et al.*, “Plasma and aerosols: Challenges, opportunities and perspectives,” *Applied Sciences*, vol. 9, no. 18, p. 3861, 2019.

[34] V. Garofano, R. Berard, X. Glad, C. Joblin, K. Makasheva, and L. Stafford, “Time-resolved analysis of the precursor fragmentation kinetics in an hybrid PVD/PECVD dusty plasma with pulsed injection of HMDSO,” *PLASMA PROCESSES AND POLYMERS*, vol. 16, no. 11, Nov. 2019, doi: 10.1002/ppap.201900044.

[35] R. Clergereaux, D. Escaich, I. S. de Larclause, B. Bernecker, and P. Raynaud, “Plasma deposition of carbon layer: Correlations between plasma parameters, film structure and properties,” *Diamond and Related Materials*, vol. 15, no. 4–8, pp. 888–892, Aug. 2006, doi: 10.1016/j.diamond.2005.10.028.

[36] L. Cacot, G. Carnide, M. L. Kahn, N. Naudé, and L. Stafford, R. Clergereaux, “Soft plasma polymerization of HMDSO droplets by coupling pulsed direct-liquid injections with dielectric barrier discharge,” *Plasma Processes and Polymers*, p. DOI 10.1002/ppap.202200165, 2022.

[37] D. Hegemann, B. Nisol, S. Gaiser, S. Watson, and M. R. Wertheimer, “Energy conversion efficiency in low-and atmospheric-pressure plasma polymerization processes with hydrocarbons,” *Physical Chemistry Chemical Physics*, vol. 21, no. 17, pp. 8698–8708, 2019.

[38] A. Kraegeloh, B. Suarez-Merino, T. Sluijters, and C. Micheletti, “Implementation of safe-by-design for nanomaterial development and safe innovation: why we need a comprehensive approach,” *Nanomaterials*, vol. 8, no. 4, p. 239, 2018.

[39] G. Carnide *et al.*, “Secured Nanosynthesis–Deposition Aerosol Process for Composite Thin Films Incorporating Highly Dispersed Nanoparticles,” *Advanced Science*, advs.202204929R2.

[40] Carnide Guillaume, Champouret Yohan, Valappil Divyendu, Vahlas Constantin, Mingotaud Anne-Françoise, Clergereaux Richard, Kahn Myrtil, “Composite Thin Films Incorporating Highly Dispersed Nanoparticles from a Secured Nanosynthesis–Deposition Aerosol Process.”

[41] O. Levasseur *et al.*, “Role of substrate outgassing on the formation dynamics of either hydrophilic or hydrophobic wood surfaces in atmospheric-pressure, organosilicon plasmas,” *Surface and Coatings Technology*, vol. 234, pp. 42–47, 2013.

[42] N. Naudé, J. Cambronne, N. Gherardi, and F. Massines, “Electrical model and analysis of the transition from an atmospheric pressure Townsend discharge to a filamentary discharge,” *Journal of physics D: applied physics*, vol. 38, no. 4, p. 530, 2005.

[43] J. Hong, A. Goullet, and G. Turban, “Ellipsometry and Raman study on hydrogenated amorphous carbon (aC: H) films deposited in a dual ECR-rf plasma,” *Thin solid films*, vol. 352, no. 1–2, pp. 41–48, 1999.

[44] D. Dowling, K. Donnelly, M. Monclus, and M. McGuinness, “The use of refractive index as a measure of diamond-like carbon film quality,” *Diamond and related materials*, vol. 7, no. 2–5, pp. 432–434, 1998.

[45] G. Lazar, K. Zellama, I. Vascan, M. Stamate, I. Lazar, and I. Rusu, “Infrared absorption properties of amorphous carbon films,” *J. Optoelectron. Adv. Mater*, vol. 7, no. 2, pp. 647–652, 2005.

[46] C. Simonnet *et al.*, “Pulsed-aerosol-assisted low-pressure plasma deposition of diamond-like carbon coatings,” *Diamond and Related Materials*, submitted 2022.

[47] A. Pastol and Y. Catherine, “Optical emission spectroscopy for diagnostic and monitoring of CH4 plasmas used for aC: H deposition,” *Journal of Physics D: Applied Physics*, vol. 23, no. 7, p. 799, 1990.

[48] S. Peter, K. Graupner, D. Grambole, and F. Richter, “Comparative experimental analysis of the a-C: H deposition processes using CH 4 and C 2 H 2 as precursors,” *Journal of applied physics*, vol. 102, no. 5, p. 053304, 2007.

[49] M. L. Kahn *et al.*, “Organometallic chemistry: an alternative approach towards metal oxide nanoparticles,” *Journal of Materials Chemistry*, vol. 19, no. 24, pp. 4044–4060, 2009.

[50] J. Berndt *et al.*, “Some Aspects of Reactive Complex Plasmas,” *Contributions to Plasma Physics*, vol. 49, no. 3, pp. 107–133, Apr. 2009, doi: 10.1002/ctpp.200910016.

[51] L. Laguardia *et al.*, “Formation of dust in low-pressure magnetized hydrocarbon plasmas,” *New Journal of Physics*, vol. 13, no. 6, p. 063006, 2011.

[52] T. Sadek *et al.*, “Time-resolved analysis of the electron temperature in RF magnetron discharges with a pulsed gas injection,” *Atoms*, vol. 10, no. 4, p. 147, 2022.

[53] M. Monge, M. L. Kahn, A. Maisonnat, and B. Chaudret, “Room-Temperature Organometallic Synthesis of Soluble and Crystalline ZnO Nanoparticles of Controlled Size and Shape,” *Angewandte Chemie International Edition*, vol. 42, no. 43, pp. 5321–5324, 2003.

[54] S. Martin, F. Massines, N. Gherardi, and C. Jimenez, “Atmospheric pressure PE-CVD of silicon based coatings using a glow dielectric barrier discharge,” *Surface and coatings Technology*, vol. 177, pp. 693–698, 2004.

[55] M. L. Kahn, T. Cardinal, B. Bousquet, M. Monge, V. Jubera, and B. Chaudret, “Optical properties of zinc oxide nanoparticles and nanorods synthesized using an organometallic method,” *ChemPhysChem*, vol. 7, no. 11, pp. 2392–2397, 2006.

[56] C. Sarra-Bournet, N. Gherardi, H. Glénat, G. Laroche, and F. Massines, “Effect of C2H4/N2 ratio in an atmospheric pressure dielectric barrier discharge on the plasma deposition of hydrogenated amorphous carbon-nitride films (aC: N: H),” *Plasma Chemistry and Plasma Processing*, vol. 30, no. 2, pp. 213–239, 2010.

[57] F. Massines, C. Sarra-Bournet, F. Fanelli, N. Naudé, and N. Gherardi, “Atmospheric pressure low temperature direct plasma technology: status and challenges for thin film deposition,” *Plasma Processes and Polymers*, vol. 9, no. 11–12, pp. 1041–1073, 2012.

[58] N. de Mejanes, J. Profili, S. Babaei, N. Naudé, and L. Stafford, “Refined analysis of current–voltage characteristics in Townsend dielectric barrier discharges in nitrogen at atmospheric pressure,” *Journal of Physics D: Applied Physics*, vol. 54, no. 9, p. 095204, Dec. 2020, doi: 10.1088/1361-6463/abcb32.

[59] N. Naudé, J.-P. Cambronne, N. Gherardi, and F. Massines, “Electrical model of an atmospheric pressure Townsend-like discharge (APTD),” *The European Physical Journal-Applied Physics*, vol. 29, no. 2, pp. 173–180, 2005.

Chapitre VI. Conclusions et perspectives

Ce travail visait à développer et étudier un procédé à la pression atmosphérique avec une injection pulsée de précurseurs sous la forme d'aérosol liquide pour le dépôt de couches minces (multi-)fonctionnelles. Le principal enjeu de cette thèse est le couplage complexe d'une décharge à barrière diélectrique avec un système d'injection pulsée qu'il a fallu étudier étape par étape. Dans cette conclusion, nous allons revenir sur chaque partie en mettant l'accent sur les réalisations les plus importantes.

L'injection pulsée de gaz dans une décharge à barrière diélectrique

La première étape a consisté à décrire et comprendre l'effet de l'injection pulsée de gaz sur la stabilité de la décharge. En effet, dans l'objectif final de dépôt de couches-minces, le régime de décharge (filamentaire ou homogène) a son importance. L'expérience a consisté à étudier l'effet d'une injection de façon pulsée d'azote dans une décharge d'azote par des caractéristiques électriques et optiques de la décharge. Plusieurs conclusions ont été tirées :

- Pour une injection d'un seul pulse de gaz, la décharge reste dans un régime homogène si la durée du pulse est inférieure au temps de résidence du gaz porteur (i.e. le flux continu d'azote) dans la zone de décharge ;
- Pour une injection d'une durée supérieure au temps de résidence du gaz, avec un taux élevé de répétition des pulses, ou avec un plus grand débit de gaz injecté, la décharge transite en régime filamentaire ;
- La spectroscopie d'émission optique a montré que ce passage en régime filamentaire est relié à la présence d'espèces oxygénées dans la décharge avec des perturbations d'une temporalité plus grande que celle liée au temps de résidence, indiquant ainsi des phénomènes d'accumulation.

Des simulations numériques bi-dimensionnelle de l'écoulement gazeux en présence d'un pulse de gaz ont montré que cette transition vers un régime filamentaire n'est pas liée à la vitesse

transitoire du gaz mais à une forte modification de l'écoulement en fonction de la géométrie du réacteur. En particulier, ce pulse de gaz induit une recirculation en amont de la décharge qui peut induire l'injection d'impuretés dans la cellule de décharge via des phénomènes de dégazage des parois. Ainsi, en présence d'une injection pulsée, le design des espaces situés en amont de la décharge est à prendre en considération pour la stabilité des décharges de Townsend.

L'injection pulsée directe de liquide dans une décharge à barrière diélectrique

La deuxième étape a consisté à décrire et comprendre l'effet de l'injection pulsée de liquide, ici HMDSO, sur la stabilité de la décharge et d'étudier les dépôts obtenus. Cette partie était découpée en deux parties, à savoir, la cinétique de dépôt ainsi que la caractérisation des couches minces obtenues.

* Lorsque le précurseur est injecté sous forme d'aérosols, la cinétique de dépôt est dépendante du temps d'interaction décharge-gouttes. Le dépôt est contrôlé par les phénomènes de transport agissant sur le précurseur indépendamment du temps d'allumage du plasma (en régime d'alimentation pulsée) ou du délai entre l'injection de l'aérosol et l'initiation de la décharge. Ceci est expliqué par la limitation de l'énergie apportée par la décharge à la quantité de précurseur injecté.

* Le dépôt se produit à partir des gouttes confinées dans la décharge (du fait de leur charge électrique) et transportées par le champ électrique. Seules les plus petites sont efficacement déposées, indiquant des effets de transport (par la force d'entrainement des neutres) des plus grosses ou des évolutions temporelles de leur taille suite à la fission Coulombienne.

* Piégées dans l'espace inter-électrodes, les gouttes sont aussi soumises à différents processus d'interaction plasma-gouttes. En fonction du temps d'interaction, le dépôt peut évoluer de deux manières :

    - A faible énergie, des couches minces lisses organosiliciées caractérisées par une forte fragmentation de HMDSO et un fort taux de réticulation ;

- A haute énergie, des couches minces microstructurées organosiliciées caractérisées par un faible taux de dissociation et de polymérisation d'HMDSO (polymérisation douce). Ces dépôts sont visqueux et croient par îlots.

L'ajustement du procédé en contrôlant les paramètres plasmas et les paramètres d'injection pour une variabilité de la couche mince

L'étape suivante a consisté à modifier les interactions plasma-gouttes en favorisant les mécanismes d'évaporation et à étudier les couches minces obtenues dans ces conditions.

* En HMDSO, l'augmentation de la fréquence de la tension appliquée vient changer la morphologie des couches, de couches visqueuses à basse fréquence vers des couches plus lisses mais montrant la présence de poudres à haute fréquence. Cette transition est attribuée au chauffage du gaz dans la décharge à plus haute fréquence pouvant favoriser l'évaporation des gouttes liquides.
* L'efficacité du procédé, c'est à dire la vitesse de dépôt normalisée par la quantité d'énergie injectée, diminue avec la fréquence d'excitation. Ce phénomène est lié au piégeage des gouttelettes dans le champ électrique oscillant et leur évacuation de la cellule de décharge par la force d'entrainement des neutres.
* Les effets de l'évaporation du précurseur sont confirmés par l'utilisation d'aérosols de pentane, où des couches minces visqueuses sont déposées mais avec une efficacité réduite attribuée à l'augmentation de la quantité de vapeurs formées en pentane. Des mesures électriques confirment toutefois que des gouttes de solvant sont confinées dans la décharge sur des temps de plusieurs secondes.

La synthèse de couche-mince nanocomposite par couplage du réacteur-injecteur avec un procédé par plasma

La dernière étape a consisté à étudier le procédé couplant une DBD avec un réacteur-injecteur de nanoparticules qui injecte de façon pulsée un aérosol de nanoparticules et à caractériser les

mécanismes et la structure des couches minces nanocomposites obtenues. Les résultats mènent aux conclusions suivantes :

* Comme à basse pression, la synthèse et le dépôt de couches minces nanocomposites est réalisable avec un réacteur-injecteur de nanoparticules couplé à un plasma à pression atmosphérique.

* La phase plasmagène étant fortement collisionnelle, le transport et le chargement des gouttes de solvant et des nanoparticules joue un rôle clé sur les mécanismes de dépôt des couches minces nanocomposites.

Perspectives dans la caractérisation de la décharge à barrière diélectriques en présence de gouttelettes

Malgré une utilisation et une configuration relativement simple du procédé de dépôt à pression atmosphérique, la présence de gouttelettes dans la décharge à barrière diélectrique constitue un système complexe. En effet, nous avons montré tout au long de ce travail que la décharge transitait d'un régime homogène vers un régime filamentaire en présence d'une injection directe de liquide (III.3, III.4 et IV.2). D'autre part, en analysant plus en détail le régime pulsé de l'injection, il a été mis en avant certains temps caractéristiques de perturbation dépendant du débit continu et du précurseur liquide (IV.2.3). En injection pulsée de gaz (II.3), nous avons vu que la déstabilisation de la décharge pouvait être observée et expliquée par une analyse de la spectroscopie d'émission optique de cette dernière couplée aux mesures électriques. La Figure 40 trace l'évolution de l'émission du N_2 SPS suite à une injection pulsée d'HMDSO avec différentes conditions de débit continu. Ces données sont comparées à l'émission avec une injection pulsée d'azote uniquement. Sans débit continu, deux types de perturbations peuvent être observée. Sur la première minute d'injection l'intensité augmente sensiblement comme pour l'injection pulsée d'azote. Par la suite l'intensité de l'émission optique va diminuer après chaque pulse sans jamais revenir à une position d'équilibre, engendrant une diminution globale de l'émission. En présence d'un débit continu, on observe uniquement une décroissance de l'intensité après chaque injection de liquide. Cette diminution arrive plus ou moins rapidement

suite à l'injection en fonction du débit. Enfin, le retour à une valeur d'équilibre se fait dans la période d'injection du pulse et donc avant le pulse suivant. Ces évolutions semblent indiqué un temps de résidence des gouttes dans la décharge comme évoqué dans la partie III.3. Ces analyses montrent à première vue une signature optique de la perturbation de la décharge par les gouttelettes.

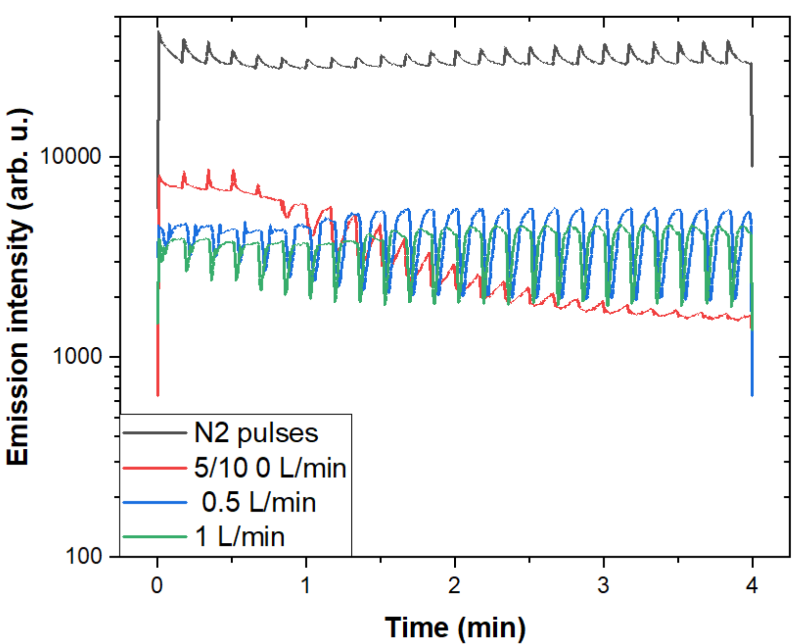

Figure 40: Évolution de l'intensité de l'émission optique du N_2 SPS avec une injection pulsée d'azote (courbe noire) et d'HMDSO pour différents débits 0L/min (courbe rouge), 0.5L/min (courbe bleue), 1L/min (courbe verte).

Un second aspect intéressant est l'analyse optique du N_2 HIR en fonction des conditions de décharge (Figure 41). En augmentant la puissance de la décharge, l'émission du N_2 SPS, relié à la densité électronique, augmente. Cependant que ce soit pour le N_2 SPS ou le N_2 HIR, une diminution arrive après chaque injection de liquide. De plus les données normalisées montrent un temps de perturbation différent pour les deux émissions, ainsi qu'un retour à l'équilibre différent en fonction des conditions de décharge pour le N_2 HIR. Ces données couplées à des analyses électriques résolues spatialement et temporellement pourraient donner plusieurs informations sur la dynamique de transport des gouttelettes dans l'espace inter-diélectriques ainsi que leurs interactions avec les espèces énergétiques du plasma (électrons et métastables).

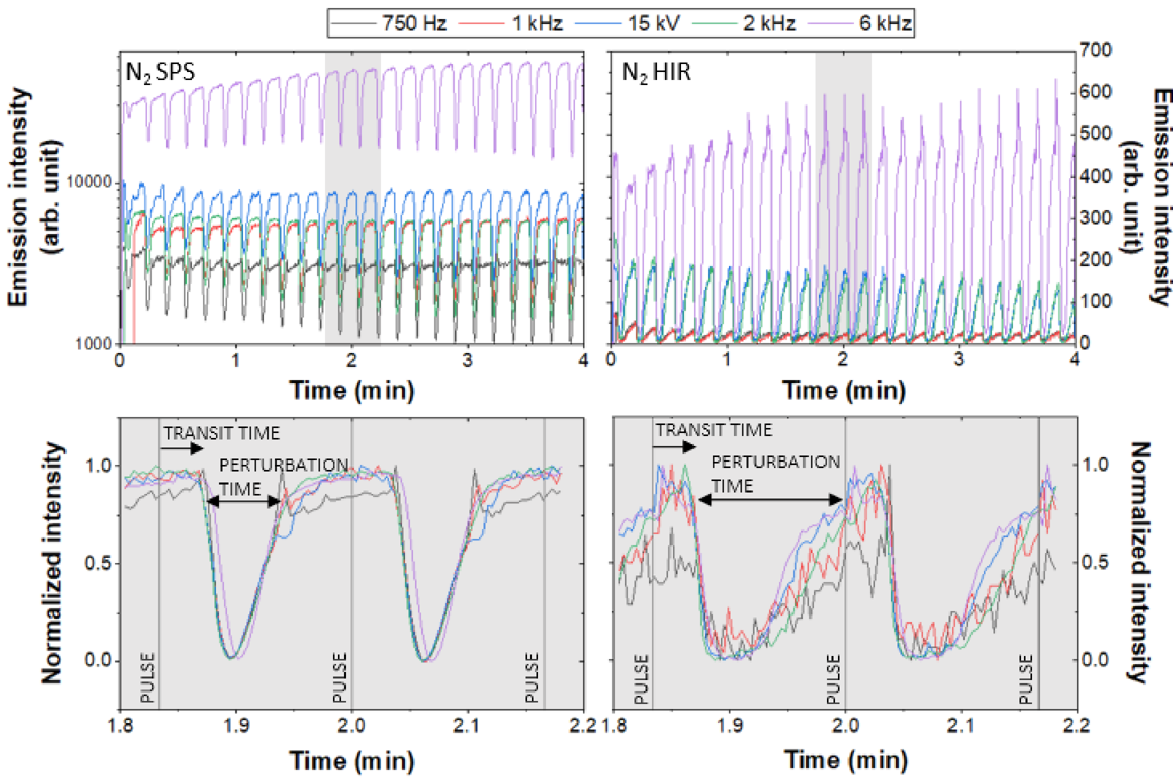

Figure 41 : Évolution temporelle des intensités des émissions N2 SPS et N2 HIR. Les intensités zoomées et normalisées des émissions sont également représentées, et les injections de liquide sont indiquées par les lignes verticales.

Perspectives dans la caractérisation de la couche mince (multi)fonctionnelle

Tout au long de ce travail, nous nous sommes principalement appuyés sur de la spectroscopie FTIR en mode transmission pour analyser les couches minces (III.3, III.4, et IV.2.2). En fonction des conditions de décharge (débit continu, temps du procédé, puissance) et des conditions d'injection (t_{liq}, précurseur), la structure et la composition des couches sont modifiées. En complément de ces résultats, il serait intéressant de caractériser plus finement ces matériaux, en particulier par chromatographie (GPC) pour définir la longueur des chaines de polymères, par spectroscopie à résonance magnétique nucléaire (RMN), pour caractériser la répétition de motifs.

Enfin nous avons ouvert des perspectives sur le transport des nanoparticules de ZnO dans la couche dans la partie 0. Il est possible d'imaginer une caractérisation plus en profondeur de ce type de couches pour différents paramètres d'injection afin de comprendre les mécanismes mis en jeu dans le procédé avec le réacteur-injecteur de nanoparticules. En effet, la Figure 42 compare

la distribution spatiale de l'épaisseur de la couche et du coefficient d'extinction le long de la cellule de décharge sur des dépôts obtenus avec une injection à 1 Hz et 0.1 Hz . Les profils très différents pour ces deux conditions suggèrent des mécanismes de transport différents des nanoparticules ainsi que de la matrice dans la décharge.

Enfin, l'ouverture vers de nouveaux matériaux (type de nanoparticules, solvant, précurseurs) ouvrent de nombreuses perspectives du point de vue matériaux et applications.

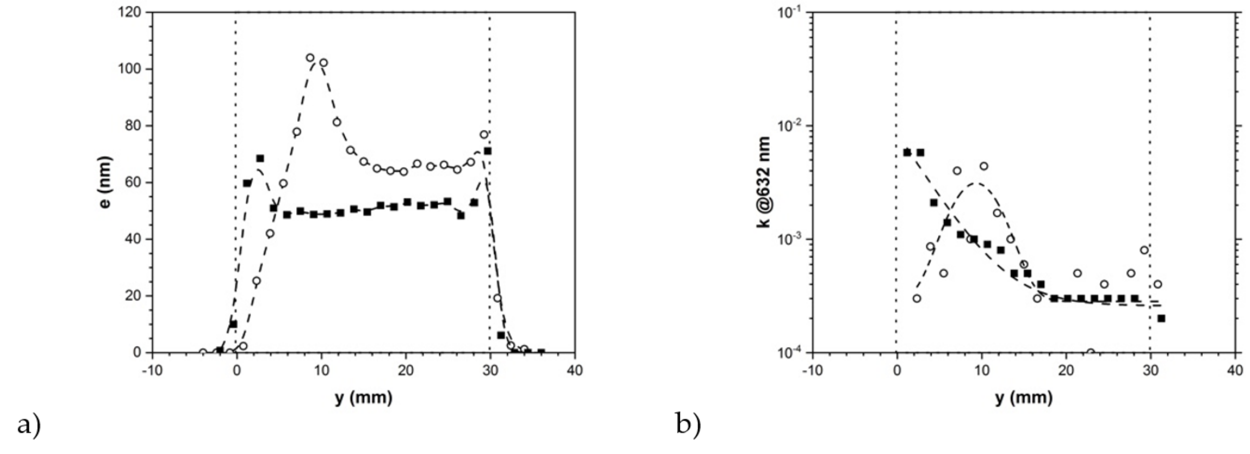

Figure 42: Comparaison des profils d'évolution spatiale de a) l'épaisseur du film et b) du coefficient d'extinction à 632 nm enregistrés aux fréquences d'injection de l'aérosol de 1 (carrés) et de 0,1 Hz (cercles ouverts).

Références bibliographiques

[1] Camargo P H C, Satyanarayana K G and Wypych F 2009 Nanocomposites: synthesis, structure, properties and new application opportunities *Materials Research* **12** 1–39

[2] Zhan C, Yu G, Lu Y, Wang L, Wujcik E and Wei S 2017 Conductive polymer nanocomposites: a critical review of modern advanced devices *J Mater Chem C Mater* **5** 1569–85

[3] Rhim J, Park H and Ha C 2013 Progress in Polymer Science Bio-nanocomposites for food packaging applications *Prog Polym Sci* **38** 1629–52

[4] Du Y, Ge J, Li Y, Ma P X and Lei B 2018 Biomimetic elastomeric, conductive and biodegradable polycitrate-based nanocomposites for guiding myogenic differentiation and skeletal muscle regeneration *Biomaterials* **157** 40–50

[5] Moussa M, El-Kady M F, Abdel-Azeim S, Kaner R B, Majewski P and Ma J 2018 Compact, flexible conducting polymer/graphene nanocomposites for supercapacitors of high volumetric energy density *Compos Sci Technol* **160** 50–9

[6] Massines F, Sarra-Bournet C, Fanelli F, Naudé N and Gherardi N 2012 Atmospheric pressure low temperature direct plasma technology: Status and challenges for thin film deposition *Plasma Processes and Polymers* **9** 1041–73

[7] Profili J, Rousselot S, Tomassi E, Briqueleur E, Aymé-Perrot D, Stafford L and Dollé M 2020 Toward More Sustainable Rechargeable Aqueous Batteries Using Plasma-Treated Cellulose-Based Li-Ion Electrodes *ACS Sustain Chem Eng* **8** 4728–33

[8] Fanelli F, Mastrangelo A M, Caputo G and Fracassi F 2019 Tuning the structure and wetting properties of organic-inorganic nanocomposite coatings prepared by aerosol-assisted atmospheric pressure cold plasma deposition *Surf Coat Technol* **358** 67–75

[9] Hanemann T and Szabó D V 2010 Polymer-Nanoparticle Composites: From Synthesis to Modern Applications *Materials* **3** 3468–517

[10] Kahn M L, Champouret Y, Clergereaux R, Vahlas C and Mingotaud A-F 2016 Process for the preparation of nanoparticles

[11] Mitronika M 2020 *Dépôt de couches minces de TiO2 – SiO2 par association plasma et sol-gel : impact du procédé de dépôt et de la composition sur les propriétés, application à l'optique intégrée*

[12] Uricchio A and Fanelli F 2021 Low-Temperature Atmospheric Pressure Plasma Processes for the Deposition of Nanocomposite Coatings *Processes* **9** 2069

[13] Kahn M L, Glaria A, Pages C, Monge M and Chaudret B 2009 Organometallic chemistry : an alternative approach towards metal oxide nanoparticles 4044–60

[14] Carnide G, Kahn M and Clergereaux R *Nanocomposite thin films : Reactor injector combine with plasma process Nanocomposite thin film : Multifunctionnal Coatings : Depending on the nanoparticle and matrix properties Field of interest Nano-objects dispersed inside a matrix*

[15] Gibson R F 2010 A review of recent research on mechanics of multifunctional composite materials and structures *Compos Struct* **92** 2793–810

[16] Okpala C C 2016 Nanocomposites: an overview *Emerging Materials Research* **5** 5–43

[17] Usuki A, Kawasumi M, Kojima Y, Okada A, Kurauchi T and Kamigaito O 1993 Swelling behavior of montmorillonite cation exchanged for ω-amino acids by -caprolactam *J Mater Res* **8** 1174–8

[18] Usuki A, Kojima Y, Kawasumi M, Okada A, Fukushima Y, Kurauchi T and Kamigaito O 1993 Synthesis of nylon 6-clay hybrid *J Mater Res* **8** 1179–84

[19] Cote D R, Nguyen S V., Stamper A K, Armbrust D S, Tobben D, Conti R A and Lee G Y 1999 Plasma-assisted chemical vapor deposition of dielectric thin films for ULSI semiconductor circuits *IBM J Res Dev* **43** 5–38

[20] Avasthi D K, Mishra Y K, Kabiraj D, Lalla N P and Pivin J C 2007 Synthesis of metal – polymer nanocomposite for optical applications *Nanotechnology* **18**

[21] Scott J F 2007 Multiferroic memories Model interfaces *Nature* **6** 256–7

[22] Díez-Pascual A, Luceño Sánchez J, Peña Capilla R and García Díaz P 2018 Recent Developments in Graphene/Polymer Nanocomposites for Application in Polymer Solar Cells *Polymers (Basel)* **10** 217

[23] Imamura H, Kusuhara M and Minami S 2003 Carbon nanocomposites synthesized by high-energy mechanical milling of graphite and magnesium for hydrogen storage **51** 6407–14

[24] Yeh J M, Liou S J, Lin C Y, Cheng C Y, Chang Y W and Lee K R 2002 Anticorrosively enhanced PMMA-clay nanocomposite materials with quaternary alkylphosphonium salt as an intercalating agent *Chemistry of Materials* **14** 154–61

[25] Levasseur O, Stafford L, Gherardi N, Naudé N, Blanchard V, Blanchet P, Riedl B and Sarkissian A 2012 Deposition of Hydrophobic Functional Groups on Wood Surfaces Using Atmospheric-Pressure Dielectric Barrier Discharge in Helium-Hexamethyldisiloxane Gas Mixtures *Plasma Processes and Polymers* **9** 1168–75

[26] Han Q, Wang R, Xing B, Zhang T, Khan M S, Wu D and Wei Q 2018 Label-free photoelectrochemical immunoassay for CEA detection based on CdS sensitized WO3@BiOI heterostructure nanocomposite *Biosens Bioelectron* **99** 493–9

[27] Mohanta D and Ahmaruzzaman Md 2018 Bio-inspired adsorption of arsenite and fluoride from aqueous solutions using activated carbon@SnO 2 nanocomposites: Isotherms, kinetics, thermodynamics, cost estimation and regeneration studies *J Environ Chem Eng* **6** 356–66

[28] Pirhashemi M and Habibi-Yangjeh A 2017 Ultrasonic-assisted preparation of plasmonic ZnO/Ag/Ag2WO4nanocomposites with high visible-light photocatalytic performance for degradation of organic pollutants *J Colloid Interface Sci* **491** 216–29

[29] Lloyd S M and Lave L B 2003 Life cycle economic and environmental implications of using nanocomposites in automobiles *Environ Sci Technol* **37** 3458–66

[30] Azeredo H M C de 2009 Nanocomposites for food packaging applications *Res J Chem Environ* **15** 721–3

[31] Robert Cammarata 2004 *Introduction to nanoscale Science and Technology* ed J R Ventra, Massimiliano, Evoy, Stephane, Heflin (Springer science)

[32] P.M.Ajayan, L.S.Schadler P V B 2003 Nanocomposite Science and Technology

[33] Chang J H and An Y U 2002 Nanocomposites of polyurethane with various organoclays: Thermomechanical properties, morphology, and gas permeability *J Polym Sci B Polym Phys* **40** 670–7

[34] Kamigaito O 1991 What can be improved by nanometer composites? *Journal of the Japan Society of Powder and Powder Metallurgy* **38** 315–21

[35] Kern W and Vossen J L 2012 *Thin Film Processes II*

[36] Konuma M 1991 *Film deposition by plasma thecniques*

[37] Lukaszkowicz K 2011 Review of Nanocomposite Thin Films and Coatings Deposited by PVD and CVD Technology *Nanomaterials* ed M Rahman pp 146–62

[38] Lieberman M A and Lichtenberg A J 2005 *principles of plasma discharges and materials processingA*

[39] Moisan M and Pelletier J 2014 *Plasma collisionnels*

[40] R.Behrish 1982 *Sputtering by particle bombardment, vol. I: Physical sputtering of single-elements solids* vol 107

[41] Carcia P F, McLean R S, Reilly M H and Nunes G 2003 Transparent ZnO thin-film transistor fabricated by rf magnetron sputtering *Appl Phys Lett* **82** 1117–9

[42] Rand M J 1979 Plasma-promoted deposition of thin inorganic films *Journal of Vacuum Science and Technology* **16** 420

[43] Yu H Z and Thompson C V 2014 Grain growth and complex stress evolution during Volmer – Weber growth of polycrystalline thin films *Acta Mater* **67** 189–98

[44] Dennler G, Houdayer A, Ségui Y and Wertheimer M R 2004 Growth and structure of hyperthin coatings on polymers Growth and structure of hyperthin SiO 2 coatings on polymers **2320**

[45] Schürmann U, Hartung W, Takele H, Zaporojtchenko V and Faupel F 2005 Controlled syntheses of Ag-polytetrafluoroethylene nanocomposite thin films by co-sputtering from two magnetron sources *Nanotechnology* **16** 1078–82

[46] Drabik M, Hanus J, Kousal J, Choukourov A, Biederman H, Slavinska D, Mackova A and Pesicka J 2007 Composite TiOx/Hydrocarbon Plasma Polymer Films Prepared by Magnetron Sputtering of TiO2 and Poly(propylene) *Plasma Processes and Polymers* **4** 654–63

[47] A.Choukourov 2002 Rf sputtering of composite SiO x /plasma polymer films and their basic properties *Surf Coat Technol* **152** 214–7

[48] Desjardins P 2006 *Croissance de couches épitaxiales: Processus de surface et modélisation*

[49] Kratochvíl J, Kuzminova A, Kylián O and Biederman H 2015 Comparison of magnetron sputtering and gas aggregation nanoparticle source used for fabrication of silver nanoparticle films *Surf Coat Technol* **275** 296–302

[50] Singh V, Jiang J C and Meletis E I 2005 Cr-diamondlike carbon nanocomposite films: Synthesis, characterization and properties *Thin Solid Films* **489** 150–8

[51] Kukiełka S, Gulbiński W, Pauleau Y, Dub S N and Grob J J 2006 Composition, mechanical properties and friction behavior of nickel/hydrogenated amorphous carbon composite films *Surf Coat Technol* **200** 6258–62

[52] Dilonardo E, Milella A, Palumbo F, Capitani G, d'Agostino R and Fracassi F 2010 One-Step Plasma Deposition of Platinum Containing Nanocomposite Coatings *Plasma Processes and Polymers* **7** 51–8

[53] Zehnder T 2000 Nanocomposite TiCra **.** C : H hard coatings deposited by reactive PVD *Surf Coat Technol* 138–44

[54] Cabril E 1992 *Films composites or-carbone obtenus par decharge luminescente radio-frequence* (Thèse à l'université Paul Sabatier, Toulouse III)

[55] Despax B and Raynaud P 2007 Deposition of "Polysiloxane" Thin Films Containing Silver Particles by an RF Asymmetrical Discharge *Plasma Processes and Polymers* **4** 127–34

[56] Spears K G, Robinson T J and Roth R M 1986 Particle Distributions and Laser-Particle Interactions Discharge of Silane 179–87

[57] Bouchoule A and Boufendi L 1993 Particulate formation and dusty plasma behaviour in argon-silane RF discharge *Plasma Sources Sci Technol* **2** 204–13

[58] Shukla P K 2001 A survey of dusty plasma physics *PHYSICS OF PLASMAS* vol 8

[59] Roca P, Fontcuberta A, Lebib S and Poissant Y 2002 Plasma production of nanocrystalline silicon particles and polymorphous silicon thin films for large-area electronic devices **74** 359–67

[60] Roca P, Gay P, Hadjadj A, Roca P, Gay P and Hadjadj A 2012 Experimental evidence for nanoparticle deposition in continuous argon – silane plasmas : Effects of silicon nanoparticles on film properties Experimental evidence for nanoparticle deposition in continuous argon – silane plasmas : Effects of silicon nanopa **655**

[61] Gruen D M 1999 Nanocrystalline diamond films *annual review mater science*

[62] Paulmier T, Bell J M and Fredericks P M 2007 Deposition of nano-crystalline graphite films by cathodic plasma electrolysis **515** 2926–34

[63] Choi S J and Kushner M J 1993 The role of negative ions in the formation of particles in low-pressure plasmas *J Appl Phys* **74** 853–61

[64] Hollenstein C, Dorier J-L, Dutta J, Sansonnens L and Howling a a 1994 Diagnostics of particle genesis and growth in RF silane plasmas by ion mass spectrometry and light scattering *Plasma Sources Sci Technol* **3** 278–85

[65] Roth C, Oberbossel G, Buitrago E, Heuberger R and Rudolf Von Rohr P 2012 Nanoparticle synthesis and growth in a continuous plasma reactor from organosilicon precursors *Plasma Processes and Polymers* **9** 119–34

[66] Nichols G, Byard S, Bloxham M J, Botterill J, Dawson N J, Dennis A, Diart V, North N C and Sherwood J D 2002 A review of the terms agglomerate and aggregate with a recommendation for nomenclature used in powder and particle characterization *J Pharm Sci* **91** 2103–9

[67] Rojo M, Glad X, Margot J, Dap S and Clergereaux R 2019 Charging and heating processes of dust particles in an electron cyclotron resonance plasma *Plasma Sources Sci Technol* **28** 085004

[68] Smirnov R D, Pigarov A Y, Rosenberg M, Krasheninnikov S I and Mendis D A 2007 Modelling of dynamics and transport of carbon dust particles in tokamaks *Plasma Phys Control Fusion* **49** 347–71

[69] Merlino R L 2006 *Dusty plasmas and applications in space and industry* vol 661

[70] Shimada M, Wang W-N and Okuyama K 2010 Synthesis of Gallium Nitride Nanoparticles by Microwave Plasma-Enhanced CVD *Chemical Vapor Deposition* **16** 151–6

[71] Massereau-guilbaud V, Géraud-grenier I, Plain A, Massereau-guilbaud V, Géraud-grenier I and Plain A 2012 Determination of the electron temperature by optical emission spectroscopy in a 13 . 56 MHz dusty methane plasma : Influence of the power Determination of the electron temperature by optical emission spectroscopy in a 13 . 56 MHz dusty methane plasma : In *J Appl Phys* **113305**

[72] Tachibana, K. and Hayashi Y 1996 Analysis of Coulomb-crystal formation process for application to tailored particle synthesis in **68** 1107–12

[73] Kitamura, K., Akutsu S 1997 Physics and Application of Dusty Low Pressure Plasmas *Proc. 3rd Int. Conf. on reactive plasmas* (Nara, Japan)

[74] C. Nessim, M. Boulos U K 2009 In flight coating of nanoparticles in amospheric pressure DBD torch plasmas *J. Appl.Phys.* **47** 22819

[75] Brunet P, Rincón R, Margot J, Massines F and Chaker M 2017 Deposition of homogeneous carbon-TiO2 composites by atmospheric pressure DBD *Plasma Processes and Polymers* **14** 1600075

[76] Nautiyal P, Seikh M M, Lebedev O I and Kundu A K 2015 Sol-gel synthesis of Fe-Co nanoparticles and magnetization study *J Magn Magn Mater* **377** 402–5

[77] Amiens C, Chaudret B, Ciuculescu-pradines D, Fajerwerg K, Fau P, Kahn M and Philippot K 2013 Organometallic approach for the synthesis of nanostructures † 3374–401

[78] Zhang D, Go B and Barcikowski S 2017 Laser Synthesis and Processing of Colloids : Fundamentals and Applications

[79] Behnajady M A, Eskandarloo H, Modirshahla N and Shokri M 2011 Investigation of the effect of sol-gel synthesis variables on structural and photocatalytic properties of TiO2nanoparticles *Desalination* **278** 10–7

[80] Profili J 2016 *Dépôt de couches minces nanocomposites par nébulisation d'une suspension colloïdale dans une décharge de Townsend à la pression atmosphérique*

[81] Burgener J A 2002 Enhanced parallel path nebulizer with a large range of flow rates

[82] Mitronika M, Granier A, Goullet A and Richard-Plouet M 2021 Hybrid approaches coupling sol–gel and plasma for the deposition of oxide-based nanocomposite thin films: a review *SN Appl Sci* **3** 665

[83] Fanelli F, Mastrangelo A M and Fracassi F 2014 Aerosol-Assisted Atmospheric Cold Plasma Deposition and Characterization of Superhydrophobic Organic–Inorganic Nanocomposite Thin Films *Langmuir* **30** 857–65

[84] Profili J, Levasseur O, Koronai A, Stafford L and Gherardi N 2017 Deposition of nanocomposite coatings on wood using cold discharges at atmospheric pressure *Surf Coat Technol* **309** 729–37

[85] Frari D Del, Bour J, Bardon J, Buchheit O, Arnoult C and Ruch D 2009 Hybrid Layers Deposited by an Atmospheric Pressure Plasma Process for Corrosion Protection of Galvanized Steel **9** 1–9

[86] Bardon J, Bour J, Frari D del, Arnoult C and Ruch D 2009 Dispersion of cerium-based nanoparticles in an organosilicon plasma polymerized coating: Effect on corrosion protection *Plasma Processes and Polymers* **6** 655–9

[87] Profili J, Levasseur O, Blaisot J-B, Koronai A, Stafford L and Gherardi N 2016 Nebulization of Nanocolloidal Suspensions for the Growth of Nanocomposite Coatings in Dielectric Barrier Discharges *Plasma Processes and Polymers* **13** 981–9

[88] Pappas D 2011 Status and potential of atmospheric plasma processing of materials *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* **29** 020801

[89] Kogelschatz U, Eliasson B, Egli W, Kogelschatz U, Eliasson B and Principle W E D D 1997 Dielectric-Barrier Discharges . Principle and Applications To cite this version : HAL Id : jpa-00255561

[90] Naudé N 2005 *Etude électrique de la physique d ' une décharge de Townsend à la pression atmosphérique et de son interaction avec un générateur : Modèle et Expérience To cite this version : HAL Id : tel-00601053*

[91] Massines F and Gouda G 1998 A comparison of polypropylene-surface treatment by filamentary, homogeneous and glow discharges in helium at atmospheric pressure *J Phys D Appl Phys* **31** 3411–20

[92] Massines F, Gherardi N, Fornelli A and Martin S 2005 Atmospheric pressure plasma deposition of thin films by Townsend dielectric barrier discharge *Surf Coat Technol* **200** 1855–61

[93] Enache I, Caquineau H, Gherardi N, Paulmier T, Maechler L and Massines F 2007 Transport Phenomena in an Atmospheric-Pressure Townsend Discharge Fed by N2/N2O/HMDSO Mixtures *Plasma Processes and Polymers* **4** 806–14

[94] Petersen J, Bechara R, Bardon J, Fouquet T, Ziarelli F, Daheron L, Ball V, Toniazzo V, Michel M, Dinia A and Ruch D 2011 Atmospheric Plasma Deposition Process_ A Versatile Tool for the Design of Tunable Siloxanes-Based Plasma Polymer *Plasma Processes and Polymers* **8** 895–903

[95] Benedikt J, Ellerweg D, Schneider S, Rügner K, Reuter R, Hersten H and Benter T Mass spectrometry of positive ions and neutral species in the effluent of an atmospheric pressure plasma with hexamethyldisiloxane and oxygen

[96] Sonnenfeld A, Tun T M, Zajíčková L, Kozlov K v., Wagner H E, Behnke J F and Hippler R 2001 Deposition process based on organosilicon precursors in Dielectric Barrier Discharges at atmospheric pressure - A comparison *Plasmas Polym* **6** 237–66

[97] Starostin S A, Premkumar P A, Creatore M, De Vries H, Paffen R M J and Van De Sanden M C M 2010 High current diffuse dielectric barrier discharge in atmospheric pressure air for the deposition of thin silica-like films *Appl Phys Lett* **96** 21–4

[98] Savin de Larclause I, Paulmier T, Enache I, Caquineau H, Raynaud P, Massines F and Gherardi N 2009 Conformity of Silica-like Thin Films Deposited by Atmospheric Pressure Townsend Discharge and Transport Mechanisms *IEEE Transactions on Plasma Science* **37** 970–8

[99] Petersen J, Bardon J, Dinia A, Ruch D and Gherardi N 2012 Organosilicon Coatings Deposited in Atmospheric Pressure Townsend Discharge for Gas Barrier Purpose: Effect of Substrate Temperature on Structure and Properties *ACS Appl Mater Interfaces* **4** 5872–82

[100] Martin S 2003 *Mécanismes de croissance et propriétés de couches minces de silice hydrogénée réalisées par décharge luminescente à la pression atmosphérique en mélange silane, protoxine d’azote, azote* (Université Toulouse III)

[101] Starostine S, Aldea E, de Vries H, Creatore M and van de Sanden M C M 2007 Atmospheric Pressure Barrier Discharge Deposition of Silica-Like Films on Polymeric Substrates *Plasma Processes and Polymers* **4** S440–4

[102] Wallimann R, Roth C and Rudolf von Rohr P 2018 Nanoparticle production from HMDSO in atmospheric pressure argon-oxygen plasma *Plasma Processes and Polymers* **15** 1700202

[103] Fanelli F, Lovascio S, d'Agostino R, Arefi-Khonsari F and Fracassi F 2010 Ar/HMDSO/O2 Fed Atmospheric Pressure DBDs: Thin Film Deposition and GC-MS Investigation of By-Products *Plasma Processes and Polymers* **7** 535–43

[104] Zhang J, Wavhal D S and Fisher E R 2004 Mechanisms of SiO2 film deposition from tetramethylcyclotetrasiloxane, dimethyldimethoxysilane, and trimethylsilane plasmas *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* **22** 201–13

[105] YOSHINARI M, HAYAKAWA T, MATSUZAKA K, INOUE T, ODA Y, SHIMONO M, IDE T and TANAKA T 2006 Oxygen plasma surface modification enhances immobilization of simvastatin acid *Biomedical Research* **27** 29–36

[106] Benedikt J, Raballand V, Yanguas-Gil A, Focke K and von Keudell A 2007 Thin film deposition by means of atmospheric pressure microplasma jet *Plasma Phys Control Fusion* **49** B419–27

[107] Siliprandi R A, Zanini S, Grimoldi E, Fumagalli F S, Barni R and Riccardi C 2011 Atmospheric pressure plasma discharge for polysiloxane thin films deposition and comparison with low pressure process *Plasma Chemistry and Plasma Processing* **31** 353–72

[108] Vautrin-Ul C, Boisse-Laporte C, Benissad N, Chausse A, Leprince P and Messina R 2000 Plasma-polymerized coatings using HMDSO precursor for iron protection *Prog Org Coat* **38** 9–15

[109] O'Neill L, Herbert P A F, Stallard C and Dowling D P 2010 Investigation of the effects of gas versus liquid deposition in an aerosol-assisted corona deposition process *Plasma Processes and Polymers* **7** 43–50

[110] Ribeiro R P, Rangel R de C C, Fernandes F O, Cruz N C and Rangel E C 2021 Effect of Plasma Oxidation Treatment on Production of a SiOx/SiOxCyHz Bilayer to Protect Carbon Steel Against Corrosion *Materials Research* **24**

[111] Tran T H, Au D B, Diawara B, Fatyeyeva K, Marais S, Ortiz J, Debarnot D and Poncin-Epaillard F 2019 How the chemical structure of the plasma-deposited SiOx film modifies its stability and barrier properties: FTIR study *Prog Org Coat* **137** 105332

[112] Suhendi A, Nandiyanto A B D, Munir M M, Ogi T, Gradon L and Okuyama K 2013 Self-assembly of colloidal nanoparticles inside charged droplets during spray-drying in the fabrication of nanostructured particles *Langmuir* **29** 13152–61

[113] Profili J, Dap S, Levasseur O, Naude N, Belinger A, Stafford L and Gherardi N 2017 Interaction of atomized colloid with an ac electric field in a dielectric barrier discharge reactor used for deposition of nanocomposite coatings *J Phys D Appl Phys* **50** 075201

[114] Brunet P, Rincón R R, Matouk Z, Chaker M and Oise Massines F 2018 Tailored Waveform of Dielectric Barrier Discharge to Control Composite Thin Film Morphology

[115] Profili J, Levasseur O, Naudé N, Chaneac C, Stafford L and Gherardi N 2016 Influence of the voltage waveform during nanocomposite layer deposition by aerosol-assisted atmospheric pressure Townsend discharge *J Appl Phys* **120** 053302

[116] Jidenko N, Jimenez C, Massines F and Borra J P 2007 Nano-particle size-dependent charging and electro-deposition in dielectric barrier discharges at atmospheric pressure for thin SiOxfilm deposition *J Phys D Appl Phys* **40** 4155–63

[117] Thomas E 2005 Analysis of the neutral drag force in a dc glow discharge dusty plasma *AIP Conference Proceedings* (AIP) pp 279–82

[118] Jimenez C 2004 *Formation de particules à partir de silane et protoxyde d'azote dans des décharges controlées par barrières diélectriques filamentaires et de townsend à la pression atmosphérique d'azote*

[119] Coppins M 2010 Electrostatic Breakup in a Misty Plasma *Phys Rev Lett* **104** 065003

[120] Coppins M 2004 The critical droplet size in a misty plasma *31st EPS Conference on Plasma Phys. Lindon*

[121] Stancampiano A, Gallingani T, Gherardi M, Machala Z, Maguire P, Colombo V, Pouvesle J-M and Robert E 2019 Plasma and Aerosols: Challenges, Opportunities and Perspectives *Applied Sciences* **9** 3861

[122] Guo Q, Mather J P, Yang P, Boden M and Mather P T 2015 Fabrication of Polymeric Coatings with Controlled Microtopographies Using an Electrospraying Technique *PLoS One* **10** e0129960

[123] Agostini P, Meffre A, Lacroix L-M, Ugnati D, Ondarçuhu T, Respaud M and Lassagne B 2016 Electrospray deposition of isolated chemically synthesized magnetic nanoparticles *Journal of Nanoparticle Research* **18** 11

[124] Ogawa D, Saraf I, Sra A, Timmons R, Goeckner M and Overzet L 2009 The direct injection of liquid droplets into low pressure plasmas *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* **27** 342–51

[125] Manley T C 1943 The Electric Characteristics of the Ozonator Discharge *Trans. Electochem. Soc.* **84** 83

[126] Manakhov A, Moreno-Couranjou M, Boscher N D, Rogé V, Choquet P and Pireaux J-J 2012 Atmospheric Pressure Pulsed Plasma Copolymerisation of Maleic Anhydride and Vinyltrimethoxysilane: Influence of Electrical Parameters on Chemistry, Morphology and Deposition Rate of the Coatings *Plasma Processes and Polymers* **9** 435–45

[127] Hilt F, Duday D, Gherardi N, Frache G, Didierjean J and Choquet P 2015 Plasma polymerisation of an allyl organophosphate monomer by atmospheric pressure pulsed-PECVD: insights into the growth mechanisms *RSC Adv* **5** 4277–85

[128] Hopf C, Schwarz-Selinger T, Jacob W and von Keudell A 2000 Surface loss probabilities of hydrocarbon radicals on amorphous hydrogenated carbon film surfaces *J Appl Phys* **87** 2719–25

[129] von Keudell A, Meier M and Hopf C 2002 Growth mechanism of amorphous hydrogenated carbon *Diam Relat Mater* **11** 969–75

[130] Erradi A, Clergereaux R and Gaboriau F 2010 H-atom interaction with amorphous hydrocarbon films: Effect of surface temperature, H flux and exposure time *J Appl Phys* **107** 093305