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## **Atmospheric pressure low temperature direct plasma technology: status and challenges for thin film deposition**

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Over the last ten years, expansion of atmospheric pressure plasma solutions for surface treatment of materials has been remarkable, however direct plasma technology for thin film deposition needs still great effort. The objective of this paper is to establish the state of the art on scientific and technologic locks, which have to be opened to consider direct atmospheric pressure plasma-enhanced chemical vapor deposition (AP-PECVD) a viable option for industrial application. Basic scientific principles to understand and optimize an AP-PECVD process are summarized. Laboratory reactor configurations are reviewed. Reference points for the design and use of AP-PECVD reactors according to the desired thin film properties are given. Finally, solutions to avoid powder formation and to increase the thin film growth rate are discussed.

# I Introduction

Over the last two decades, non-equilibrium (“cold”) atmospheric pressure plasma-enhanced chemical vapor deposition (AP-PECVD) has been touted as a promising alternative to replace some of the low pressure (LP) plasma processes employed for thin film deposition. The main motivations and expectations for this approach were principally to (i) allow continuous processing, (ii) allow easier processing, (iii) reduce the equipment costs by avoiding the need for expensive pumping systems of conventional low-pressure plasma devices and (iv) use open systems. The atmospheric pressure operation adds the possibility of employing easy-to-handle apparatuses to the advantages of the PECVD technology, well known as an easy solution to realize materials in the form of thin films, with a fine tuning of properties (chemistry, morphology, etc.) of the deposited coatings as a function of the process conditions and with a low environmental impact.

There are many other advantages to work with AP-PECVD such as the possibility of (i) using low-volatility liquid compounds, solutions and dispersions in form of aerosols as precursors,<sup>[1-4]</sup> (ii) treating large surface substrates with small linear plasma sources, (iii) depositing in small volumes (compatible with micro- or nano-scale processes),<sup>[5,6]</sup> (iv) localizing pollution of the reactor walls due to low diffusion, (v) treating living tissues (i.e. plasma medicine).<sup>[7,8]</sup> However, it needs to be said that LP plasmas present some key properties that are not present in cold atmospheric pressure plasmas and could still be the best options in some applications. Hence, at low pressure (LP) it is easier to deposit a large variety of coatings on substrates of any type (dielectric, semiconductor, and conductor) and shape (e.g. 3D substrates). For instance, at LP high ion energy allows sputter-assisted processes, and also the deposition of crystalline and denser films compared to the amorphous organic and/or hydrogenated coatings obtained at AP.

All AP-PECVD processes benefit from the fact that the substrate or the plasma source can easily be moved allowing the treatment of large surfaces with relative small plasma sources. Two general and radically different approaches need to be defined for cold atmospheric pressure plasma deposition processes:

- (i) the use of a “direct” plasma on the substrate, where the active species are created directly near the substrate, with the substrate placed between the electrodes, and
- (ii) the use of an “indirect” plasma, where the active species are created remotely in a plasma and pushed onto the substrate. This second approach is also commonly known as atmospheric pressure plasma jet (APPJ) or “post-discharge” deposition process and is suitable for complex 3D substrates of any shape and thickness as there is no electrode spatial confinement.

APPJ technologies and applications have been extensively discussed in other excellent reviews.<sup>[9-11]</sup> While the APPJ approach already presents interesting industrial applications, this is not the case for “direct” plasma deposition process even if it is obvious that a “direct” plasma deposition process would be more efficient in terms of creating and delivering reactive species to the substrate. The difficulty is related to the direct influence of the substrate on the plasma and the need of a tight control of both the plasma and the gas injection to obtain the desired coating. This paper is centered on large 2D surface treatment by direct AP-PECVD.

The fundamental needs to be satisfied by “direct” AP-PECVD processes in industrial applications are:

1. Large-area deposition;
2. High throughput of material to be treated (m/s);
3. Smooth and uniform film on the whole surface;
4. High deposition rates;
5. Reliable and stable process for continuous production (24h/24h);

6. Low gas consumption and utilization of inexpensive and/or easily recycled/reused gases.

AP-PECVD is fully adapted to fulfil the first point. Configurations inspired by roll-to-roll corona treaters<sup>[12,13]</sup> with the substrate crossing linear plasma zones are suitable for large-area deposition. In such reactors, the substrate width determines the electrodes length; meters are fully possible. Substrate displacement allows treating kilometers of soft substrates like polymer films or metal sheet, as well as rigid substrates like glass plates, silicon wafers, and metal plates. This approach is actually working well for surface activation; however the points 2 to 6 also have to be fulfilled to consider AP-PECVD development and these points are still under development. A lot of progress has been done to realize dense and homogeneous powder-free coatings. Throughput depends on the number of substrates simultaneously treated, on the dimension and number of the electrodes and on the growth rate which still have to be improved. Solutions are under study to increase the power which would improve the precursor dissociation rate, and to enhance the transfer of reactive species to the surface.

The aim of this paper is to review the different plasma solutions and to establish the state of the art on the scientific and technological locks, which have to be opened to consider direct AP-PECVD viable option for industrial applications.

Writing the literature review on AP-PECVD reactors is not easy because most of the apparatuses are homemade and are usually not clearly described in the papers. However, their configurations largely determine the thin film properties through the discharge physics and the reactive species transport to the surface. For example, the discharge homogeneity, the secondary chemistry and powder contributions which largely determine the chemical composition and morphology of the thin films are directly related to the reactor configuration. A number of general review articles have already been published on cold atmospheric pressure plasmas and on the physical and chemical properties of the films obtained with such

technology,<sup>[11,14-20]</sup> and thus these themes will not be the focus of this work. The main aim of this review is to establish a common ground of parameters for choosing reactor configuration according to the required properties of the thin films: from polymeric to inorganic dense layers, from ultra smooth to rough nanostructured coatings, from nanoparticle- to biomolecule-containing coatings, etc.

The objective is to give reference points for the design and use of AP-PECVD according to the desired thin film properties. Based on the literature and on the experience of the authors, this review is addressed to those who begin to work on AP-PECVD, those who need to improve AP-PECVD process performances (e.g., thin film properties and growth rate) and those who want to develop industrial solutions.

The paper is composed of four sections. The first two sections summarize the basic scientific principles to have in mind to understand and optimize an AP-PECVD process. First, the different discharge regimes suitable for AP-PECVD are defined and explained; the consequences of the discharge regime, the feed mixture chemical composition and the substrate on the energetic species created by the plasma are detailed (Section II). Then, the chemistry and precursor deposition are discussed (Section III). As one of the advantages of AP-PECVD is the possibility to use gas but also vapor, liquid droplet and even powders as thin film precursors, the consequence of the precursor nature is detailed. Finally surface reactions and mechanisms of powder formation in the plasma are also commented. The last two sections present more practical issues. Section IV concerns the AP-PECVD reactors, which are considered as an assembly of the substrate holder, gas injection system, electrodes and power supply; the control of ambient air is also discussed. Section V is focused on the AP-PECVD process. It begins with a literature review and finally gives some rules to choose the discharge regime and the feed gas, as well to avoid powder formation and to increase the growth rate. The consequence of the substrate displacement is also discussed.

## II Discharge regimes and energetic species

Not every cold atmospheric pressure discharges are suitable for direct AP-PECVD. Thus, in the first part of this section, discharge regimes allowing the deposition of uniform coatings on large surfaces are described (Section II.1). The way the energy injected into the plasma is transformed into energetic species is presented, pointing out the consequences on electrons, metastable states, photons, ions and gas heating (Section II.2). In an AP-PECVD process, the thin film precursor is usually diluted in a main gas; this dilution gas (among He, Ar, N<sub>2</sub> and in a few cases air) is necessary to limit the collision between reactive species and, thus, powder formation. The dilution of the precursor is high, ranging from a few ppm to a few percent. The role of the dilution gas and of reactive additives (e.g. the thin film precursor) in the discharge regimes is presented (Section II.3). As in direct AP-PECVD, the substrate is located inside the discharge zone, the substrate influence on the discharge behaviour is also discussed (Section II.4).

### II.1. Discharges for direct AP-PECVD

At atmospheric pressure, the density of atoms/molecules is as high as  $2.3 \cdot 10^{19} \text{ cm}^{-3}$  at 300K (room temperature), hence, collision frequency between electron and neutrals in the gas phase is high, typically in the  $10^{10}$ - $10^{12} \text{ s}^{-1}$  range. This causes a rapid thermalization of the energetic electrons and gas heating, leading to thermal plasma. As a consequence, solutions to get AP low-temperature plasmas consist in limiting the current amplitude or the duration of the discharge. Depending on the excitation frequency, different discharge mechanisms and solutions are used, thus, this discussion will be split in two parts, one devoted to low-frequency ( $f < 1 \text{ MHz}$ ) discharges, the other to high-frequency ( $f > 1 \text{ MHz}$ ) ones. For low frequency excitation, gas heating is avoided by reducing, "pulsing", the discharge at a time scale varying

between 100 ns and 1 ms; for high frequency excitation, it is the current amplitude which has to be limited because the discharge is always on.

#### II.1.1. Low-frequency discharges ( $f < 1$ MHz)

For excitation frequency lower than 1 MHz, a robust solution to limit discharge duration consists in pulsing the discharge by adding a solid dielectric in the current path to stop the discharge as soon as breakdown occurs, i.e. before electron thermalization.<sup>[14]</sup> This discharge is referred to as dielectric barrier discharge (DBD). The dielectric acts as the insulating part of a capacitor (solid dielectric capacitance,  $C_{sd}$ ), which is charged by the discharge current ( $V_d = \int i(t)dt/C_{sd}$  where  $V_d$  is the dielectric voltage and  $i(t)$  the current), inducing a decrease of the gas voltage and the extinction of the discharge. Higher is the current increase, quicker is the discharge extinction which explained the correlation between the discharge duration and the maximum current density (Table 1). In PECVD process based on such discharges, the gas temperature can remain lower than 330K as typically required for the treatment of thermolabile substrates (e.g., polymers).

Since the frequency is lower than 1 MHz, AP low-temperature DBDs turn on and off each half cycle. Although there is a period in between two consecutive half-cycles for which there is no more ionisation, this off-time is an active period during which efficient energy transfer and chemical reactions occur, due to the existence of long lifetime species like metastable states or radicals. To give an order of magnitude, for a 1 kHz excitation, the off-time is about 250  $\mu$ s, while the time for the gas to return at rest is longer than 1 ms. From a physical point of view, this is at the origin of memory effects from one discharge to the next;<sup>[21]</sup> from a physico-chemical process point of view, this has consequences on the chemistry on the gas phase and on the deposition mechanisms, similarly to what is observed in LP-PECVD modulated process.<sup>[22,23]</sup>

Four different regimes leading to very different energetic species densities (Table 1) can be observed in DBDs:

- (i) Atmospheric Pressure **Filamentary DBD** (FDBD) is made of a multitude of microdischarges reaching high electron density up to  $10^{14} \text{ cm}^{-3}$  but for a very short time (typically 100 ns) and in a small volume, having a radius of 100  $\mu\text{m}$ .<sup>[14,24]</sup> A microdischarge has a typical current density of some  $\text{A} \cdot \text{cm}^{-2}$  (but its section is really lower than  $1 \text{ cm}^2$ ) and is constituted of a strong cathode fall and a plasma zone. It starts with one large electronic avalanche initiating a streamer, which connects the two electrodes to form a single microdischarge channel. Thus, in this regime the electron energy largely varies in time and space. In AP-PECVD configuration, a huge number of microdischarges randomly distributed over time and space cover the whole dielectric surface; this random distribution allows the deposition of a relatively uniform coating because the process time scale is long compared to the microdischarges repetition time.
- (ii) Atmospheric Pressure **Glow-like DBD** (GLDBD) is made of a constrict discharge which propagates up to cover the entire electrode. These discharges have been developed by Van de Sanden and his co-workers, through the use of a 130 kHz excitation, a dynamic power matching and a discharge stabilisation network.<sup>[25,26]</sup> Unfortunately, there is only a few data concerning this discharge and the information given in the papers is not sufficiently detailed to give the opportunity to other research teams to reproduce it. However it is presented here because it is probably an interesting solution for AP-PECVD development. The discharge looks visually uniform like in the case of large number of microdischarges but the coating uniformity is much higher than in FDBDs.<sup>[27,28]</sup> Indeed, the discharge formation process is fully different from a filamentary discharge: the discharge is initiated by a Townsend breakdown of the gaseous gap over the entire electrode surface, followed by a Townsend–glow transition, in which glow-like current spots first form at one or several locations and then laterally expand along the electrodes.<sup>[29]</sup> A cathode fall is always

observed. The glow-like current spot is momentarily occupying only a small part of the electrode surface area; however, due to its dynamics, it provides a uniform treatment of the whole substrate (and electrode surface) within a single unipolar current pulse lasting a few hundreds of ns. The off-time between two discharges is  $\sim 3 \mu\text{s}$ . The current density is one order of magnitude lower than in a microdischarge ( $\sim 1 \text{ A}\cdot\text{cm}^{-2}$ ).

(iii) Atmospheric Pressure **Glow DBD** (GDBD) or Glow Discharge (APGD) is defined by a  $10^{11} \text{ cm}^{-3}$  electron density<sup>[30,31]</sup> in the volume over the whole electrode surface. It starts with a Townsend breakdown initiating a Townsend discharge, which transits to a glow discharge having a cathode fall and a positive column if the gas gap is larger than 2 mm.<sup>[32]</sup> Differently from the FDBD and the GLDBD, at each moment of its development, the discharge uniformly covers the surface of electrodes. The discharge duration is a few microseconds, i.e. for a 10 kHz excitation the discharge is on 10% of the time (i.e. of the period, T). Higher is the frequency, higher is the on-time to off-time ratio and higher is the power, up to the point where the RF regime (i.e. discharge always on) is reached. The ionisation level in a GDBD is lower than in a FDBD or in a GLDBD but the whole volume is ionised and this for a time at least 10 times longer than in a FDBD; thus the deposited power per electrode surface is not so different than for these discharge regimes.

(iv) Atmospheric Pressure **Townsend DBD** (TDBD) or Townsend Discharges (APTD) leads to an electron density of  $10^8 \text{ cm}^{-3}$  in the volume defined by the electrode surface.<sup>[32,33]</sup> Similarly to the GDBD, the discharge is perfectly uniform over the electrodes. This discharge also starts with a Townsend breakdown initiating a Townsend discharge. However, here, the ionisation level remains too low to allow the formation of a cathode fall<sup>[34]</sup> and the electric field is uniform through the gas gap during the entire discharge duration (i.e. the discharge current pulse). Thus, the electron energy is rather constant in time and space. A consequence of the low ionization level is the high electric field, which can favour streamer formation even after gas breakdown.<sup>[35]</sup> Moreover, due to the fact that

the gas voltage is constant during the discharge current pulse,<sup>[32]</sup> the discharge current is proportional to the slope of the applied voltage,  $dV/dt$  (see ref.<sup>[35]</sup> for more details). Higher is the excitation frequency, higher is  $dV/dt$ , and higher is the current along with the risk of reaching a too high ionization level to maintain a homogeneous discharge (transition to a filamentary discharge). The electron density is low along with the current density ( $\sim \text{mA}\cdot\text{cm}^{-2}$ ), but the discharge is turned on for a few 100  $\mu\text{s}$  ( $\sim$  half of the period for a kHz excitation frequency) so the deposited power is similar to that of FDBD (Table 1).

Besides the FDBD, randomly distributed over the entire electrode surface, the GLDBD, progressively covering the entire electrode, the GDBD and TDBD homogeneous over the whole electrode surface, the recent improvement of **nanosecond repetitive pulsed** (NRP) power supplies opens the field to the NRP discharge. A NRP discharge, in DBD configuration or not, is more complicated to install and control than a DBD which operates with a low frequency sinusoidal power supply and dielectrics on the electrodes. In NRP discharges, breakdown occurs under very large overvoltage shifting the electron energy to higher values.<sup>[36,37]</sup> The discharge duration is about the same or even shorter than in FDBD but each discharge can cover the whole electrode surface. In case of NRP DBDs, the pulse duration influence has been studied. Values shorter than tens of nanoseconds are more suitable to get homogeneous DBD.<sup>[38]</sup> In fact, homogeneous pulsed DBD have been observed in helium as carrier gas<sup>[39,40]</sup> or with very short pulses (10-100 ns).<sup>[41,42]</sup> Other conditions lead to filamentary discharges.<sup>[43-47]</sup> NRPD is a promising solution for PECVD.

### II.1.2. High-frequency discharges ( $f > 1 \text{ MHz}$ )

For a frequency higher than 1 MHz (e.g. radiofrequencies), the discharge is always on and the current density should be typically lower than  $50 \text{ mA}\cdot\text{cm}^{-2}$ , otherwise significant gas heating

occurs.<sup>[48]</sup> Similarly to low pressure, AP **radio-frequency glow discharges** (RFGD) can operate in two regimes: the  $\alpha$  mode and the  $\gamma$  one. The  $\gamma$  mode tends to make the discharge localised, so the  $\alpha$  mode only is suitable for PECVD. At atmospheric pressure, this mode ( $\alpha$ -RFGD) is characterised by a volumetric ionisation of the gas occurring both in the sheath and the bulk regions of the interelectrode gap.<sup>[49]</sup> Cathode secondary electron contribution is negligible and the cathode emissivity does not influence the plasma. Dielectric layers covering the electrodes are no more necessary to get a homogeneous discharge. Edge effects related to the shape of the electrode or of the substrate (i.e. increasing of the local field), are also negligible.<sup>[50]</sup> Temperatures lower than 500K are achieved as for instance in helium or argon.<sup>[50,51]</sup> In N<sub>2</sub> or air, gas temperature would increase more significantly through the vibrational excitation. In this case, very large gas flows cools the plasma gas but this is not a really suitable solution for industrial applications due to the gas cost. According to numerical modeling by Shi *et al.*,<sup>[49]</sup> Park *et al.*<sup>[50]</sup> and Yuan *et al.*,<sup>[48]</sup> electron density in  $\alpha$  mode RF discharges is in the range of  $10^{12}$  cm<sup>-3</sup>. It is interesting to point out that the power density dissipated in RFGD is in the same order of magnitude than in low frequency DBDs even if the discharge is always turn on. This is related to the gas heating limitation.

The physics of the discharge changes when the ultra high frequencies range (UHF range of 100 MHz) is reached. The literature about low-temperature atmospheric pressure plasmas at these excitation frequencies is poor and there is no information on the discharge itself (ultra high frequency discharge, UHFD), however it is with such a discharge that the highest growth rates were obtained in AP-PECVD processes.<sup>[52,53]</sup>

## **II.2. Energetic species and energy transfer**

The different discharges that have been presented in the previous section are candidates for direct AP-PECVD. However data concerning energetic species are available only for: FDBD,

randomly distributed over the entire electrode surface, and GDBD, TDBD,  $\alpha$ -RFGD homogeneous over the whole electrode surface. The advantages and drawbacks of the different discharges will be discussed in the AP-PECVD processes section (Section V). Beforehand, the present section deals with the energetic transfers occurring in these discharges, from the creation of the energetic species, namely electron, metastable states, photons and ions, to the gas heating effect. The use of the atmospheric pressure induces specificities common to the different discharge regimes. These specificities are related (i) to the high collision rate inducing a rapid transfer of electron energy to the gas, (ii) to the pulsed character of the FDBD, GLDBD, GDBD and TDBD, with on-time mainly dominated by electrons and off-time dominated by long lifetime excited species.

### II.2.1. Electrons

The maximum electron densities of the different DBDs are very different (Table 1) but they lead to about the same mean power ( $1$  to  $10 \text{ W}\cdot\text{cm}^{-2}$ ) because higher is the ionisation level, more rapid is the current increase, and thus the gas voltage decrease and the discharge extinction. The highest electron densities are also spatially localised in volume having a section as low as few  $100 \mu\text{m}^2$  in the case of FDBDs. Moreover, stronger is the cathode fall, higher is the maximum electron energy reached, but also greater is the variation of this energy in the gas gap. This illustrates the difficulty of comparing maximum electron density and energy from a transient discharge to another one. Numerical modelling and experimental measurements have been done to determine these values (Table 1 and **Figure 1**). The models need to take into account the electron energy loss due to collisions with the background gas. Indeed, this phenomenon is sometimes negligible in low-pressure glow discharges, while it has been shown that at atmospheric pressure, inelastic collisions are not the sole responsible of electron energy losses and these elastic collisions can even be a dominant process, as in the case of helium-fed discharges.<sup>[48]</sup>

For the sake of comparison, Figure 1 shows the electron temperature and electron densities of various atmospheric pressure discharges. Compared with low pressure glow discharges, which presents electron density and energy in the range of  $10^8$ - $10^{11}$   $\text{cm}^{-3}$  and 1-10 eV, respectively,<sup>[57]</sup> it can be seen that atmospheric pressure plasmas show comparable or higher electron densities with relatively comparable energies. For DBDs, the higher electron densities ( $> 10^{12}$   $\text{cm}^{-3}$ ) are obtained in filamentary discharges, while homogeneous DBDs show lower values. In a RFGD the density of electrons is higher than in a GDBD but the energy is generally lower, the reduced field being lower. The sheath-to-bulk electron energy ratio in an AP-RFGD is rather limited ( $\sim 3$ ), with a maximum value in the sheath ranging between 2 and 5 eV depending on the current or the voltage. The electron energy of low frequency DBDs is similar to that of RFGD sheath. There is no data for GLDBD, UHFD and NRP DBD. Concerning the GLDBD, taking into account the current density, the discharge duration and the discharge section, one can expect electron densities and energies in between GDBDs and FDBDs.

### II.2.2. Dilution gas metastable states

In a DBD, the off-time is usually longer than the on-time, therefore during the off-time, energetic species having long lifetime play a dominant role in the chemistry initiation. As previously written, the gas is usually a mixture of a film precursor and a dilution gas among He, Ar,  $\text{N}_2$  and, in a few cases, air. The most important metastable states are those of the dilution gas. Indeed, the high partial pressure of the dilution gas increases the probability of collision of electrons with dilution gas atoms or molecules favouring the formation of metastables. The metastable states have a well-defined energy ( $\text{N}_2^m \sim 6$  eV,  $\text{Ar}^m \sim 11.5$  eV,  $\text{He}^m \sim 20$  eV) and their concentration can be high enough (Figure 1) to make them the main contributors to the plasma chemistry, and thus to tailor the deposition mechanisms. Their density reflects more their lifetime than their creation rate; longer is the species lifetime, larger is its maximum density

value because of the accumulation over several discharge pulses. An example is the concentration of  $N_2(A^3 \Sigma_u^+)$  metastable molecules ( $N_2^m$ ) in a nitrogen-fed TDBD. For instance, at 1 kHz, the off-time is about 250  $\mu$ s, and since the metastable lifetime is about 4 ms, the  $N_2(A^3 \Sigma_u^+)$  metastables accumulate over several discharges and result in a density five orders of magnitude larger than that of electrons (Table 1 or ref.<sup>[32]</sup>). From Figure 1, in a first approximation it can be considered that in a FDBD, electrons play the dominant role while in a GDBD and RFGD, both electrons and metastables are important, and in a TDBD, metastables are dominant.

As mentioned above, the density of the metastable states largely depends on their destruction rate. Among the possible reactions, a very important one is the Penning ionization. Penning ionization is an ionization process that involves two or more neutral gas phase species, with at least one of them being in an excited metastable state. This is a two-step process consisting of an initial production of the metastable state (for example  $e + Ar \rightarrow Ar^m + e$ ), followed by the Penning ionization in itself ( $Ar^m + X \rightarrow Ar + X^+ + e$ ). High efficiency of this ionization process is obtained if there is a good adequacy between the first ionization potential of X and the energy of the metastable species. As a direct consequence of the importance of metastable states, such process can play a dominant role in the production of electrons in an AP low-temperature plasma. The other consequence is that in the case that X is the starting precursor, the ion created by Penning ionization can contribute directly to the thin film deposition.

Metastable states are also quenched by collisional deexcitations. Quenching reactions play a dominant role in atmospheric pressure discharges when the quencher is an atom or molecule in the fundamental level. For instance: (i) the quenching of metastable states  $N_2(a' \ ^1\Sigma_u^-)$  by  $N_2$  significantly reduces its contribution to the off-time chemistry,<sup>[33,58]</sup> (ii) quenching of  $N_2(A^3 \Sigma_u^+)$

metastables state by O<sub>2</sub> becomes a dominant loss pathway for O<sub>2</sub> concentration as low as 20 ppm.<sup>[59]</sup> Indeed, even if 20 ppm is a very low concentration, it corresponds to a partial pressure of 2 Pa and molecules density of  $5 \cdot 10^{14} \text{ cm}^{-3}$ , which is an order of magnitude larger than the metastables one. This is a point to always keep in mind: in an AP low-temperature plasma, the density of the energetic species is always very low compared to the gas density, even the additives one.

In noble gases, another important transformation of metastable species initially created by electron collision is the dimer formation. This is mainly a 3-body association reaction in which a third body play the role of catalyser:  $A^* + B + C \rightarrow AB^* + C$ . The third body being an atom or a molecule of the dilution gas, the frequency of these reactions increases proportionally with the pressure. These reactions, which can be often neglected in low-pressure processes, play a dominant role at atmospheric pressure. The dimers exist only in the excited state; they are also referred to as excimers. They can be metastable or radiative species, neutral or ionised species.<sup>[48]</sup> For example, using noble gases, there is always a strong contribution of dimers, He<sub>2</sub><sup>\*</sup> or Ar<sub>2</sub><sup>\*</sup>. Indeed, at atmospheric pressure, and due to the formation of dimers, the lifetime of He(2<sup>3</sup>S) metastable decreases to 2 μs<sup>[60]</sup> and that of Ar(<sup>3</sup>P) metastable decreases below 0.1 μs.<sup>[61,62]</sup> A direct consequence is that in Ar AP discharges, the [Ar<sub>2</sub><sup>\*</sup>]/[Ar<sup>\*</sup>] ratio can be of several thousand,<sup>[63]</sup> Ar<sub>2</sub><sup>\*</sup> becoming the main actor in the Penning ionization process. Similarly to the other metastables states, neutral excimers can also play a dominant role some microseconds after the end of the discharge: for example the lifetime of Ar<sub>2</sub><sup>\*</sup>(3Σ<sub>u</sub>) state at high pressure is longer than 3 μs.<sup>[62]</sup>

In noble gases, in the same way than for the neutral dimers, dimer ions are usually formed by a 3-body reaction involving an atomic ion. This reaction rate can be really high: in Ar at atmospheric pressure and at room temperature, the dimer ion formation takes place in less than 10 ns.<sup>[62]</sup> As a consequence, in noble gases, if the main ion is not the one created by Penning ionisation, the dimer ion is usually dominant over the atomic ion.



### II.2.3. Photons

Radiative dimers are at the origin of an important VUV radiation. This is particularly intense in Ar AP discharges where dimer radiative deexcitation leads to an emission centred at 126 nm.<sup>[62]</sup> Moreover, resonant energy transfer from argon dimers to atomic oxygen impurities allows the emission of oxygen triplet lines around 130 nm.<sup>[64-66]</sup>

Another remark concerning light emission is that quenching of radiative states, in particular for those states with relatively long vacuum lifetime ( $> 100$  ns), is enhanced. A direct consequence is that some radiative species, usually observed at low pressure, may not be observed in DBDs at atmospheric pressure even if they are created; for example emissions of the  $B^2\Delta-X^2\Pi$  CF system<sup>[67]</sup> or of the  $H_\alpha$  line<sup>[68]</sup> are scarcely observed at AP.

The third point to take into account is the absorption of resonance radiation: when the light emission is due to a resonant transition directly from an excited state to the fundamental state, the emitted photon may be reabsorbed by another atom in the ground state, and thus create a new radiative state. A first approximation of the distance travelled by a resonant photon before being absorbed is given by the inverse of the absorption coefficient: in the case of argon at atmospheric pressure and room temperature, this mean free path is around  $1 \mu\text{m}$  for the  $\text{Ar}(4s)$  states, which is by far smaller than the characteristic lengths in a DBD reactor. Thus these self-absorption effects can play a significant contribution in discharge physics. In contrast, the gas phase is always optically thin (i.e. transparent) for the dimers because dimers fundamental state is dissociative.

### II.2.4. Ions

In most low pressure discharges, ions are considered as energetic species due to their kinetic energy. At AP, they can be considered mainly as chemical species. At atmospheric pressure, their kinetic energy is limited by elastic collision losses; therefore, due to the very small mean free path (typically less than 100 nm regardless of the ion and the gas) the ions lose most of

their kinetic energy in elastic collisions with the surrounding gas, in the volume of the discharge as well as in the sheaths. Thus, even if the applied fields are high, the kinetic energy of ions impinging the surfaces is always very low ( $< 1$  eV).<sup>[48,65,66,69,70]</sup> This means that the surface activation cannot be done by the kinetic energy of the species that come into contact, and physical etching (i.e. sputtering) is generally not observed in a cold plasma process at AP. This lack of energetic ion bombardment may result in less cross-linked coatings compared with hard coatings deposited in LP plasma with negative substrate bias.<sup>[71]</sup> On the other hand, at AP, the defects generally induced in the layers and at the interface between the substrate and the layer by the ion bombardment are not observed.

However, and despite their low kinetic energy, it is worth mentioning that these ions do interact with the surface. Their flux on the surface is in the range of  $10^{15}$   $\text{cm}^{-2}\cdot\text{s}^{-1}$ ,<sup>[31,32]</sup> which is the same order of magnitude as in typical LP plasma processes. During their interaction with the surface, the ions release their potential energy through their electric neutralisation, which has to be taken into account for the understanding of the whole process. For example, the recombination of  $\text{N}_2^+$  ions with electrons from the surface is an exoenergetic process which plays a significant role (i) in the creation of N atoms by a  $\text{N}_2$  Townsend DBD,<sup>[72]</sup> and (ii) in the grafting of N atoms at the surface of a polymer in a He- $\text{N}_2$  fed GDBD.  $\text{N}_2^+$  dissociation releases in fact enough energy to break a polymer bond and to create, at the same time and at the same place, radicals in the gas and on the surface.<sup>[73]</sup> Moreover, due to their high mobility compared to neutrals (time scale for the ion transport is  $\mu\text{s}$  while it is  $\text{ms}$  for a neutral), the ions may also directly contribute to the growth of the layer, as it will be discussed later on.

#### II.2.5. Gas temperature

The gas temperature is always a key parameter as some of the applications are concerned with temperature sensitive materials. In a first approximation, higher is the power, higher is the gas temperature which means, considering the different discharges, that RFGD ( $\sim 150^\circ\text{C}$ )  $>$  FDBD

( $\sim 100^\circ\text{C}$ )  $\geq$  GLDBD  $>$  TDBD ( $\sim 50^\circ\text{C}$ )  $>$  GDBD ( $\sim 30^\circ\text{C}$ ). At atmospheric pressure, in most cases, it is possible to assume that the number of collisions between the molecules is large enough to ensure that the gas temperature and the rotational temperature are in equilibrium. In the case of nitrogen, it was showed that the balance between the translational and rotational levels is achieved in a few collisions.<sup>[74]</sup> The second positive system of nitrogen is thus generally considered an excellent candidate to probe the gas temperature. However, it is worth mentioning here the case of OH(A-X), which is more often questionable, although it is sometimes used with success.<sup>[75,76]</sup> Despite the AP, in fact, the rotational structure of the excited state (A) of OH can be influenced by its process of formation,<sup>[77,78]</sup> which means that the rotational temperature of OH(A-X) can sometimes not be considered a kinetic temperature.

### **II.3. Dilution gas**

In AP-PECVD processes, the thin film precursor is diluted in a main gas. The choice of this dilution gas is crucial both for the discharge physics and the process cost since it is the primary consumable product (Table 2).

The main gases utilized in AP-PECVD processes are He, Ar or N<sub>2</sub> and in a very few cases air.<sup>[81,82]</sup> As it can be seen in Table 2, not all the homogeneous discharges (GDBD, TDBD, or RFGD) can be obtained in any gas. On the other hand, it is always possible to generate a homogeneous DBD whatever the gas, even if it is easier in He and N<sub>2</sub>. The specificities of Ar, He and N<sub>2</sub> discharges are summarized below.

#### **II.3.1. Helium**

Although helium is the most expensive gas, about half of the published works on AP-PECVD use it as the dilution gas. The primary advantage of using helium is its low breakdown voltage (usually around 4 kV·cm<sup>-1</sup> in an AP-PECVD process). This low value simplifies the development of the power supply. Another advantage is that diffuse discharges are rather easy

to obtain in this gas and microdischarges in filamentary discharges have larger radii than in other gases. This is related to the larger mean free path of electrons due to the smaller size of the He atoms. The mean free path of the different species is important: higher it is, longer are both the diffusion length and the mean free path of all the species. One of the consequences is that, for a given electric field, the energy of electrons is higher. This explains why, helium, namely the gas having the highest ionization energy (25 eV), has one of the lowest breakdown voltages. The energy of the first excited metastable state is also high (19.6 eV). This energy is higher than the ionization level of all the other gases and vapors, thus in low power discharges, He<sup>m</sup> largely participate to the ionization (through Penning ionization) whatever the gas mixture and even in "pure" helium because of surface desorption; this mainly occurs in diffuse regime (see section II.2 and Figure 1), characterized by He<sup>m</sup> density comparable or even higher than the electron density.

In a PECVD reactor and process, helium can be always considered as a so-called "Penning mixture" (i.e. a mixture characterized by good adequation between the energy of He<sup>m</sup> atoms and the ionization potential of the precursor or the impurities). There is always a precursor quantity, usually below the threshold concentration of about 10<sup>4</sup> ppm, for which a diffuse plasma can be obtained as far as the excitation is high enough ( $\geq 1$  kHz). On the other hand there is also a maximum concentration of precursors over which the discharge widely involves the reactive gas, which means that ions are mainly formed from direct electronic ionization of the reactive gases; in these conditions the transition to filamentary regimes is usually favored. It was reported for instance that in the case of deposition processes in He-based DBDs of fluorocarbon and hydrocarbon polymers, the typical features of a GDBD can be obtained at precursor concentrations lower than 0.01 %, 0.025 % and 0.5 % for hexafluoropropene (C<sub>3</sub>F<sub>6</sub>), octafluoropropane (C<sub>3</sub>F<sub>8</sub>) and ethylene (C<sub>2</sub>H<sub>4</sub>), respectively.<sup>[67,83]</sup> It is worth mentioning that these threshold limits depend on the feed mixture, which are related to the reactor utilized (considering both mechanical and electrical part) and should be assessed through careful

monitoring of the discharge operation over time during the deposition process, when the surfaces exposed to the discharge (e.g. the dielectric surface in DBDs) are gradually coated by the growing coating.

Another peculiarity of He is that it has a large thermal transfer coefficient allowing a quick dissipation of local gas heating, which is helpful to limit the discharge localization. Thus (i) high ionization levels are obtained in He without formation of streamers and GDBD is easily working, while (ii) in case of He FDBD microdischarges reignition at the same locations (e.g. memory effects) is unlikely. Of course, in He, as  $\text{He}^m$  ionizes most of the other component of the feed mixture, the dominant ions are usually those of the reactive gases.

### II.3.2. Argon

Ar is suitable for RFGD generation. For GDBDs, the employment of Ar as main gas strictly requires the utilization of a Penning mixture. This means that one needs to add a gas/vapor whose ionization potential is in good adequation with the energy of the metastable Ar atoms (11.55 eV and 11.71 eV) or the metastable  $\text{Ar}_2^*$  dimers (10.85 eV). Contrary to He, this condition is very restrictive in Ar, and up to now only  $\text{NH}_3$ <sup>[32,84,85]</sup> or ketone<sup>[86]</sup> has been used for the successful generation of a GDBD. Similarly to He, in an argon Penning mixture, the breakdown voltage is around two times lower than in pure argon. As explained before, another specificity of Ar is the large VUV emission related to radiative  $\text{Ar}_2$  states deexcitation, which largely participate to photoemission.

It has also to be noted that in Ar-fed FDBDs, the energy of a microdischarge is higher than for the other gases. For example, degradation of silicon wafer by such Ar FDBD has been observed.<sup>[87]</sup> It is also in an Ar atmosphere that GLDBDs have been first observed,<sup>[26]</sup> even if, according to the most recent publications, Ar is not necessary to get this regime.<sup>[82]</sup>

When both helium and argon are suitable, argon is preferable because of its lower cost. This is the case of RFGD.

### II.3.3. Nitrogen

In  $N_2$ , the only solution to get a homogeneous plasma is the TDBD. The breakdown value is high, 35 kV/cm, which is not so easy to obtain when the current is limited to mA. Penning ionization can occur by collision between the two metastables states  $N_2(a^1 \Sigma_u^-)$  and  $N_2(A^3 \Sigma_u^+)$ , however due to the strong quenching of  $N_2(a^1 \Sigma_u^-)$ ,<sup>[33,58]</sup> this process is not relevant; thus the most important mechanism involving metastables is the secondary emission of electrons induced by  $N_2(A^3 \Sigma_u^+)$  metastables diffusion to the cathode before breakdown.<sup>[21,33]</sup> One of the differences with noble gases is that the dominant ions ( $N_2^+$  and  $N_4^+$ ) in  $N_2$  TDBDs derive from the main gas and not from the precursors.

As mentioned earlier,  $N_2(A^3 \Sigma_u^+)$  is the important species for the discharge stability. In pure  $N_2$ , it reaches high density ( $10^{13} \text{ cm}^{-3}$ ) where the electron density is 5 orders of magnitude lower.  $N_2(A^3 \Sigma_u^+)$  energy is not so high (6.2 eV) and thus its sensitivity to gas pollution is limited. For example, Brandenburg *et al.* showed that a considerable amount of noble gases (up to 90%) could be added in nitrogen without change in the discharge regime<sup>[88]</sup> and TDBD in  $N_2$  and air are fully similar.<sup>[89]</sup> Hence, due to  $N_2(A^3 \Sigma_u^+)$  metastables, TDBD in  $N_2$  is much more stable than a GDBD in noble gases, which is more dependent on the gas contamination or transformation. On the other hand, addition of precursors able to quench the 6.2 eV metastable always destabilizes the discharge,<sup>[21,32]</sup> this energy being too low to ionize the reactive component. For instance, it was demonstrated that a small addition of quenchers like  $O_2$  or  $NH_3$  considerably limits the minimum frequency under which the TDBD occurs. In the case of the  $SiO_2$ -like film deposition from hexamethyldisiloxane (HMDSO), Massines *et al.*<sup>[90]</sup> found out that with  $N_2$ -HMDSO- $N_2O$  mixtures, the Townsend regime can be successfully obtained at HMDSO concentrations lower than 50 ppm, while the  $N_2O$  content can be as high as few hundreds of

ppm. In this mixture,  $N_2(A^3\Sigma_u^+)$  dominates the chemistry initiation<sup>[91]</sup> as long as 6.2 eV is enough to dissociate the HMDSO molecules.

#### II.4. Substrate

At atmospheric pressure, one could assume that the gas collisions are so numerous that the substrate does not influence the plasma development. Experience shows that this is not the case. For example, in FDBDs, photoemission from the substrate usually plays an important role in the streamer developments.

Substrate importance is even enhanced in homogeneous DBDs as it determines:

- (i) The cathode secondary emission coefficient,  $\gamma$ . When the surface charge is neutralized or the surface is positively charged, this coefficient is that of the intrinsic material. For an insulator it is usually lower than for a metal or a semiconductor, because of the higher energy difference between the Fermi and the void levels (i.e.  $\gamma$  is scaled in the order metal > semiconductor > insulator). Higher is  $\gamma$ , higher is the discharge current for constant electron energy. In other words, due to secondary electron emission increase, a given ionization level is reached with a lower gas bulk ionization and thus a lower voltage. Such effect is clearly observed in a parallel-plate DBD configuration with the two electrodes covered by a dielectric and a silicon wafer added on one of the dielectrics. Breakdown is not significantly affected because the negative charges deposited during the previous half cycle increase dielectric  $\gamma$  coefficient to more or less the same level as that of a semiconductor or a metal. The difference occurs during the discharge development. When the negative charges have been neutralized,  $\gamma$  goes back to the value of the intrinsic material. In the case of a dielectric substrate,  $\gamma$  decreases, in case of semiconducting or metallic substrate  $\gamma$  is not significantly affected by the surface charge. Consequently, a dielectric substrate limits the discharge amplification by decreasing  $\gamma$  contribution. The absence of this mechanism implies a larger voltage decrease to reach the same result with

semiconducting or metallic substrates. Hence, the addition of a conducting substrate in the discharge cell implies an electron energy decrease to get the same current amplitude i.e. the gas ionization has to be limited, otherwise the transition to FDBD or even to arc easily occurs.

- (ii) The value of the capacitance in series with the discharge. This capacitance ( $C$ ) is determined by thickness ( $d$ ) and permittivity ( $\epsilon$ ) of a solid dielectric introduced between the plasma and the electrodes, and by the surface covered by the plasma ( $S$ ). This surface is lower or equal to that of the electrodes. More details on electrical model of DBDs can be found in ref.<sup>[92]</sup> Adding an insulating substrate increases the total dielectric thickness ( $d$ ) and decreases the capacitance ( $C = \epsilon \cdot S/d$ ), and so increases the gas voltage decrease ( $V_g = V_a - Q/C$  where  $V_a$  is the potential applied to the electrodes and  $Q$  the charge deposited by the plasma on the dielectrics). When a conductive surface is added on the dielectric, whatever the part of the surface interacting with the discharge, the charge is distributed over the entire surface. If the substrate is larger than the discharge,  $S$  is no more the surface covered by the dielectric but the substrate surface. Thus the introduction of a conductive substrate induces an increase of  $S$  that becomes equal to the one of the substrate surface, increasing  $C$ ; finally for a given  $Q$  value,  $C$  increases and so  $V_g$ . To summarize, when the surface of the conductive substrate is larger than the discharge, the capacitance increases and the decrease of the gas voltage is lower. As  $\gamma$  is not reduced during the discharge development (metallic surface), the gas ionization can lead to discharge localization. Hence locally, current density high enough to induce silicon wafer degradation can be reached.<sup>[87]</sup>

In conclusion, the discharge regime of a low frequency DBD is affected by the electrical properties of the substrate. In GDBD or TDBD, mean electron energy is higher when the cathode is covered by a dielectric material. Working domain is limited by the addition of a conductive or semi-conductive material. The influence is more important in GDBD in which

the gas voltage has to significantly decrease to stop the discharge. In FDBD-based processes, when conductive or semiconductive substrates are used, microdischarges repeatedly ignite at the same position in form of bright localized filaments.<sup>[19,87]</sup> Thus the coating uniformity in AP-PECVD processes is no more possible.

Substrate conductivity has no influence on  $\alpha$ -RFGD, and this is one of the reasons for interest in these discharges. This is related to the low contribution of secondary emission to ionization. The discharge is fully controlled by the gas bulk ionization. Not only substrate electrical characteristics effects disappear when the  $\alpha$ -RFGD regime is reached but also edge effects related to the local field enhancement due to sharp angles.

The influence of the substrate roughness, flatness and displacement are issues to be considered in AP-PECVD processes. When the roughness reach the level of 10  $\mu\text{m}$ , the coating conformity is no longer obvious because of the high collision level<sup>[93]</sup> but there is no influence on the discharge and uniformity at a larger scale. Lack of flatness could be more significant if it is higher than typically 100  $\mu\text{m}$  and not corrected to maintain a constant gas gap value. As AP gaps are small, usually shorter than 5 mm, 10% gas gap variation over the substrate (electrode) surface have consequences on the coating uniformity due to gas flow modification and to transition from a GDBD covering the whole electrode to a regime similar to GLDBD with a breakdown localized where the gap is minimum and then a discharge extension up to cover the entire surface.

Substrate displacement speeds up to m/s have no effect since the displacement is negligible at the discharge time scale ( $\mu\text{s}$ ). Substrate temperature is more important. Heating the substrate heats the gas. Large gradients are observed even for 1 mm gas gap: more than  $200^\circ\text{C}\cdot\text{mm}^{-1}$  for a substrate heated at  $400^\circ\text{C}$  can be achieved. Such a gradient induces a significant variation of the gas density, which largely influences the electrons energy across the gap and the ionization localization. Ionization mainly occurs in the high temperature region.

### **III Chemistry and precursor deposition**

Now that the energetic species generated by the discharge have been discussed, the reactive species will be considered. The consequence of the dilution gas on the overall plasma chemistry is introduced, drawing attention to molecular gases such as nitrogen and air (Section III.1). The nature and physical state of the precursor is considered (Section III.2) and surface reactions are commented (Section III.3). Reactive species lead to heterogeneous growth at the surface but can also lead to homogeneous growth in the gas phase. The latter finally leads to powder formation (Section III.4). This is a key point in AP-PECVD because nanopowder-dominated growth generally results in coatings with poor density and even nonadherent coatings; thus the adequate control of the powder contribution to the coating growth is decisive to achieve the required coating properties.

#### **III.1. Reactive or inert dilution gas**

As already mentioned, the choice of the feed mixture, and more specifically the selection of the different components (i.e. dilution gas, thin film precursor and additives) and of their relative concentrations, highly affects the discharge regime and behavior. However, it has also a strong influence on the chemical composition and properties of the deposited coating. In fact, molecular gases, such as air and nitrogen, can seriously influence the composition of the deposited coating.

The employment of nitrogen as main gas can result in N-uptake in the coatings. For this reason, the deposition process of polymeric coatings such as hydrocarbon, fluorocarbon or silicon hydride coatings<sup>[52,67,83]</sup> is generally performed in noble gases (e.g. He, Ar). On the other hand

the employment of N<sub>2</sub> as main gas can be exploited in the deposition of coatings with N-containing functionalities. For instance, Girard-Lauriault *et al.*<sup>[94]</sup> deposited nitrogen-rich plasma-polymerised ethylene films using feed gas mixtures of N<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> (about 10 slm and 10 sccm, respectively).

Nitrogen can also be utilized as main gas in the deposition of oxide coatings like SiO<sub>x</sub> from a mixture of a silicon-containing precursors and an oxidant (e.g. O<sub>2</sub>, and N<sub>2</sub>O) diluted in N<sub>2</sub>; in this reactive system, the higher energy of Si-O bond as opposed to the Si-N one (e.g. 800 and 437 kJ·mol<sup>-1</sup> in silica and silicon nitride, respectively) favors the O-uptake in the coating at relatively low oxidant-to-precursor feed ratios.<sup>[90]</sup> Analogous considerations allow concluding that the utilization of air as main gas is convenient in the deposition of oxide coatings, even if in this case the deposition process needs a serious optimization to avoid or control the filamentary character of the air-fed AP-PECVD which can seriously compromise the quality of the deposited layer.

### III.2. Nature and physical state of the precursor

Thin film deposition by atmospheric pressure cold plasmas is accomplished either by adding the precursor gas or vapor to feed mixture, as in the classical PECVD, or by injecting a liquid precursor, as in the aerosol-assisted plasma deposition (AAPD), namely a atmospheric plasma liquid deposition (APLD) technique in which the liquid precursor is introduced in the discharge as a finely dispersed aerosol.

The aerosols is usually generated by pneumatic and ultrasonic atomizers; while the first approach is based on Venturi effect and requires an atomizing gas as for instance the dilution gas of the discharge feed mixture, the second technology allows the direct atomization of the liquid introduced into an ultrasonic nozzle which can be either integrated in the discharge cell or located outside (i.e. upstream) the discharge area.

First, Badyal *et al.* in 2003<sup>[4,95]</sup> developed a polymerization process at atmospheric pressure in which a He GDBD was combined with the aerosol of a liquid precursor injected through a ultrasonic nozzle integrated in the ground electrode of the discharge cell; afterwards several groups reported the employment of aerosol for the deposition of functional coating.<sup>[3,95-103]</sup> Utilizing acrylic acid as precursor, Badyal *et al.*<sup>[95]</sup> demonstrated the possibility of obtaining a high retention of the precursor carboxylic acid group in the coatings.

The employment of aerosols generally seems to favor a soft plasma-assisted polymerization resulting in polymeric thin films characterized by a high retention degree of the precursor molecular structure.<sup>[96,97]</sup> In fact, for the soft plasma-assisted polymerization, the precursor molecules undergo limited fragmentation, while they are activated predominantly at particular reaction sites; they hence undergo a controlled polymerization, which allows the retention in the deposited coating of important chemical functionalities.

The injection in the discharge of a liquid precursor, in the form of finely dispersed drops of liquid, is thought to protect the precursor structure from the action of the energetic species in the plasma, minimizing the fragmentation with respect to the classical PECVD process in which

the precursor molecules in the vapor phase are directly exposed to the plasma. It is supposed that, in the aerosol-assisted thin film deposition, most precursor in the liquid phase is shielded from the plasma, and probably also on the substrate surface when the droplets wet it out.<sup>[96,97]</sup>

Herbert *et al.*<sup>[96]</sup> investigated the aerosol-assisted deposition utilizing 1H, 1H, 2H, 2H-heptadecafluorodecylacrylate characterized by a “polymerization site” and a “functional site” represented by the vinyl group and the long chain perfluorinated functional group, respectively.

The employment of the aerosol coupled with the low specific energy of the discharge (i.e. point-to-plane corona discharge) allowed the deposition of a coating with minimal fragmentation of the precursor molecule and high retention of the perfluorinated chain in the coating.

A successive study evaluated how the physical state of the precursor (vapor or liquid), i.e. the 1H, 1H, 2H-perfluoro-1-decene, influences the fragmentation of the precursor in the discharge and the subsequent coating properties.<sup>[97]</sup> In this case, due to the low discharge power, high retention of the precursor structure was obtained both with the vapor and liquid precursor; however the film deposited by the vapor was more stable and exhibited a higher level of cross-linking degree with respect to the one deposited by the liquid precursor.

Differently from PECVD processes, new mechanisms have to be considered in the rationalization of aerosol-assisted AP processes, and deserve a deeper investigation, as for instance:

- (i) The gas phase plasma/liquid droplet interaction in the gas phase, which can cause charging of the droplet, vaporization of the liquid, formation of activated precursor molecules in the gas phase;
- (ii) The relative importance of two possible pathways that can lead to coating formation, namely the deposition of thin film precursor formed in the plasma phase due to the plasma/droplet interaction, and the action of the plasma on the liquid layer that can form on the substrate due to the direct impact and spread out of the liquid droplet over the surface.

As highlighted by O'Neill *et al.* in ref.<sup>[98]</sup>, there is little direct evidence of how the polymerisable liquid aerosol droplet interacts with the non-thermal atmospheric plasma; it is actually unknown if the liquid aerosol droplets shatter, evaporate or coalesce within the plasma phase during the polymerisation process. They hence reported the direct laser imaging of droplet behavior within a non-thermal plasma polymerisation device.<sup>[98]</sup> The relatively volatile HMDSO and non-volatile polymethylhydrogensiloxane (PHMS) were chosen as model precursors for this study. It was demonstrated that at low aerosol flow rates, no droplets associated with the HMDSO monomer were detected in the plasma, indicating that the droplets were vaporized; while with the non volatile PHMS, droplet particles were detected, indicating that precursor volatility significantly influenced vaporization of the droplets in the discharge. On the other hand, a droplet-dominated process was observed for both HMDS and PHMS at high aerosol flow rates; in this case, droplets can also impact directly on the substrate highly influencing the coating morphology (e.g. forming large polymeric protrusions and drop-like surface).

All these evidences outline some general indications concerning the employment of PECVD and AAPD processes:

- (i) At high power densities, aerosol-assisted processes limit the fragmentation of the precursor molecules, while the employment of vapors results in a deep fragmentation of the precursor and even lead to powder formation, in particular for very reactive precursors. Results similar to the classical PECVD should be expected with low concentrations of aerosols of high volatile precursors.
- (ii) At low power densities, the use of the precursor both in the vapor or aerosol form can lead to good retention of the precursor molecular structure; however in the case of aerosols, the process has to be carefully optimized since there is a risk of obtaining coatings with poor stability or even liquid layers (in particular at high aerosol concentration and for low volatile precursors).

Beside the different considerations that can be helpful in evaluating the utilization of precursors in form of vapor or liquid as a function of the properties of the coatings to be deposited, it is beyond dispute that aerosol-assisted processes are particularly convenient, and can even offer the only possible solution, in the following specific cases:

- (i) When non-volatile (and eventually thermolabile) precursors are utilized. If the precursor vapor pressure is very low as in the case of octamethylcyclotetrasiloxane<sup>[4,98,99]</sup> polymethyldisiloxane,<sup>[100]</sup> this avoids the heating of the precursor delivery system as required for PECVD processes.
- (ii) When biomolecules are injected in the discharge, as reported by Heyse *et al.*<sup>[101]</sup> for bio-functional film fabrication. In this work, organic coating precursors, such as acetylene or pyrrole, are injected simultaneously with an atomized enzyme water solution directly in the discharge. By atomizing the enzyme solution, the very sensitive enzyme molecules are surrounded by a watery shell. It is envisioned that such droplets act as “shuttles”, delivering the enzymes to the discharge while protecting them from the harsh plasma conditions. In the discharge, polymerization of the added organic coating precursor takes place and consequently, the enzyme molecules become trapped in the growing polymer network.
- (iii) When solutions or dispersions are injected in the plasma. For instance, Tynan *et al.*<sup>[102]</sup> deposited a plasma polymerized polycaprolactone (PCL) film nebulizing a solution of a PCL diol in chloroform, while Bardon *et al.*<sup>[103]</sup> reported the deposition of a nanocomposite coating in which aluminum–cerium oxide nanoparticles are incorporated in a silicone-like matrix coating by injecting in a parallel plate DBD dispersions of the nanoparticles in the liquid organosilicon precursor (HMDSO).

Beside the aerosol-assisted AP plasma deposition in which the liquid precursor is directly injected in the discharge, a large variety of atmospheric plasma liquid deposition (APLD) techniques propose to couple the utilization of liquid precursors with AP cold plasma technology; in these processes for instance the liquid precursor is sprayed on the substrate right

before or straight after the AP plasma treatment. It is worth mentioning, for instance, the work by Tatoulian *et al.*<sup>[104]</sup> on the deposition of polymerised acrylic acid films deposited by electrospray on a polymeric film which has been pre-treated with a DBD plasma in air; in this process, the DBD generates reactive groups that will initiate the graft polymerisation of vinyl organic precursor and the interlocking between the coating and the substrate. Likewise, Nisol *et al.*<sup>[105]</sup> deposited a polyethyleneglycol-like film with a three-step process in which after a short duration argon plasma treatment for surface activation, tetraglyme precursor was injected directly into the AP discharge by means of a one-shot spray, and finally the resulting liquid film was exposed for 10 min to argon plasma which leads to the coating formation.

### **III.3. Surface reactions**

Despite the high pressure and the reduced diffusion, not only the gas phase reactions have to be taken into account for the understanding of the AP-PECVD processes. Indeed, several studies have shown that the gas decomposition is rather low in a DBD, and that the gas-surface reactions often play the major role in the polymerization process.<sup>[19,83,106-113]</sup> Even in organosilicon/oxygen mixtures for the deposition of SiO<sub>2</sub> thin films, no evidence of strong reactions in the gas phase between O atoms and organosilicon molecules have been shown,<sup>[106,110]</sup> and this, even in the case of powder formation evidence in the gas phase. This is in accordance with Reuter *et al.* studies which demonstrate that in such mixtures, despite the high pressure, the carbon removal takes place mainly at the surface.<sup>[112,113]</sup> If such results may seem surprising or even counter-intuitive at first, they must be analysed keeping in mind the densities of precursor (typically a few 10<sup>14</sup> cm<sup>-3</sup>) and energetic species (10<sup>11</sup> – 10<sup>12</sup> cm<sup>-3</sup>) in the discharges studied in these papers. In this case, one can note that these concentrations are similar to those observed in a plasma process operating at very low pressure (mTorr range) in which the surface processes dominate the whole deposition process. Some specificities of low temperature atmospheric pressure plasmas are listed below:

- (i) Reactions involving dilution gas and even precursor molecules in the fundamental level rapidly occur because of the relatively high density of the species in the fundamental level. On the other hand, reactions involving two active species resulting from a transformation of the initial gas have the same lower probability than in LP plasmas as the densities are the same.
- (ii) The gas gap is small, typically one millimetre, thus the ratio between the surfaces and the gas bulk is much higher than for LP plasma processes, which could enhance the role of the surface compared to the gas bulk.<sup>[19]</sup>
- (iii) Ions are chemically active. In most cases, the excitation frequency is low and so ions transfer to the surface is high.<sup>[61,62]</sup>
- (iv) Long lifetime species can play a crucial role in the discharge physics occurring at the surface and also in the surface chemistry. Their lifetime gives them the possibility of diffusing towards the surface on which they react. For example, this is the case of N atoms, which reacts with surface oxygen to form NO desorbed in the gas phase.<sup>[114]</sup> Moreover, the surface reactions are influenced by temperature of the sample. For example, in case of Si:H coating from SiH<sub>4</sub> and H<sub>2</sub> diluted in He, a temperature increase enhances the growth rate due to the increase of the adsorption coefficients.<sup>[52]</sup>

#### **III.4. Mechanism of powder formation**

A critical point when using a PECVD process at atmospheric pressure is dust formation.<sup>[3,31,106,109,115-118]</sup> Hence, an important variable to be considered when designing the process is the balance between homogeneous growth in the plasma phase (which finally results in the formation of powders) and heterogeneous growth at the surface. As this balance depends strongly on the partial pressure of the reactive gases, it is always possible to inhibit the dust formation by decreasing the precursor partial pressure.<sup>[119]</sup> However, as this results in an

important decrease of the growth rate,<sup>[31,116]</sup> complementary strategies have been developed, as it will be described in section V.3.

The kinetic pathways for particle formation are still not fully known, but it is likely that mechanisms similar to those observed at low pressure (for example negative ion accumulation) take place also at atmospheric pressure. In particular, it was shown that in the case of SiH<sub>4</sub>, the dynamic of powder formation can be decomposed in nucleation and aggregation mode: at first, the nucleation of condensable species leads to nanoparticles with diameter around 10 nm; then these particles grow by Brownian agglomeration as similarly observed in LP processes.<sup>[120]</sup> Comparing filamentary and Townsend DBDs, Jidenko *et al.* concluded that this dynamic is identical in both types of discharge.<sup>[121]</sup> The only difference concerns the amount of particles, which is higher in the filamentary case, due to a higher local volume energy density, leading to a higher reactive species concentration, implying faster formation kinetics of condensable species and finally resulting in a higher nucleation frequency. This higher local concentration of primary nanoparticles in filamentary discharges than in Townsend discharges leads in turn to a higher agglomeration rate and so to a faster particle growth. In filamentary discharges micrometric powder can also be formed.

An interesting point to pay attention to is the balance between the main forces acting on the nanoparticles which would be produced in a AP-PECVD: as long as the powder does not have a fixed electrostatic charge, the main force is the neutral drag which pushes the powder out of the plasma along the gas flow, in a direction parallel to the surfaces; gravity can be neglected, as well as the ion drag. Moreover, in most cases, the increase in gas and surface temperatures is only a few tenths of Kelvin; thermophoresis force can thus also be neglected. Besides, diffusion losses to the wall are usually negligible within the transit time of the particles in the reactor. As soon as the particle gets charged, which occurs for particle size higher than 10-20 nm,<sup>[43]</sup> the electrostatic force becomes another dominant force, pushing the particles on the surface (i.e. electro-deposition process). As a result, for low frequency excitation (some kHz),

electro-deposition is largely involved in the film formation.<sup>[121]</sup> For example, a powder with a diameter of a few tenths of nm, charged with 10 charges, and located in a field of  $30 \text{ kV}\cdot\text{cm}^{-1}$  should move by more than 1 mm in less than 100  $\mu\text{s}$ . This has two consequences: the first one is that in such conditions (excitation frequency in the kHz range), no big particles are synthesized. Indeed, particles larger than 10 nm get rapidly charged, and so, their transit time in the gas before being collected on the surface becomes shorter than the characteristic agglomeration time for the 20–50 nm particles preventing further growth.<sup>[121]</sup> A second consequence is that it becomes possible to get large growth rate due to the inclusion of nanopowders. Of course, these effects should decrease with an increase of the excitation frequency.

#### **IV AP-PECVD reactors**

After the overview of physics and chemistry controlling AP-PECVD, we will try to give reference points to set-up an AP-PECVD reactor. They concern the different part of a reactor: the gas injection, the shape and number of electrodes (section IV.1), the design of the substrate holder (section IV.2), the power supply (section IV.3), the employment of open-air or closed reactors (section IV.4), the plasma and in-situ thin film diagnostics (section IV.5).

## IV.1. Gas injection and electrodes

### IV.1.1. Different configurations

There have been many different designs and implementations of atmospheric pressure plasma reactors for thin film deposition and it is a real challenge to find comparative parameters to evaluate the efficiency of one design toward another. **Figure 2** shows the three main categories of reactor design when classified through their gas injection and plasma zones organization philosophy, namely the lateral, central and showerhead injection systems.

The lateral and central gas injection configurations (Figure 2a and b) are the most common ones. Gas gaps range generally between 1 and 5 mm. Gas flow is usually laminar with typical velocity of  $\text{m}\cdot\text{s}^{-1}$ . Plasma zones are of some centimeters in the gas flow direction (i.e. electrode width) and as long as necessary in the other direction to treat the entire substrate surface (i.e. electrode length). In laboratory set-ups, electrode length values are usually between 2 and 30 cm, but meters are possible and in the industrial apparatuses this allows the simultaneous treatment of several substrates.

Variable film properties and thicknesses as a function of the gas residence time in the discharge are observed. To obtain uniform films on a large scale, the substrate holder has to be moved parallel to the gas flow direction, which has the effect of “averaging” the film properties and obtaining uniform thicknesses on the whole surface.

In a first approximation, a central gas injection can be considered as two lateral injections. However, there are two significant differences related to the substrate displacement which is required to get uniform coatings. With lateral injection, the direction of the substrate movement with respect to the gas flow direction determines the interface between the substrate and the thin film. If the gas and the substrate enter the plasma zone at the same place (parallel direction), the first step of the coating is due to a slightly activated gas. If the gas flows in the opposite

direction (antiparallel direction) with respect to the substrate movement, a largely activated plasma gas initiates the thin film deposition. With a central gas injection, there is not such a choice: the interface between the substrate and the thin film is always controlled by highly activated species. The other difference is that in the central injection configuration, when the sample run through the space between the two plasma zones, the reactive surface is exposed to the flow of the initial gas mixture when reactive molecules in the feed are not still activated by the plasma, but they can react with the surface, forming a specific layer between each layer deposited in the plasma zone.

The gas is injected in the form of a blade that fits between the two electrodes. Controlled injection and extraction on each side of the plasma is a solution to force the gas in the plasma zone, limiting the losses without adding sidewalls. Of course the injector and extractor should allow the substrate displacement. In most of the reactors the substrate is moving on or with the lower electrode and the high voltage electrode as well as the gas injection system are on the counterpart. The optimum configuration has not yet been defined. Configuration in Figure 2b is the simplest one because the same elements constitute both electrodes and the gas injection system, there is no reduction of the gas gap related to the gas injection, the symmetry helps the gas to enter the plasma zone and one injection system feeding two plasma zones is less expensive than one injection for each plasma zone like the configuration in Figure 2a.

Electrodes can be plane or cylindrical. The main difference is the width of the treatment zone. When at least one of the electrodes is a rod, the discharge width is spatially limited (in the region at minimum distance between the rod electrode and the flat counter electrode) by the gap increase due to the electrode curvature. When electrodes are flat, the treatment zone is determined by the smaller electrode. So the drawback of a cylindrical electrode is that electrode width is no more an adjustable parameter to optimize the coating deposition. The main advantage is the possibility of using the cylinder rotation to force the gas in the discharge area,<sup>[52]</sup> which is suitable with low gaps (e.g. less than 1 mm).

The third configuration category, commonly named showerhead gas injection, consists of gas injection through one of the electrodes (Figure 2c) and uniformly directs the reactive species on the substrate to be treated, which is more akin to a jet configuration. Holes and electrode size and distribution are critical to avoid holes obstruction and to get uniform coatings. Such configuration limits severe gradients in coating thickness due to lateral gas injection, but it is more complicated to get thickness and properties homogeneity at the whole surface scale. Sintered fine metal powders<sup>[122]</sup> or the use of a wire<sup>[123]</sup> mesh are solutions to make a diffuse showerhead electrode. Another possibility consists in utilizing small capillary holes in the dielectric plate (alumina<sup>[124]</sup> or other insulating materials<sup>[69]</sup>). Concentric organization of the holes seems a good solution to have uniform coatings<sup>[124]</sup> on round samples without any displacement for small electrode areas (about a few cm<sup>2</sup>).

#### IV.1.2. Importance of the fluid dynamics

As far as the transport is concerned, since the PECVD processes at atmospheric pressure generally utilize a laminar flow, the laminar diffusion is extremely limited compared to the convection (i.e. the drift with the carrier flow).<sup>[11,27,91]</sup> This can be estimated by calculating the Péclet number,  $Pe = vL/D$ , where  $v$  is the mean gas velocity,  $L$  a characteristic length of the reactor (for example the gas gap) and  $D$  the diffusion coefficient of the species. Velocities are usually in the order of hundreds of cm·s<sup>-1</sup>, gas gaps in the range of a few mm; for the diffusion coefficient of neutral radicals, Savin de Larclause *et al.*<sup>[93]</sup> and Premkumar *et al.*<sup>[27]</sup> found values in the range of 10<sup>-1</sup> cm<sup>2</sup>·s<sup>-1</sup> for HMDSO fragments diffusing respectively in N<sub>2</sub> and Ar-N<sub>2</sub> mixtures. Hence, in most cases, the Péclet number is much higher than 1, which indicates that the diffusion strongly limits the transport of neutrals towards the surfaces: therefore, only the neutrals radicals which are close to the surface are efficiently transferred to it. As an example, it has been shown that in the case of a Townsend DBD in N<sub>2</sub>-HMDSO-N<sub>2</sub>O, using a lateral gas injection between two dielectric plates spaced by 1 mm (Figure 2a configuration), for a mean

gas velocity of  $2.3 \text{ m}\cdot\text{s}^{-1}$  and a 3 cm electrode only the reactive species located closer than 200  $\mu\text{m}$  from the surface actually contributes to the coating growth.<sup>[174]</sup> Thus, in the case of a deposition process using a laminar flow (most of the studies), the gas injection has to be designed in order to optimise the transfer of the neutrals film precursors towards the surface. Also, the fact that the convection largely defines the growth rate implies that the thickness of the layer reflects all the defects of the gas injection. Thus, to get a homogeneous layer not only the power should be homogeneously distributed over the discharge area, but also the gas. If there is a gas recirculation zone (due to vortex formation), it will be reflected on the layer homogeneity. This is illustrated in **Figure 3** which shows two coatings deposited using the same homogenous plasma conditions (TDBD) and the same mean gas velocity; however Figure 3a is obtained in the case of the presence of gas recirculations close to the discharge, while these recirculations are removed in Figure 3b.

Recirculation can occur each time the gas confinement is modified, like at the end of the electrodes, or in the configuration of Figure 2b when the gas impacts the surface. To avoid it, these modifications have to be smoothed, for example by having a distance between the two upper electrodes equal to 2 times the spacing of gas injection slit in configuration of Figure 2b, or by limiting the aperture of the gas flow channel at the outlet side of the discharge zone. It is worth mentioning that, in case of sample displacement, a recirculation involving activated precursors is reflected on the coating even if the phenomenon occurs after the end of the plasma as soon as the substrate reaches that zone. Thus, both the gas injection and extraction have to be well designed to avoid gas recirculation close to or in the plasma zone.<sup>[125]</sup> This indicates the need of an effective exhaust gas pumping in some specific AP-PECVD processes as it will be discussed later on (Section IV.4).

## **IV.2. Substrate and substrate holder**

The size of the substrate is an important parameter. Even if this paper addresses “direct” AP-PECVD on large surfaces, at the lab-scale this can typically mean substrate areas ranging from 3x3 cm<sup>2</sup> to an A4 page size. For laboratory studies, the substrate surface is determined by the final application and the needs for coating characterization. However, surface of some cm<sup>2</sup> are representative of larger surface because:

- (i) Most of the non uniformity problems occur at the scale of millimeters. One thing to keep in mind when working at atmospheric pressure is that the minimum space scale is that of a microdischarge, 100 μm, and that microdischarges are generally separated by one or two millimetres. Because of these characteristic dimensions, up-scaling from millimetres to centimetres is really more difficult than up-scaling from centimetres to meters. AP-PECVD reactor leading to homogeneous coating on 10 cm<sup>2</sup> should be working on m<sup>2</sup>. The first and main barriers to overcome to get a homogeneous coating concern the homogeneity of both the discharge energy (e.g. in the case of filamentary regimes) and the gas injection. Because of the reactive species low mean free path at atmospheric pressure, the coating is a good image of the plasma non-uniformity. If plasma homogeneity and gas injection are well mastered at the scale of some centimeters, then there could be up-scaling problems like the level of parallelism between the two electrodes, but no modification of the discharge or of gas injection which are the key reactor parameters.
- (ii) The substrate displacement allows large surface treatment with rather small plasmas area. An AP-PECVD reactor should include a system to move the sample or to move the plasma. In direct plasma configuration, it is usually the sample which is moved to uniformly treat the surface. Of course it is of great interest to study the properties of coatings deposited on static samples (static mode) because these properties can change moving along the sample surface, namely as a function of the gas residence time inside the discharge region. Coatings deposited with substrate displacement (dynamic mode) integrate at each point all the coatings properties obtained in static mode over the whole surface of the sample. The

consequence of getting uniform coatings thanks to substrate displacement will be detailed in section V.2. If the substrate is soft, like a polymer or metal sheet, roll-to-roll system are useful to control the substrate displacement allowing to treat large surfaces without increasing too much the reactor size. If the substrate is a rigid material like silicon wafers or glass plates, linear displacement system are used. A displacement length equal to the substrate length that has to be treated uniformly, plus one electrode length, can be considered as the minimum value to always have part of the sample in the plasma zone and to not perturb the plasma during the deposition process. The substrate length that has to be treated uniformly needs to be increased of two electrode lengths if the sample needs to be moved back and forth under the electrodes to get the desired coating thickness.

It has to be mentioned that smaller is the sample, larger is the contribution of edge effects related to eventual sharp angle and surface level variation at the end of the sample. Gas flow perturbation or electrical field enhancement, and thus discharge localization, could be consequences of sample edge effect. Larger is the sample surface, lower is the disturbance induced by such effect. So, in some ways, it could be easier to treat larger surfaces than small ones. If the whole sample is in the plasma area, attention should be paid in the design of the substrate holder to limit these edge effects.

In addition to the size and shape of the substrate, the structure of the substrate holder has to be defined considering the displacement system and the conditions of the electrode on which the sample is located. Does this electrode need to be covered by a dielectric? Does the thickness of this dielectric, or of the sample, need to be varied? These are also important questions to be answered. The substrate holder usually supports the low voltage electrode; however it is not always connected to the ground implying the use of insulating material to make at least part of it.

### IV.3. Power supply

The power supply is a critical part of atmospheric pressure plasma reactors firstly because filamentary discharges can be prevented by special designs of both the plasma source and the power supply.<sup>[126-128]</sup> Differently from low-pressure plasmas, some kilovolts are usually necessary to turn on the discharge while the current are rather low usually lower than 100mA. Many types (low frequency, high frequency, RF, pulsed, etc.) and structures (transformer, resonant, linear amplifier, etc.) of power supplies can be used. The choice depends on:

- (i) The type of electrical source (current or voltage source). Most of the literature deals with voltage sources. However, there is some research related to current power supplies for DBDs.<sup>[129-131]</sup> The main benefits are a better control of the discharge current, an increase of the discharge duration and therefore an increase of the discharge power without transition to thermal plasma.<sup>[132]</sup>
- (ii) The shape (sinusoidal, square, nano- micro- pulsed, etc.) and the frequency of the signal.
- (iii) The amplitude of the voltage, which depends on the carrier gas utilized in the process and on the pressure-distance product,  $p \cdot d$ , according to the Paschen's law.<sup>[80]</sup> For example, at atmospheric pressure and ambient temperature, for a 1 mm gas gap the breakdown voltage in helium is around 300 V whereas it is equal to 4 kV in nitrogen.<sup>[79,80]</sup> Usually, this requires the use of a transformer to generate the high voltage. It is worth noting that the first breakdown voltage could be considerably higher than the maintenance voltage and that breakdown voltage decreases with the frequency.<sup>[65]</sup> Thus, a solution to reduce the maximal voltage of the power supply is to use an ignition system. Bárdos *et al.* show an example of ignition of hybrid microwave plasma by a high-voltage spark produced by a Tesla coil.<sup>[133]</sup>

#### IV.3.1. Different types of power supplies

Most of the literature is on low frequency sinusoidal voltage DBD systems. Below are presented the main types and structures of power supplies used for atmospheric pressure plasma

processes. The choice depends on the application, the carrier gas and the discharge type. However, the power supply technology changes around 200 kHz.

(i) Low frequency (up to 200 kHz) sinusoidal voltage source

In laboratory experiments, the power supply is often made of a low frequency generator providing the reference waveform which is then amplified by a linear amplifier whose low voltage output is applied to the primary winding of a high voltage transformer delivering the required voltage amplitude (**Figure 4**).<sup>[35,67]</sup> This allows an easy and independent adjustment of the shape, the frequency and the amplitude of the applied voltage. This is the less expensive solution.

An alternative to this multipart solution is to use a high voltage linear amplifier.<sup>[134,135]</sup> For example, it is possible to find high voltage amplifiers that deliver a voltage up to 50 kV peak, a current of some hundred of mA and a bandwidth up to 60 kHz.

Although these power supplies are easy to implement and to use, the efficiency is too low for an industrial reactor or a large-scale reactor. This is mainly due to switching losses in the semiconductor devices. To improve the power supply efficiency, the soft switching regime, in which switching of the power semiconductor occurs only when either the voltage or current is zero, is more appropriate.<sup>[136]</sup> This regime occurs in serial and parallel resonant converter.<sup>[137-141]</sup> The resonant circuit is realized by adding an inductance (in series or parallel) with the discharge cell. The main goal of this electrical circuit is to use forced oscillation to increase voltage on cell discharge ( $V_s$ ) and create the plasma. The oscillating circuit enhances the effective power transfer to the discharge at the resonance frequency and for this reason, these power supplies are nowadays the most common and robust solution for industrial reactors as for instance large scale roll-to-roll treaters utilizing air-fed corona discharges or DBDs. This solution is energy efficient but inflexible and suitable mainly for large-scale processing.

(ii) High frequency (higher than 200 kHz) and RF sources (MHz range):

For frequency higher than a few hundred kHz, the structure of the transformer should be modified because the magnetic circuit is not well adapted. Bazinette *et al.* show a solution using a resonant circuit<sup>[142]</sup> with a transformer made of two coils coupled with air. This solution is interesting but inflexible (e.g. in terms of operating frequency) and suitable for laboratory reactors only. For higher frequency, this solution is no longer usable and the discharge is generated using an RF power supply typically at 13.56 MHz. In this case, an impedance matching is required to transfer the power to the plasma.<sup>[143,144]</sup>

(iii) Current sources:

Nowadays, current source inverters are not used for atmospheric pressure PECVD. However, they are successfully used for DBD lamps.<sup>[129-131]</sup> They allow the control of the current duration and amplitude, thus, the real operational phase of the discharge.

#### IV.3.2. Suppression of microdischarges

There are several options to suppress or even to avoid streamers.<sup>[21,133,145]</sup> The most useful approaches are listed below:

- (i) Using sinusoidal voltage at a frequency higher than 10 kHz in noble gas or lower than 20 kHz in nitrogen.<sup>[21]</sup>
- (ii) Using pulses shorter than streamer development, *i.e.* shorter than 100 ns.<sup>[146]</sup>
- (iii) Using an electronic device (*e.g.* dynamic matching) to control and/or limit the current. For GLDBD generation, Starostin *et al.*<sup>[25,26]</sup> use a discharge stabilization sub-circuit to sustain a uniform discharge avoiding transition to a filamentary regime. This circuit consists of a choke coil in series with the discharge, it is working in the saturation regime and prevents the fast current increase.

- (iv) Improving the coupling between the power supply and the discharge. In the case of a TDBD, a solution to avoid the transition in filamentary discharge is to act on the ratio of the solid dielectric capacity to the gas capacity ( $C_{sd}/C_{gas}$ ).<sup>[35]</sup> A decrease (by decreasing the dielectric permittivity or increasing the dielectric thickness) of this factor allows an increase of the maximal frequency and the discharge power.
- (v) Using special electrode connection. At low frequency, Okazaki *et al.*<sup>[126]</sup> and Trunec *et al.*<sup>[147]</sup> have reported homogeneous discharge in a DBD with a wire mesh sandwiched between the dielectric and metal conductor.

#### **IV.4. Open-air or closed reactor**

One of the main advantages of AP-PECVD is that it can work in open-air. Working in open-air implies finding solutions to control air entrance in the plasma zone and to extract the exhaust gas which contains precursor by-products, including nano-powders. Such technical problems are far away from the fundamental understanding of the AP-PECVD and of plasmas-surface interactions, however it is a crucial issue in reactor design when considering the perspective of employing AP-PECVD processes in an industrial environment. Thus, in laboratory reactors, the discharge set-up is often located in a closed container akin to a glove box or a vessel equipped with pumping systems like those of low pressure plasmas. The core idea is that the understanding of the plasmas physics and chemistry is easier if the gas chemical composition is well controlled through the use of an airtight container and a pumping system. While a pumping system is not really indispensable for removing air from the enclosure (in general, air scavenging with high flow rates of main gas is enough), extraction of plasma by-product is necessary.

Some efforts have been directed recently to determine the influence of air contamination on the overall PECVD processes. These studies aim at evaluating if atmospheric pressure DBDs can be competitive with the low pressure plasma technology for some specific processes that require

feed gases different from air. The knowledge of the highest level of contamination compatible with acceptable performances is essential to reduce the cost of processes and reactors.

The presence of air as impurity, besides influencing the discharge regime and operation, could have a serious detrimental effect on the reproducibility and overall performance of the plasma process. For example, in the case of TDBD fed by  $N_2$ -HMDSO- $N_2O$  or  $N_2$ - $SiH_4$ - $N_2O$  mixtures,<sup>[90]</sup> the presence of atmospheric oxygen contaminations does not influence the final composition of the coating, however, a few tens of  $O_2$  ppm cause TDBD destabilization and powder inclusion in the coating. The effect of air is enhanced when O and N incorporation in the coating is considered deleterious (e.g. polyethylene-like or teflon-like coatings). In the case of the deposition of polyethylene-like coatings by He- $C_2H_4$  GDBD,<sup>[83]</sup> thin film chemical composition is modified by air addition. However, increasing the ethylene concentration in He from 0.1% to 0.5% decreased the oxygen up-take in the coating from 8% to less than 1%. The contaminant concentration in the reactor is likely always the same and the important parameter is the ratio of this contamination and the thin film precursor. Another important point to have in mind is oxygen etching: the investigation of influence of air and water vapor contaminations on the AP deposition of fluorocarbon coatings in Ar- $C_3F_6$  FDBDs<sup>[148]</sup> have shown, surprisingly, that the contaminants addition (at contaminant-to- $C_3F_6$  feed ratios as high as 0.5) did not appreciably affect the chemical composition (i.e. constant XPS F/C ratio and O- and N-uptake lower than 1%) and the hydrophobic character of the deposited coatings. On the other hand, it resulted in a decrease of the discharge power, of the deposition rate and the appearance of a certain roughness; these changes were more evident for the addition of  $O_2$ , air, and  $H_2O$  than for  $N_2$ . It was hence supposed that oxygen is the main responsible and surface roughness could be ascribed to the etching of the growing polymer.

It is worth mentioning that the careful design of the DBD reactor, as far as the particular the fluid dynamic aspects are concerned, can reduce the risk of air entrainment in the discharge cell even in the case of open-air reactors, and the duration of the purging of the reactor chamber

and/or the discharge cell before performing the deposition process. It is also important to highlight that in particular in open-air systems the choice of argon and nitrogen should be preferred with respect to helium; indeed, due to the low atomic mass, at the same flow rate, helium pushes away the ambient air less effectively than argon and nitrogen.

In the optimization of AP plasma deposition processes with open-air roll-to-roll systems, particular attention should be paid to the air entrainment in the discharge zone due to fast moving webs, as well as the fact the plasma deposited coating immediately exits the discharge zone and is exposed to air when it is still reactive.

#### **IV.5. Plasma diagnostics and in-situ thin film characterization**

Plasma and thin film diagnostics will not be discussed in detail in this paper but it is of course important to keep in mind that on-line diagnostics are indispensable for process monitoring.<sup>[149]</sup>

For plasmas at atmospheric pressure, all the optical techniques (e.g. emission, absorption, fluorescence, high speed photography) are of great interest because they are not intrusive and often time and space resolved, important prerequisites for monitoring of pulsed and possibly localized plasmas. More specifically, emission, absorption and fluorescence techniques allow to have indications on the chemistry during the discharge as well as during the off-time, while high speed imaging allow to determine the plasma homogeneity, power and hence to observe discharge localization and filamentation.

For process monitoring, emission spectroscopy is certainly a solution as correlation between plasma emission and thin film chemistry have been observed.<sup>[19,67,166]</sup>

Electrical measurements are limited to Lissajous figures or current-voltage oscillograms which are not easy to analyze when the frequency increases at values higher than a few hundreds of kHz. However, at lower frequency they allow the determination of the power dissipated into the discharge as well as to have on line indications on the discharge regime. In the case of

homogeneous discharge, they also allow the determination of the voltage applied to the gas. On the other hand, Langmuir probes are not adapted because of the collisional sheath.

The gas phase chemistry can be investigated by mass spectrometry however this technique is not easy to set-up and results interpretation is not obvious.

For the substrate, ellipsometry is a powerful technique for determining for instance the film density thickness, refractive index, etc. As the gap is usually too small, ellipsometry measurement is made outside the plasma zone using the substrate displacement to move the sample at the measurement point.

## **V AP-PECVD process**

Different kind of thin films can be deposited in the same reactor. The desired thin film properties are achieved thanks to the discharge regime, the feed mixture and the power delivered to the plasma. In the previous sections, the different discharges, feed mixtures and power supply have been presented. The panel is large and choices are not obvious. Hence, the aim of this section is to give some clues to make the more appropriate choices according to the required thin film characteristics and substrate.

First, a literature review of what can be done is rapidly presented, pointing out the experimental conditions (section V.1). As one advantage of AP-PECVD is to treat large surface thanks to the substrate displacement, consequences of the substrate displacement on the layer properties are discussed (section V.2). The three main locks for AP-PECVD development are (i) the complexity of plasma panel, too many possibilities, which are not so well identified and the fact that, as of today, no plasma configuration has been found which works, whatever the application, that could be interesting for a reactor manufacturer, (ii) powder formation and inclusion in the thin film associated to AP and (iii) too low thin film growth rate compared to

the expected values. These 3 points are still under study so hints are given to choose the discharge regime and the feed gas (section V.3), to avoid powders formation which limits the layer density (section V.4) and to increase growth rate (section V.5).

### **V.1. Literature review**

The best way to identify the industrial challenges and important parameters of direct AP-PECVD processes is to present an overview of the scientific literature. Thus, in Tables 3-5, a selection of published works on the deposition of thin films for lateral, central and showerhead gas injection configuration are listed, respectively. The deposition rate is reported along with some key parameters of the process such as the discharge regime, the excitation frequency, the precursor and the carrier gas. Deposited power per coated unit area is also given when data are clearly reported in the papers. Minimum values (down to  $3 \text{ mW}\cdot\text{cm}^{-2}$ ) correspond to low frequency microsecond pulsed excitation, while larger values (up to  $50 \text{ W}\cdot\text{cm}^{-2}$ ) are observed with radio frequency excitation. As it can be seen, in most cases, power remains below  $10 \text{ W}\cdot\text{cm}^{-2}$ .

Gaseous or liquid precursors (injected as vapours or aerosols) are usually diluted in a main gas having a flow rate usually in the range between 0.5 and 20 slm. Helium is the most frequent; argon is used in particular for RFGDs;  $\text{N}_2$  is utilized for low frequency excitation and only a few papers present results with air as dilution gas. Several precursors are reported. Their concentration is varying between 10 ppm and few percentage points which means between 10 and  $10^3 \text{ Pa}$ .

As it can be observed, except for a few cases such as the use of high frequency<sup>[52,150]</sup> or of pure precursor-based plasmas,<sup>[151]</sup> the deposition rates are always lower than  $10 \text{ nm}\cdot\text{s}^{-1}$  and closer to  $1 \text{ nm}\cdot\text{s}^{-1}$ . Generally, too much increase in power<sup>[124]</sup> or oxygen addition<sup>[152-154]</sup> led to filamentary, unstable discharges and an increase in powder formation in the gas phase, which then deposits on the coating.

As far as DBDs are concerned, there does not seem to be a clear correlation on the deposition rate obtained with filamentary and homogeneous discharges. However, the discharge regime has a huge influence on the uniformity, density and smoothness of the film as filamentary discharges tends to deposit too much energy locally and enhance gas phase production of powders.<sup>[71,117,122,124]</sup> Therefore, it is necessary to evaluate the influence of each of the process parameters on coating deposition, as changes in one of them can have a significant effect on the resultant quality of the coating.

It is important to highlight the fact that the reading of the scientific literature on AP-PECVD is not easy and does not allow immediate comparison, and the common effort of the scientific community mainly involved in this field should be directed to:

- (i) Avoid some confusing heterogeneities in the nomenclature (e.g. discharge type and regime) which are very often present in the literature of AP cold plasmas;
- (ii) More clearly describe the AP-PECVD reactors that are usually homemade apparatuses (e.g. gas injection system, electrode configuration, power supply, etc.);
- (iii) Report without omissions the most important process parameters and conditions. As evident in tables 3-5, too often, published works do not report crucial process conditions such as the power density and the precursor concentration in the feed mixture, as well as they do not clearly specify the discharge regime.

This could actually favor the scientific debate, enhance the understanding of AP-PECVD processes, and allow establishing a common ground of parameters for choosing reactor configuration and processes conditions for the required thin film properties.

## **V.2. Consequences of substrate displacement**

The consequence of obtaining thickness uniformity over the entire surface by moving the substrate in the discharge is that the coating can be non-uniform along its thickness. Indeed, as already mentioned in section IV.1.1, chemical composition and density of the thin film depends

on the reactive species reaching the surface and these species depends on the gas residence time in the plasma. This is the consequence of (i) the time needed to dissociate the precursor gas and transport the radicals to the surface, (ii) the reactive gas consumption, (iii) the secondary chemistry becoming more and more important for longer residence times, (iv) the time needed to form powders. As an example, **Figure 5a** presents SiH content per thickness unit of a static sample of  $\text{SiN}_x\text{:H}$  as a function of the position in the discharge. The coating has been made in GDBDs fed by  $\text{SiH}_4$  and  $\text{NH}_3$  diluted in Ar, in the configuration presented in figure 2b and results concern one of the two plasma zones. The position 0 mm corresponds to the gas entrance in the plasma zone. The SiH content, evaluated as FTIR absorbance normalized to the thin film thickness, increases from 0 to 5 mm, which is related to the progressive  $\text{SiH}_4$  dissociation and transport to the surface, then there is more or less a plateau and a decrease related to the end of the plasma (10 mm). The consequence of this variation on a moving sample is clearly shown by SIMS results as a function of the sample thickness (Figure 5b). To produce this thin film, the substrate makes five runs back and forth in the plasma zones. SIMS  $\text{Si}_3^-$  ions oscillations as a function of the sample thickness are correlated to these runs. The coating is the same on the whole surface but the chemical composition in thickness is varying. This variation has consequences on the final properties of the layer.

This example has been chosen because it clearly illustrates the possible chemical gradient induced in dynamic mode deposition by the chemistry evolution with the gas residence time. However, the amplitude of this phenomenon depends on the process conditions, like precursor concentration. Figure 5b shows that Si concentration oscillation decreases when  $\text{SiH}_4$  concentration in the plasma increases. For reducing the gradient due to the entrance region of the plasma, a solution could be to reduce the transport time to the surface by modifying the gas flow injection, by replacing neutral radicals by ions choosing a dilution gas having excited state able to ionize the precursor. At least in low frequency excitation, ions have a transport time scale of  $\mu\text{s}$  to be compared to the ms for radicals. Higher power will also reduce the gradient at

the entrance of the plasma but depletion of reactive gas will occur more rapidly and secondary chemistry and powder formation will be enhanced. So gradient on the exhaust side could be larger. Choosing a less reactive precursor or experimental conditions limiting powder formation could reduce this effect.<sup>[174]</sup> Of course, the total gas residence time defined by the gas flow and the electrode length is an important parameter.

Using the configuration of Figure 2a, Premkumar *et al.*<sup>[27]</sup> evidenced similar effects during the deposition of thin films from HMDSO in a GLDBD: for short residence times a smooth SiO<sub>x</sub> film is deposited whereas for long residence time, due to HMDSO depletion in the plasma phase, non-depositing species interact with the polymeric substrate and induce rough deposits with high carbon content. This has strong consequences on the film quality when using web roll conditions: when the web rolls in the same direction than the gas flow injection, a dense smooth inorganic film is obtained.<sup>[27]</sup> When the web moves in the opposite direction, the polymer is first etched and modified in the precursor depletion zone by the non-depositing radicals. The SiO<sub>x</sub> deposition only occurs near precursor injection region and on a surface already pretreated. Result is a very rough film.<sup>[27]</sup> A similar effect has been observed by Maechler *et al.*: using a TDBD in N<sub>2</sub>/HMDSO, the organic behavior of the deposited film increases with respect to the gas residence time.<sup>[170]</sup> This has been turned in a benefit to make a gradient between a polymer substrate and an inorganic SiO<sub>x</sub> layer deposited in a second step, as it is shown in **Figure 6**.

### **V.3. How to choose the discharge regime and the dilution gas**

When working at atmospheric pressure, one should keep in mind that the time scale of the process can be as short as the microdischarge duration (a few ns) and as long as the whole thin film growth time scale (from seconds to minutes). Indeed there are several time scales to consider: that of the discharge (from 10 ns - microdischarge duration in FDBDs, to 100μs -

discharge pulse duration in TDBDs), that between two discharges, that of the chemistry induced by long life time species (a few ms), that of the gas residence time in the discharge zone (10 to 100 ms), and finally the time scale of the whole process. This difference explains why a discharge of low diameter but whose occurrence is randomly distributed in space can produce a homogeneous treatment at a time scale long compare to the discharge repetition rate i.e. why a FDBD can make rather uniform coating.

The first question when defining an AP-PECVD process is: do I need homogeneity over the entire surface better than 10%? As a general rule, it can be stated that getting homogeneous coating with a homogeneous GDBD, TDBD and RFGD is easier than with a FDBD.<sup>[117]</sup> According to the literature, GLDBD regime, intermediate between homogeneous and filamentary discharge is also useful. The second question is: do I need a dense layer which according to AP-PECVD literature means a layer free of powders?

- (i) If the answer to these two first questions concerning homogeneity and density is no, FDBD processing should be at least tried as it is the easiest to set-up. Microdischarges should be randomly distributed and the process time scale should be long compared to the excitation frequency to statistically allow the production of a homogeneous coating. The other consequence of the high energy level and small radius of microdischarges is that the probability of incurring into homogeneous growth, thus into powder formation is larger. Since a lot of radicals are being created at the same place and at the same time by a microdischarge, their probability of reacting in the gas phase is larger compared to that of diffusing to the surface. In that case, large clusters and even powders contribute to film growth, large growth rate are hence reached but the layer density is limited. Substrate displacement surely helps in obtaining more homogeneous coating in the case of FDBDs however problems due to the reduced coatings density and to powder formation cannot be easily solved.

(ii) If the answer is yes, each discharge should cover the entire surface. In this case GDBD and TDBD are solutions easy to set-up but implying restrictive conditions (Table 6) including a limited amount of reactive gases, a dielectric on each electrodes and a careful selection of the excitation frequency and voltage. RFGDs are an efficient solution, since they are not sensitive to the substrate; even discharge localisation related to edge effect disappears. Their drawback is the gas heating and the need of an impedance adaptation between the plasma and the power supply which complicates the set-up and the up-scaling. GLDBD is another solution but the difficulty to reproduce the results indicates that there are restrictive conditions at least concerning the electrical circuit. The recent improvement of nanorepetitive pulsed (NRP) power supply makes NRP discharge achievable even if it is really more complicate to install and manipulate than a low frequency sinusoidal power supply and dielectrics on the electrodes.

The previous considerations highlight the fact that the production of homogeneous and dense layers almost strictly requires the utilization of homogeneous regimes. On the other hand, it is worth mentioning that the huge interest in employing FDBDs in direct thin film deposition resides in:

- (i) the utilization of air as main gas; indeed, a lot of work is done to get homogeneous discharge in air and there are promising results but today conditions are still more restrictive than in nitrogen,<sup>[82,89,172]</sup>
- (ii) the utilization of high reactive gas (i.e. precursor and additives) concentrations, exceeding the threshold value for homogeneous regimes generation;
- (iii) the need of depositing porous rough and even nanostructured coatings. This can be achieved by the simple inclusion of nanoparticles in the growing coating or by the localized material growth induced by the higher local volume energy density of FDBDs.<sup>[46]</sup>

Beside the question on homogeneity and density (having in mind that up to now dense film have not be obtained with FDBDs) other question should be answered to choose the most appropriate discharge regime to make a given thin film on a given substrate:

- (i) The thermal stability of the substrate: the order of the discharge according to ascending temperature is TDBD < GDBD < GLDBD < RFGD. FDBD temperature increases with the power up to values of RFGD. Treatment of thermolabile substrate is possible as far the FDBD power is limited.
- (ii) The substrate electrical conductivity: RFGD is not affected by the substrate conductivity. The other discharges are more localized with conductive substrates than with insulating ones.
- (iii) The chemical composition of the thin film: is it an oxide, a nitride or a film free of O and N? All the gases and then all the discharges are suitable for oxides. N<sub>2</sub> can be the dilution gas for coatings free of N as far as an O-containing gas is added. Neither O nor N in the thin film implies the use of Ar or He as dilution gas and thus only GDBD and GLDBD as homogeneous discharges. For nitride O-containing gas should be avoided but every discharge regimes are available.

Up to now, the choice of the plasma source discharge regime depends on the required thin film quality and the substrate, which complicate the development of direct AP-PECVD. Conversely, according to the literature, GLDBD are convenient whatever the thin film, NRPD have not been explored, the possibilities of RFGD have not been extensively studied and new low frequency DBD power supply opens new avenues to explore.

#### **V.4. How to avoid powder in AP-PECVD**

Layer density is significantly affected by powder inclusion in the thin film. Deposition of coatings formed by agglomerated or even nonadherent nanoparticles can highly limit the employment of AP plasma processes. Powder formation compromises, in fact, the quality of

the deposited layers, while it causes serious practical troubles, such as the apparatus dirtiness, undesirable in continuous processing.

Considering the mechanisms leading to the formation of powders (Section III.4) it can be generally stated that homogeneous regimes are more suitable for the deposition of powder-free coatings rather than filamentary regimes. However significant studies in the literature demonstrate that experimental conditions leads to powder whatever the discharge regime, however it is possible to control and limit dust formation even with filamentary discharge, and hence deposit high quality powder-free coatings. Apart precursor having low reactivity, inventive solutions have been studied at the laboratory scale to avoid powder formation with high radical concentration like pulsed plasma, high flow rate, droplet injection as discussed below:

(i) Modulated power supplies

Starostin *et al.*<sup>[29]</sup> reported the deposition of uniform SiO<sub>2</sub>-like coatings in a GLDBD discharge and demonstrated that the formation of powders can be avoided by using a modulated power supply and adequate gas residence time in the discharge zone. More specifically, it was demonstrated that it is possible to suppress dust formation by using an on-time lower than 1 ms; this value seems to be lower than the gas residence time in the discharge which equals approximately 2 ms. It was argued that, as demonstrated for low pressure plasmas, dust formation is induced by negative ions accumulation or by high radical densities in the atmospheric discharge. In order to prevent the dust formation it is hence necessary to limit the dissociation of the molecules by the plasma, which leads to the formation of dust coagulation centers. Pulsing the power supply is a straightforward way to diminish plasma reactivity by decreasing the average energy transferred to the plasma per unit time.

As reported in a related patent,<sup>[173]</sup> the proposed method is based on the suppression of the formation of dust coagulation centers from the initial phase during the power on-time  $t_{on}$ . It was

found that dust formation can be prevented when the on-time is shorter than the time necessary for forming charged particles in the treatment space e.g. less than 0.5 ms, while the duty cycle can vary from 1 to 50 % and the sum of the on-time and off-time can substantially correspond to the gas residence time in the discharge region, but can also be shorter than it.

In the case of a filamentary DBD, Boscher *et al.*<sup>[107]</sup> demonstrated that the employment of a modulated power supply enhances the film homogeneity also on metallic substrates, allowing the growth of pinhole-free films. In FDBDs, the local higher power density at the filament position induces fast precursor depletion and nucleation of particles; the pulsed excitation mode reduces the powders formation and surface damaging since it improves the statistical distribution of filaments, and hence reduces the memory effects related to local overheating, which contribute to anchoring and reappearing of the filaments, on the substrate hot spots or in gas region preheated by filaments.

#### (ii) Precursor recirculation

In AP plasma reactors for thin film deposition, the presence of gas containing precursor recirculation zones has to be avoided and limited in the discharge zone as well as downstream. Caquineau *et al.*<sup>[125]</sup> reported that gas fluid dynamics influences the discharge stability and the uniformity of the AP-PECVD of thin films. In the case of DBD reactors in which the feed gas is injected uniformly parallel to the substrate (Figure 2a) the obtained layer is always uniform along the substrate length, while when the gas is injected perpendicularly to the substrate, as in Figure 2b, thin film non uniformity can be observed due to the penetration of the gas recirculation into the discharge zone. This recirculation usually takes place just at the right angle defined by the vertical gas channel and the upper dielectric electrode. As reported in **Figure 7**, the higher the flow rate, the larger the recirculation zone and the deeper the recirculation penetrates in the discharge zone.

The layer non-uniformity is related to the penetration of gas recirculation containing precursor into the discharge zone. The recirculation induces an increase in the gas residence time at this location; hence a plausible hypothesis for the layer uniformity dependence on the recirculation is the possible enhancement of powder formation (which requires a typical mean formation time of 5 ms in the experimental conditions of this study) and growth in the recirculation zone. Once created, these powders could possibly be trapped in the recirculation zone; when their particle size is large enough, electrons may attach on the powder, inducing electron depletion at the origin of the discharge instabilities. These instabilities can result in coating non-uniformity but also in powder deposition on the coating. The penetration of recirculation zone in the discharge zone can be reduced both by decreasing the flow rate and by moving away the discharge from the recirculation zone.

In ref.<sup>[85]</sup>, the deposition of silicon nitride coatings was reported with a DBD cell similar to Figure 2b, comparing processes performed in static and in dynamic mode (namely without and with substrate displacement, respectively). Modeling of the gas flow in the reactor showed recirculation areas outside the plasma, downstream of the discharge zone. Aggregates are created in these recirculation zones when they can grow and reach a critical mass. In dynamic mode, as the substrate is moving back and forth in the plasma areas, aggregates formed in the recirculation zones located on both side of the plasma zones are deposited on the growing layer whose surface is reactive. Then, during the following run in the plasma, the aggregates are included in the growing layer. This means that in the case of DBD reactors, for deposition in dynamic mode, the presence of recirculation zones has to be avoided also outside the plasma region.

### (iii) Precursor reactivity and physical state

It is possible to avoid powder formation by a careful selection of the precursor reactivity. The investigation of the PECVD process of silicon oxide thin film properties with SiH<sub>4</sub>- and

HMDSO-containing TDBD<sup>[90]</sup> allowed the observation that the relative contribution of homogeneous and heterogeneous growth mechanisms is very dependent on the nature of the precursor. Because of its high reactivity, SiH<sub>4</sub> induces particles formation in the plasma. These particles are efficiently included in the coating, decreasing drastically the layer density. Thin films made with HMDSO are always dense. Moreover as reported in section III.2, the injection of the liquid precursor in aerosol form can modulate the precursor reactivity in the plasma. It seems in fact that in aerosol-assisted plasma deposition processes, the fragmentation of the precursor molecules is generally limited, with respect to the classical PECVD, and hence powder formation is unlikely to occur.

(iv) Gas residence time and rotary electrodes.

As it was said beforehand, formation of nanoparticles by gas phase reactions (involving the precursor and reactive species formed by precursor fragmentation in the discharge) can be limited by decreasing the concentration and gas residence time of the precursor in the discharge zone. The main gas flow rate determines, in fact, the amount of precursor that goes through the discharge and the mean time that the precursor molecule spends in the discharge cell, i.e., its residence time. In general the increase of the main gas flow rate (at constant precursor concentration) decreases the residence time of the precursor molecule and lower the chance of powder formation.

Mori *et al.*<sup>[52]</sup> found an original solution to decrease the residence time. They deposited homogeneous and high-quality thin films utilizing a rotary cylindrical electrode. In this apparatus the reactive molecules are carried by high-speed viscous flow and homogeneously introduced into the plasma area between the cylindrical electrode and the substrate (gas gap of 0.5 mm) by rotating the electrode at a maximum rotation speed of 5000 rpm; the nanoparticles generated in the plasma are easily removed from the plasma area along with the high speed flow.

## V.5. How to increase the growth rate

Higher is the growth rate, lower is the cost of the thin film deposition process. For a given precursor and substrate, the growth rate mainly depends on the precursor concentration, the energy per precursor molecule and the transport of the reactive species to the surface. Here are listed possible solutions for increasing the growth rate in AP-PECVD processes:

### (i) Precursor concentration

The precursor concentration is limited by powders formation or by the discharge regime stability. In the first case, smoother is the energy injection in the gas larger is the threshold concentration. If radicals can react with the initial precursor like  $\text{SiH}_4$ , the quantity of precursor is really limited (e.g. 2 ppm in  $\text{SiH}_4/\text{N}_2\text{O}/\text{N}_2$ ). Decreasing the precursor reactivity is a solution to shift the threshold to higher values. In case of limitation related to the discharge stability, lower is the ability of precursor to quench the dilution gas metastable higher is the threshold. For example, in  $\text{N}_2$  TDBD, the concentration of  $\text{NH}_3$  is limited to 20 ppm while in an Ar GDBD concentrations higher than 300 ppm are acceptable.

Other possibilities to be considered are the increase of the precursor size, replacing gases by vapour, droplet or powders. Larger is the size of the species interacting with the surface higher is the growth rate. However, large molecules slowly diffuse which reduce their transport to the surface.

### (ii) Transport of the reactive species to the surface

The reactive transport to the surface can also be the limiting step. Radical transport is controlled by convection and diffusion. As discussed previously, diffusion is limited and all the solutions to increase the convection to the surface or to modify the ratio of diffusion other convection are interesting avenues. Among them, there is the double injections configuration (**Figure 8**). This solution<sup>[118,174]</sup> consists in coupling two layers of gases, the first containing the reactive gases,

the latter being free of them, and being used to press the first layer close to the surface where the sample is located. Figure 8 shows the calculated profile of mass fraction of HMDSO precursor in a double injection system in which the first layer of gas contains HMDSO and N<sub>2</sub>O in N<sub>2</sub> as dilution gas, while the second one contains only N<sub>2</sub>; the HMDSO profile is higher close to the surface where the substrate is located. **Figure 8** evidences the increase of the experimental growth rate by moving from a simple single injection to a double injection.

The cylindrical electrode<sup>[53]</sup> is also interesting as the high speed of the surface modifies the gas velocity profile in the gas gap decreasing the value close to the substrate changing the ratio between convection and diffusion.

Another way to get rid of this limitation due to the intrinsic low diffusion at atmospheric pressure is to tune the process in order to have a strong contribution of ions to the coating growth. As an example, Foest *et al.* have shown that in a He-HMDSO discharge, the mass transport by precursor ions could be important for film formation, these ions being created either by direct electron impact (higher cross section of HMDSO compared to He, and lower ionization threshold) or more probably through Penning ionization.<sup>[31]</sup> This mechanism is easier to get in He because He<sup>m</sup> is able to ionise all the other gases. In other gases, the precursors have to be carefully chosen to be ionised by the metastable states.

The plasma length is also important. In an on-line PECVD the coating duration is determined by substrate velocity and the plasma length. Longer is the plasma; longer is this duration, as far as there is still precursor or no serious powder formation. So the plasma length should be as long as possible taken into account the variation of the layer chemistry with the variation of the of gas chemistry. Of course several gas injection and electrodes can be installed to improve the treatment time but this has a cost.

(iii) Power

Increasing the discharge power can result in microdischarges, which are strongly non-uniform and in some cases are not suitable for the deposition of smooth thin film, because the microdischarges can locally heat and damage the forming film, especially for soft materials such as polymers or conductive materials like silicon. This requires an understanding of the electrical behavior of the whole system, not only considering the discharge but also the power supply, the electrical circuit and the electrodes (with substrate and dielectrics in case of a DBD). For homogeneous discharges, the origin of the power limitation is different between TDBD and GDBD (or GLDBD). For TDBD, the discharge power is limited due to limitations of the slope of the voltage versus time and the maximal discharge current.<sup>[35]</sup> Thus, in the case of sinusoidal excitation, the amplitude and frequency of the applied voltage that allows a TDBD discharge regime are limited. A solution to increase the discharge power is to limit the current and increase the discharge duration. This could be realized using a square-wave current inverter source.<sup>[132]</sup> **Figure 9** presents a comparison between experimental waveforms for a sinusoidal voltage source and a simulation of a square-wave current inverter source for the same discharge current amplitude. The simulation is realized with PSpice software using a macroscopic electrical model of the discharge.<sup>[35]</sup> In this case, this increases the duration of the discharge ignition from 64 to 90% and the power from 1.6 to 3.8 W·cm<sup>-2</sup>.

For GDBD (or GLDBD), the problematic is different. Power increases proportionally to the excitation frequency up to point where the electrons are trapped in the gas gap and the radiofrequency regime is reached. The upper frequency limit (around 1 MHz) is not due to a transition in filamentary regime but to a transition in RFGD regime, which is homogeneous too. For a GDBD or RFGD, increasing the frequency does increase the plasma density, which can lead to an increase deposition rate but also an increase of the gas temperature. The RFGD is also limited in power, if it increase too much,  $\gamma$  mode (large contribution of electron secondary emission from the cathode) is reached and the discharge becomes instable.

However, there are some heating concerns;<sup>[52,111,175]</sup> the electrodes temperature can increase by several hundred Kelvin degrees. Thus, a cooling system may be required for coating on thermal sensitive substrates.

In addition of using an RF power supply, Baars-Hibbe *et al.*, applied a bias of 500-1300 V<sub>pk-pk</sub> (9.5 kHz) to accelerate the charges particles to the substrate. They observed that the plasma volume is extended by the bias potential towards the substrate.<sup>[167]</sup>

## **VI Conclusion**

A state of the art of the different plasmas, reactors and processes solutions to get uniform dense coating by direct AP-PECVD has been presented. Five different discharge modes have been identified: FDBD, TDBD, GDBD, GLDBD and RFGD. At a glance, the most suitable one for a PECVD application depends on the required density of the thin film (FDBD acceptable or not), on the maximum thin film cost, mainly determined by the dilution gas (nitrogen or air TDBD, GLDBD or noble gases GDBD, RFGD), on the substrate conductivity (RFGD preferable or not) and thermolability (FDBD, RFGD acceptable or not). The other criterion to have in mind is that the discharge mode and the dilution gas not only influence the physics of the discharge but also its chemistry. Dilution gas acts as a reactive or a catalyst.

Whatever the discharge mode, the second key point when designing a plasma reactor is the gas flow injection which should be carefully considered to enhance the thin film growth rate and homogeneity. Consequences of substrate displacement (the solution to coat large surface) have also to be taken into account.

If solutions to get homogeneous dense coating free of powder have been found, growth rate is still a lock to lift; the ideal reactor configuration is still not clear. The ease of implementation of the reactors has led to the development of a very rich panel of homemade reactors and it is difficult to compare them to derive the ideal one. Thus, it would be really fruitful if in scientific

publications each of us systematically makes an effort of giving more information such as: discharge regime, power/cm<sup>3</sup> and /cm<sup>2</sup>, gas residence time, thin film precursor concentration, thin film homogeneity, powder free or not and detail information concerning injection gas, electrode configuration, power supply and which set-up and process parameters influence the thin film quality or growth rate.

This complexity limits up to now the industrial development of AP-PECVD. Work is still in progress to find a universal solution; GLDBD appears like a promising option, NRPD (nano repetitive pulsed discharge), which begins to be studied for AP-PECVD, is another perspective. Radio frequency homogeneous discharges also open new possibilities mainly for conductive and not thermolabile substrates. Moreover, the replacement of industrial processes by AP-PECVD will occurs when this method will bring a unique feature. Today, research efforts are directed in that way. AP operation are not only suitable for in-line process but also for introducing liquid droplets, nanopowders, living matters in the plasma opening new fields to PECVD applications.

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[1] J. P. Borra, *J. Phys. D: Appl. Phys.* **2006**, *39*, R19.

[2] D. Vangeneugden, S. Paulussen, O. Goossens, R. Rego, K. Rose, *Chem. Vap. Deposition* **2005**, *11*, 491.

- [3] L. O'Neill, L. A. O'Hare, S. R. Leadley, A. J. Goodwin, *Chem. Vap. Deposition* **2005**, *11*, 477.
- [4] L. J. Ward, W. C. E. Schofield, J. P. S. Badyal, A. J. Goodwin, P. J. Merlin, *Langmuir* **2003**, *19*, 2110.
- [5] D. Mariotti, R. M. Sankaran, *J. Phys. D: Appl. Phys.* **2010**, *43*, 323001.
- [6] T. Belmonte, G. Arnoult, G. Henrion, T. Gries, *J. Phys. D: Appl. Phys.* **2011**, *44*, 363001.
- [7] M. G. Kong, G. Kroesen, G. Morfill, T. Nosenko, T. Shimizu, J. van Dijk, J. L. Zimmermann, *New Journal of Physics* **2009**, *11*, 115012.
- [8] E. Stoffels, Y. Sakiyama, D. B. Graves, *IEEE Trans. Plasma Sci.* **2008**, *36*, 1441.
- [9] M. Laroussi, T. Akan, *Plasma Process. Polym.* **2007**, *4*, 777.
- [10] A. Schutze, J. Y. Jeong, S. E. Babayan, J. Park, G. S. Selwyn, R. F. Hicks, *IEEE Trans. Plasma Sci.* **1998**, *26*, 1685.
- [11] T. Belmonte, G. Henrion, T. Gries, *J. Thermal Spray Technol.* **2011**, *20*, 744.
- [12] A. Villermet, P. Cocolios, G. Rames-Langlade, F. Coeuret, J. L. Gelot, E. Prinz, F. Förster, *Surf. Coat. Technol.* **2003**, *174*, 899.
- [13] J. R. Roth, *Industrial Plasma Engineering, Volume 2 - Applications to nonthermal Plasma Processing*, IOP publishing, Philadelphia, PA, USA, **2001**.
- [14] U. Kogelschatz, *Plasma Chem. Plasma Process.* **2003**, *23*, 1.
- [15] S. E. Alexandrov, M. L. Hitchman, *Chem. Vap. Deposition* **2005**, *11*, 491.
- [16] A. Fridman, A. Chirokov, A. Gutsol, *J. Phys. D: Appl. Phys.* **2005**, *38*, R1.
- [17] C. Tendero, C. Tixier, P. Tristant, J. Desmaison, P. Leprince, *Spectrochimica Acta Part B* **2006**, *61*, 2.
- [18] R. Foest, M. Schmidt, K. Becker, *Internat. J. Mass Spectrometry* **2006**, *248*, 87.
- [19] F. Fanelli, *Surf. Coat. Technol.* **2010**, *205*, 1536.
- [20] D. Merche, N. Vandencastele, F. Reniers, *Thin Solid Films* **2012**, DOI: 10.1016/j.tsf.2012.01.026

- [21] F. Massines, N. Gherardi, N. Naudé, P. Ségur, *Eur. Phys. J. Appl. Phys.* **2009**, *47*, 22805.
- [22] G. Cicala, M. Creatore, P. Favia, R. Lamendola, R. d'Agostino, *Appl. Phys. Lett.* **1999**, *75*, 37.
- [23] A. Bousquet, V. Bursikova, A. Goulet, A. Djouadi, L. Zajickova, A. Granier, *Surf. Coat. Technol.* **2006**, *200*, 6517.
- [24] H. E. Wagner, R. Brandenburg, K. V. Kozlov, A. Sonnenfeld, P. Michel, J. F. Behnke, *Vacuum* **2003**, *71*, 417.
- [25] E. Aldea, J. Bastiaan, M. C. M. van de Sanden, H. de Vries, *US 2007210721*, **2007**.
- [26] E. Aldea, P. Peeters, H. de Vries, M.C.M van de Sanden , *Surf. Coat. Technol.* **2005**, *200*, 46.
- [27] P. A. Premkumar, S. A. Starostin, H. de Vries, R. M. J. Paffen, M. Creatore, T. J. Eijkemans, P. M. Koenraad, M. C. M. van de Sanden, *Plasma Process. Polym.* **2009**, *6*, 693.
- [28] P. A. Premkumar, S. A. Starostin, M. Creatore, H. de Vries, R. M. J. Paffen, P. M. Koenraad, M. C. M. van de Sanden, *Plasma Process. Polym.* **2010**, *7*, 635.
- [29] S. A. Starostin, P. A. Premkumar, M. Creatore, E. M. van Veldhuizen, H. de Vries, R. M. J. Paffen, M. C. M. van de Sanden, *Plasma Sources Sci. Technol.* **2009**, *18*, 045021.
- [30] F. Massines, A. Rabehi, Ph. Decomps, R. Ben Gadri, P. Ségur, C. Mayoux, *J. Appl. Phys.* **1998**, *83*, 2950.
- [31] R. Foest, F. Adler, F. Sigeneger, M. Schmidt, *Surf. Coat. Technol.* **2003**, *163–164*, 323.
- [32] F. Massines, N. Gherardi, N. Naudé, P. Ségur, *Plasma Phys. Controlled Fusion* **2005**, *47*, B577.
- [33] F. Massines, P. Ségur, N. Gherardi, C. Khamphan, A. Ricard, *Surf. Coat. Technol.* **2003**, *174–175*, 8.
- [34] N. Gherardi, G. Gouda, E. Gat, A. Ricard, F Massines, *Plasma Sources Sci. Technol.* **2000**, *9*, 340.

- [35] N. Naudé, J. P. Cambronner, N. Gherardi, F. Massines, *J. Phys. D: Appl. Phys.* **2005**, *38*, 530.
- [36] R. H. Stark, K. H. Schoenbach, *J. Appl. Phys.* **2001**, *89*, 3568.
- [37] S. O. Macheret, M. N. Shneider, R. B. Miles, *IEEE Trans. Plasma Sci.* **2002**, *30*, 1301.
- [38] H. Ayan, G. Fridman, A. F. Gutsol, V. N. Vasilets, A. Fridman, G. Friedman, *IEEE Trans. Plasma Sci.* **2008**, *36*, 504.
- [39] I. Topala, M. Asandulesa, D. Spridon, N. Dumitrascu, *IEEE Trans. Plasma Sci.* **2009**, *37*, 6.
- [40] Y. Suzuki, S. Ejima, T. Shikama, S. Azuma, O. Tanaka, T. Kajitani, H. Koinuma, *Thin Solid Films* **2006**, *506–507*, 155.
- [41] D. Z. Pai, D. A. Lacoste, C. O. Laux, *J. Appl. Phys.* **2010**, *107*, 093303.
- [42] F. Tholin, D. L. Rusterholtz, D. A. Lacoste, D. Z. Pai, S. Celestin, J. Jarrige, G. D. Stancu, A. Bourdon, C. O. Laux, *IEEE Trans. Plasma Sci.* **2011**, *39*, 11.
- [43] K. G. Donohoe, T. Wydeven, *J. Appl. Polymer Sci.* **1979**, *23*, 2591.
- [44] U. Reitz, J. G. H. Salge, R. Schwarz, *Surf. Coat. Technol.* **1993**, *59*, 144.
- [45] S. P. Bugaev, A. D. Korotaev, K. V. Oskomov, N. S. Sochugov, *Surf. Coat. Technol.* **1997**, *96*, 123.
- [46] V. Rohani, G. Bauville, B. Lacour, V. Puech, F. D. Duminica, E. Silberberg, *Surf. Coat. Technol.* **2008**, *203*, 862.
- [47] X. W. Zhang, G. R. Han, *Thin Solid Films* **2008**, *516*, 6140.
- [48] X. Yuan, L. L. Raja, *IEEE Trans. Plasma Sci.* **2003**, *31*, 495.
- [49] J. J. Shi, M. G. Kong, *J. Appl. Phys.* **2005**, *97*, 023306.
- [50] J. Park, I. Henins, H. W. Hermann, G. S. Selwyn, R. F. Hicks, *J. Appl. Phys.* **2001**, *89*, 20.
- [51] J. J. Shi, M. G. Kong, *Appl. Phys. Lett.* **2007**, *90*, 111502.
- [52] Y. Mori, K. Yoshii, H. Kakuichi, K. Yasutake, *Rev. Sci. Instrum.* **2000**, *71*, 3173.

- [53] H. Kakiuchi, H. Ohmi, K. Nakamura, Y. Yamaguchi, K. Yasutake, *Plasma Chem. Plasma Process.* **2010**, *30*, 579.
- [54] A. Fateev, F. Leipold, Y. Kusano, B. Stenum, E. Tsakadze, H. Bindslev, *Plasma Process. Polym.* **2005**, *2*, 193.
- [55] A. Sarani, A. Yu. Nikiforov, C. Leys, *Phys. Plasmas* **2010**, *17*, 063504.
- [56] G. Uchida, S. Uchida, H. Kajiyama, T. Shinoda, *J. Appl. Phys.* **2010**, *107*, 023305.
- [57] M. A. Lieberman, A. J. Lichtenberg, *Principles of Plasma Discharges and Materials Processing*, Wiley, Hoboken, NJ, USA, **2005**.
- [58] Yu B. Golubovskii, V. A. Maiorov, J. Behnke, J. F. Behnke, *J. Phys. D: Appl. Phys.* **2002**, *35*, 751.
- [59] R. Brandenburg, V. A. Maiorov, Yu B. Golubovskii, H. E. Wagner, J. Behnke, J. F. Behnke, *J. Phys. D: Appl. Phys.* **2005**, *38*, 2187.
- [60] P. C. Hill, P. R. Herman, *Phys. Rev. A*, **1993**, *47*, 4837.
- [61] A. Bogaerts, R. Gijbels, *Phys. Rev. A*, **1995**, *52*, 3743.
- [62] S. K. Lam, C. E. Zheng, D. Lo, A. Demyanov, A. P. Napartovich, *J. Phys. D: Appl. Phys.* **2000**, *33*, 242.
- [63] H. Furuya, S. Kambara, K. Nishidate, S. Fujimaki, Y. Hashimoto, S. Suzuki, T. Iwama, K. Hiraoka, *J. Mass Spectrom. Soc. Jpn.* **2010**, *58*, 211.
- [64] M. Laroussi, M. C. Gupta, A. El Dakrouy, J. Yan, K. H. Becker, K. Martus, in *Proc. 29th Int. Conf. on Plasma Science (ICOPS)*, 2002. DOI: 10.1109/PLASMA.2002.1030419
- [65] H. Barankova, L. Bardos, in *Handbook of Deposition Technologies for Films and Coatings*, Third Edition Science Application and Technology, edited by Peter M. Martin (Elsevier, William Andrew, Oxford, December **2009**), Ch. 17. IBSN: 978-0-8155-2031-3.
- [66] L. Bardos, H. Barankova, *Vacuum* **2009**, *83*, 522.
- [67] F. Fanelli, R. d'Agostino, F. Fracassi, *Plasma Process. Polym.* **2007**, *4*, 797.

- [68] B. Twomey, A. Nindrayog, K. Niemi, W. G. Graham, D. P. Dowling, *Plasma Chem. Plasma Process.* **2011**, *31*, 139.
- [69] S. Kyung, Y. Lee, C. Kim, J. Lee, G. Yeom, *Thin Solid Films* **2006**, *506*, 268.
- [70] T. Nozaki, T. Goto, K. Okazaki, K. Ohnishi, L. Mangolini, J. Heberlein, U. Kortshagen, *J. Appl. Phys.* **2006**, *99*, 024310.
- [71] R. Thyen, A. Weber, C. P. Klages, *Surf. Coat. Technol.* **1997**, *97*, 426.
- [72] Et-T. Es-Sebbar, C. Sarra-Bournet, N. Naudé, F. Massines, N. Gherardi, *J. Appl. Phys.* **2009**, *106*, 073302.
- [72] F. Massines, R. Messaoudi, C. Mayoux, *Plasmas Polym.* **1998**, *3*, 43.
- [74] P. C. Jain, *J. Phys. D: Appl. Phys.* **1980**, *13*, 25.
- [75] O. Motret, C. Hibert, S. Pellerin, J. M. Pouvesle, *J. Phys. D: Appl. Phys.* **2000**, *33*, 1493.
- [76] N. K. Bibinov, A. A. Fateev, K. Wiesemann, *J. Phys. D: Appl. Phys.* **2001**, *34*, 1819.
- [77] P. Bruggeman, D. C. Schram, M. G. Kong, C. Leys, *Plasma Process. Polym.* **2009**, *6*, 751.
- [78] S. Hofmann, A. F. H. van Gessel, T. Verreycken, P. Bruggeman, *Plasma Sources Sci. Technol.* **2011**, *20*, 065010.
- [79] V. Borg Dezani, J. L. Ginoux, *Phys. Plasmas* **1994**, *1*, 1060.
- [80] Yu. P. Raizer, in *Gas Discharge Physics*, Springer-Verlag, Berlin, Germany, **1991**.
- [81] S. Sarghini, S. Paulussen, H. Terry, *Plasma Process. Polym.* **2011**, *8*, 59.
- [82] S. A. Starostin, P. A. Premkumar, M. Creatore, H. de Vries, R. M. J. Paffen, M. C. M. van de Sanden, *Appl. Phys. Lett.* **2010**, *96*, 061502.
- [83] F. Fanelli, F. Fracassi, R. d'Agostino, *Plasma Process. Polym.* **2005**, *2*, 688.
- [84] P. Lecouvreux, J. Larrieu, N. Naudé, S. Quoizola, S. Pouliquen, C. Picard, E. Bêche, N. Bererd, N. Gherardi, R. Monna, M. Pirot, D. Jahan, A. Cuevas, F. Massines, in *Proc. 23rd EU PVSEC*, Valencia, Spain, Sept. **2008**.
- [85] S. Quoizola, P. Lecouvreux, S. Pouliquen, D. Bruyère, H. Glenat, R. Bazinette, F. Massines, in *Proc. 25th EU PVSEC*, Valencia, Spain, Sept. **2010**.

- [86] S. Okazaki, M. Kogoma, M. Uehara, Y. Kimura, *J. Phys. D: Appl. Phys.* **1993**, *26*, 889.
- [87] N. Naudé, F. Massines, *IEEE Trans. Plasma Sci.* **2008**, *36*, 1322.
- [88] R. Brandenburg, Z. Navratil, J. Jansky, P. Stahel, D. Trunec, H. E. Wagner, *J. Phys. D: Appl. Phys.* **2009**, *42*, 085208.
- [89] N. Naudé, S. Okazaki, N. Gherardi and F. Massines, in *Proc. 18<sup>th</sup> International Symposium on Plasma Chemistry*, **2007**.
- [90] F. Massines, N. Gherardi, A. Fornelli, S. Martin, *Surf. Coat. Technol.* **2005**, *200*, 1855.
- [91] I. Enache, H. Caquineau, N. Gherardi, T. Paulmier, L. Maechler, F. Massines, *Plasma Process. Polym.* **2007**, *4*, 806.
- [92] J. P. Cambronne, N. Gherardi, F. Massines, *Eur. Phys. J. Appl. Phys.* **2005**, *29*, 173.
- [93] I. Savin de Larclause, Th. Paulmier, I. Enache, H. Caquineau, P. Raynaud, F. Massines, N. Gherardi, *IEEE Trans. Plasma Sci.* **2009**, *37*, 970.
- [94] P. L. Girard-Lauriault, F. Mwale, M. Iordanova, C. Demers, P. Desjardins, M. R. Wertheimer, *Plasma Process. Polym.* **2005**, *2*, 263.
- [95] L. J. Ward, W. C. E. Schofield, J. P. S. Badyal, *Chem. Mater.* **2003**, *15*, 1466.
- [96] P. A. Herbert, L. O'Neill, J. Jaroszynska-Wolinska, *Chem Mater.* **2009**, *21*, 4401.
- [97] P. A. Herbert, L. O'Neill, J. Jaroszynska-Wolinska, C. P. Stallard, A. Ramamoorthy, D. P. Dowling, *Plasma Process. Polym.* **2011**, *8*, 230.
- [98] L. O'Neill, P. A. Herbert, C. Stallard, D. P. Dowling, *Plasma Process. Polym.* **2010**, *7*, 43.
- [99] A. J. Beck, R. D. Short, A. Matthews, *Surf. Coat. Technol.* **2008**, *203*, 822.
- [100] B. Twomey, M. Rahman, G. Byrne, A. Hynes, L.-A. O'Hare, L. O'Neill, D. Dowling, *Plasma Process. Polym.* **2008**, *5*, 737.
- [101] P. Heyse, A. Van Hoeck, M. B. J. Roeffaers, J. P. Raffin, A. Steinbuchel, T. Stoveken, J. Lammertyn, P. Verboven, P. A. Jacobs, J. Hofkens, S. Paulussen, B. F. Sels, *Plasma Process. Polym.* **2011**, *8*, 965.
- [102] J. Tynan, P. Ward, G. Byrne, D. P. Dowling, *Plasma Process. Polym.* **2009**, *6*, S51.

- [103] J. Bardon, J. Bour, D. Del Frari, C. Arnoult, D. Ruch, *Plasma Process. Polym.* **2009**, *6*, S655.
- [104] M. Tatoulian, F. Arefi-Khonsari, J.-P. Borra, *Plasma Process. Polym.* **2007**, *4*, 360.
- [105] B. Nisol, C. Poleunis, P. Bertrand, F. Reniers, *Plasma Process. Polym.* **2010**, *7*, 715.
- [106] F. Fanelli, S. Lovascio, R. d'Agostino, F. Arefi-Khonsari, F. Fracassi, *Plasma Process. Polym.* **2010**, *7*, 535.
- [107] N. D. Boscher, P. Choquet, D. Duday, S. Verdier, *Plasma Process. Polym.* **2010**, *7*, 163.
- [108] Y. Sawada, S. Ogawa, M. Kogoma, *J. Phys. D: Appl. Phys.* **1995**, *28*, 1661.
- [109] K. Schmidt-Szalowski, Z. Rzanek-Boroch, J. Sentek, Z. Rymuza, Z. Kusznierevich, M. Misiak, *Plasmas Polym.* **2000**, *5*, 173.
- [110] A. Sonnenfeld, T. M. Tun, L. Zajickova, K. V. Kozlov, H. E. Wagner, J. F. Behnke, R. Hippler, *Plasmas Polym.* **2001**, *6*, 237.
- [111] X. Xu, L. Li, S. Wang, L. Zhao, T. Ye, *Plasma Sources Sci. Technol.* **2007**, *16*, 372.
- [112] R. Reuter, D. Ellerweg, A. von Keudell, J. Benedikt, *Appl. Phys. Lett.* **2011**, *98*, 111502.
- [113] R. Reuter, K. Rugner, D. Ellerweg, T. de los Arcos, A. von Keudell, J. Benedikt, *Plasma Process. Polym.* **2012**, *9*, DOI: 10.1002/ppap.201100146
- [114] I. P. Vinogradov, K. Wieseemann, *Plasma Sources Sci. Technol.* **1997**, *6*, 307.
- [115] K. G. Donohoe, T. Wydeven, *J. Appl. Polym. Sci.* **1979**, *23*, 2591.
- [116] K. K. Mishra, R. K. Khardekar, Rashmi Singh, H. C. Pant, *Rev. Sci. Instrum.* **2002**, *73*, 3251.
- [117] D. Trunec, Z. Navratil, P. Stahel, L. Zajickova, V. Bursikova, J. Cech, *J. Phys. D: Appl. Phys.* **2004**, *37*, 2112.
- [118] V. Hopfe, D. W. Sheel, *IEEE Trans. Plasma Sci.* **2007**, *35*, 204.
- [119] S. Martin, F. Massines, N. Gherardi, C. Jimenez, *Surf. Coat. Technol.* **2004**, *177-178*, 693.
- [120] J. P. Boeuf, C. Punset, in *Dusty Plasmas*, A. Bouchoule, ed., Wiley, New York, **1999**.

- [121] N. Jidenko, C. Jimenez, F. Massines, J. P. Borra, *J. Phys. D: Appl. Phys.* **2008**, *40*, 4155.
- [122] T. Nozaki, Y. Kimura, K. Okazaki, *J. Phys. D: Appl. Phys.* **2002**, *35*, 2779.
- [123] N. De Geyter, R. Morent, S. Van Vlierberghe, M. Frère-Trentesaux, P. Dubruel, E. Payen, *Prog. Org. Coat.* **2011**, *70*, 293.
- [124] T. Yokoyama, M. Kogoma, S. Kanazawa, T. Moriwaki, S. Okazaki, *J. Phys. D: Appl. Phys.* **1990**, *23*, 374.
- [125] H. Caquineau, I. Enache, N. Gherardi, N. Naudé, F. Massines, *J. Phys. D: Appl. Phys.* **2009**, *42*, 125201.
- [126] S. Okazaki, M. Kogoma, M. Uehara, Y. Kimura, *J. Phys. D: Appl. Phys.* **1993**, *26*, 889.
- [127] A. Larsson, *J. Phys. D: Appl. Phys.* **1998**, *31*, 1100.
- [128] F. Massines, A. Rabehi, P. Decomps, R. B. Gadri, P. Segur, C. Mayoux, *J. Appl. Phys.* **1998**, *83*, 2950.
- [129] R. Diez, H. Piquet, M. Cousineau, S. Bhosle, *IEEE Trans. Indus. Electron.* **2012**, *59*, 1912.
- [130] H. Piquet, S. Bhosle, R. Diez, M.V. Erofeev, *IEEE Trans. Plasma Sci.* **2010**, *38*, 2531.
- [131] M. Cousineau, R. Diez, H. Piquet, O. Durrieu, *IEEE Trans. Indus. Electron.* **2012**, *59*, 1920.
- [132] S. Vongphouthone, H. Piquet, H. Foch, *Eur. Phys. J. Appl. Phys.* **2001**, *15*, 123.
- [133] L. Bardos, H. Barankova, *J. Vac. Sci. Technol. A* **2005**, *23*, 933.
- [134] I. Topala, M. Asandulesa, D. Spridon, N. Dumitrascu, *IEEE Trans. Plasma Sci.* **2009**, *37*, 6.
- [135] L. Mangolini, C. Anderson, J. Heberlein, U. Kortshagen, *J. Phys. D: Appl. Phys.* **2004**, *37*, 1021.
- [136] K. H. Liu, F. C. Lee, *IEEE Internat. Telecommunications Energy Conference*, VPEC Seminar proceedings, **1984**, 344.

- [137] O. Koudriavtsev, W. Shengpei, M. Nakaoka, in *Proc. IEEE Industry Applications Conference* **2000**, 1, 581.
- [138] M. Littlefair, J. Richardson, R.T. Rakowski, in *Proc. 8<sup>th</sup> International Conference on Power Electronics and Variable Speed Drives* **2000**, 63.
- [139] P. Yan, J. Wang, Y. Sun, G. Sun, in *Proc. 31<sup>st</sup> IEEE International Conference on Plasma Science (ICOPS)*, **2004**.
- [140] H. Yushui, W. Liqiao, X. Yu, Z. Zhongchao, in *Proc. IEEE Applied Power Electronics Conference and Exposition (APEC '04)* **2004**, 1642-1646.
- [141] J. O. Pacheco-Soltelo, R. Valdivia Barrientos, M. Pacheco-Pacheco, J. F. Ramos Flores, M. A. Duran Garcia, J. S. Benitez-Read, R. Pena-Eguiluz, R. Lopez-Callejas, *IEEE Trans. Plasma Sci.*, **2004**, 32, 2105.
- [142] R. Bazinette, R. Subileau, J. Vallade, J. Paillol, S. Pouliquen, F. Massines, in *Proc. 20<sup>th</sup> International Symposium on Plasma Chemistry*, **2011**.
- [143] P. Chabert, N. Braithwaite, *Physics of Radiofrequency Plasmas*, Cambridge University Press, **2011**.
- [144] J. E. Harry, *Introduction to Plasma Technology*, Wiley-Ch Verlag GmbH & Co. KGaA, Weinheim, **2010**.
- [145] L. Bardos, H. Baránková, *Thin Solid Films* **2010**, 518, 6705.
- [146] M. M. Kekez, M. R. Barrault, J. D. Craggs, *J. Phys. D: Appl. Phys.* **1970**, 3, 1886.
- [147] D. Trunec, A. Brablec, F. Stantsy, *Contrib. Plasma Phys.* **1998**, 38, 435.
- [148] F. Fanelli, R. d'Agostino, F. Fracassi, *Plasma Process. Polym.* **2011**, 8, 557.
- [149] F. Massines, P. Ségur, in *Proc. APP spring meeting*, Bad Honnef, Germany, February, **2001**.
- [150] H. Schlemm, D. Roth, *Surf. Coat. Technol.* **2001**, 142, 272.
- [151] H. Kodama, A. Shirakura, A. Hotta, T. Suzuki, *Surf. Coat. Technol.* **2006**, 201, 913.
- [152] Y. Sawada, S. Ogawa, M. Kogoma, *J. Phys. D: Appl. Phys.* **1995**, 28, 1661.

- [153] C. P. Klages, K. Höpfner, N. Kläke, R. Thyen, *Plasmas Polym.* **2000**, *5*, 79.
- [154] A. Sonnenfeld, T. M. Tun, L. Zajickova, K. V. Kozlov, H.-E. Wagner, J. F. Behnke, R. Hippler, *Plasmas Polym.* **2001**, *6*, 237.
- [155] O. Goossens, E. Dekempeneer, D. Vangeneugden, R. van de Leest, C. Leys, *Surf. Coat. Technol.* **2001**, *142*, 474.
- [156] K. K. Mishra, R. K. Khardekar, R. Singh, H. C. Pant, *Rev. Sci. Instrum.* **2002**, *73*, 3251.
- [157] R. Morent, N. De geyter, S. Van Vlierberghe, E. Vanderleyden, P. Dubruel, C. Leys, E. Schacht, *Plasma Chem. Plasma Process.* **2009**, *29*, 103.
- [158] I. Topala, M. Asandulesa, D. Spridon, N. Dumitrascu, *IEEE Trans. Plasma Sci.* **2009**, *37*, 946.
- [159] R. Morent, N. de Geyter, S. van Vlierberghe, P. Dubruel, C. Leys, L. Gengembre, E. Schacht, E. Payen, *Progress in Organic Coatings*, **2009**, *64*, 304.
- [160] R. Morent, N. De Geyter, T. Jacobs, S. Van Vlierberghe, P. Dubruel, C. Leys, E. Schacht, *Plasma Process. Polym.* **2009**, *6*, S537.
- [161] J. L. Hodgkinson, D. W. Sheel, H. M. Yates, M. E. Pemble, *Plasma Process. Polym.* **2006**, *3*, 597.
- [162] A. M. Zhu, L. H. Nie, Q. H. Wu, X. L. Zhang, X. F. Yang, Y. Xu, C. Shi, *Chem. Vap. Deposition* **2007**, *13*, 141.
- [163] C. Sarra-Bournet, N. Gherardi, S. Turgeon, G. Laroche, F. Massines, *Eur. Phys. J. Appl. Phys.* **2009**, *47*, 22820.
- [164] D. Merche, J. Hubert, C. Poleunis, S. Yunus, P. Bertrandt, P. De Keyzer, R. Reniers, *Plasma Process. Polym.* **2010**, *7*, 836.
- [165] I. P. Vinogradov, A. Dinkelmann, A. Lunk, *Surf. Coat. Technol.* **2003**, *174*, 509.
- [166] E. Gil, J. B. Park, J. S. Oh, G. Y. Yeom, *Thin Solid Films* **2010**, *518*, 6403.
- [167] L. Baars-Hibbe, P. Sichler, C. Schrader, C. Geßner, K. H. Gericke, S. Büttgenbach, *Surf. Coat. Technol.* **2003**, *174*, 519.

- [168] K. Tanaka, M. Kogoma, *Plasmas Polym.* **2003**, *8*, 199.
- [169] J. H. Lee., T. T. T. Pham, Y. S. Kim, J. T. Lim, S. J. Kyung, G. Y. Yeom, *J. Electrochem. Soc.* **2008**, *155*, D163
- [170] L. Maechler, C. Cioarec, I. Enache, N. Naudé, H. Caquineau, F. Massines, N. Gherardi, in *54th Annual Technical Conference Proceedings*, Chicago, IL, USA, April, **2011**. ISSN 0737-5921
- [171] L. Maechler, C. Sarra-Bournet, P. Chevallier, N. Gherardi, G. Laroche, *Plasma Chem. Plasma Process.* **2011**, *31*, 175.
- [172] N. Osawa, Y. Yoshioka, *IEEE Trans. Plasma Sci.* **2012**, *40*, 2.
- [173] H. W. De Vries, E. Aldea, S. Starostin, S. Alexandrovich, M. Creatore, M. C. M. van de Sanden, WO 2007/139379 A9, **2007**.
- [174] F. Massines, N. Gherardi, in *Recent Progress in Thin Film: Deposition and Characterization*, Research Signpost Ed., Trivandrum, India, **2010**, Ch. 1.
- [175] H. Schlemm, D. Roth, *Surf. Coat. Technol.* **2001**, *142*, 272.

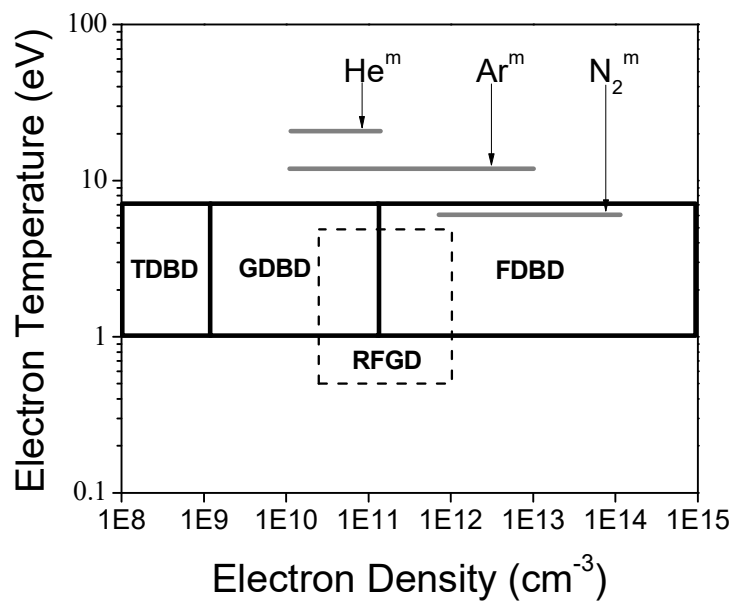
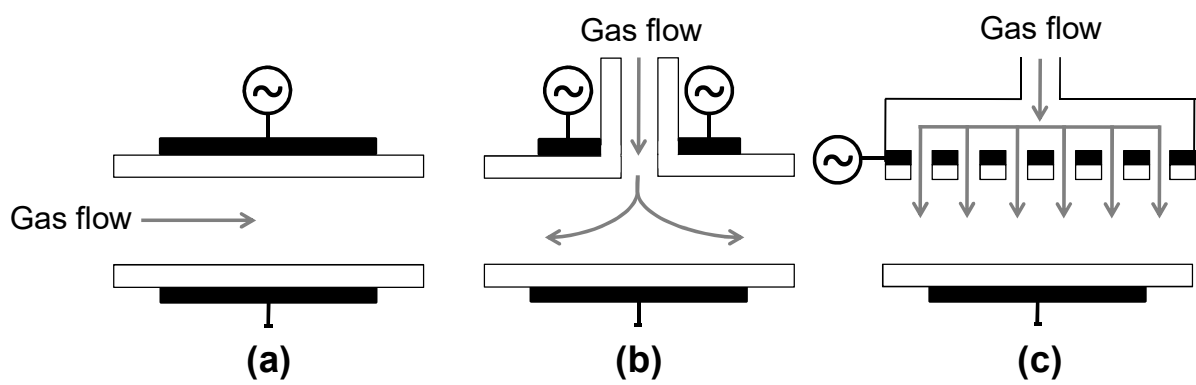
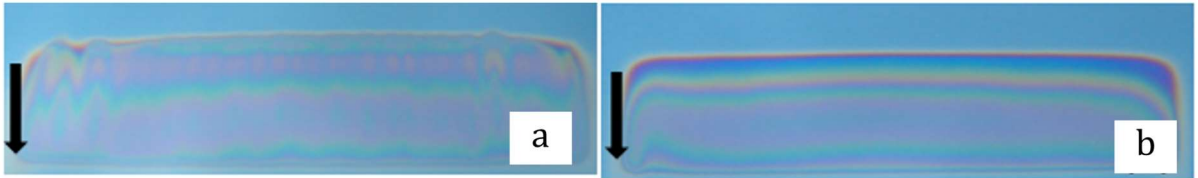


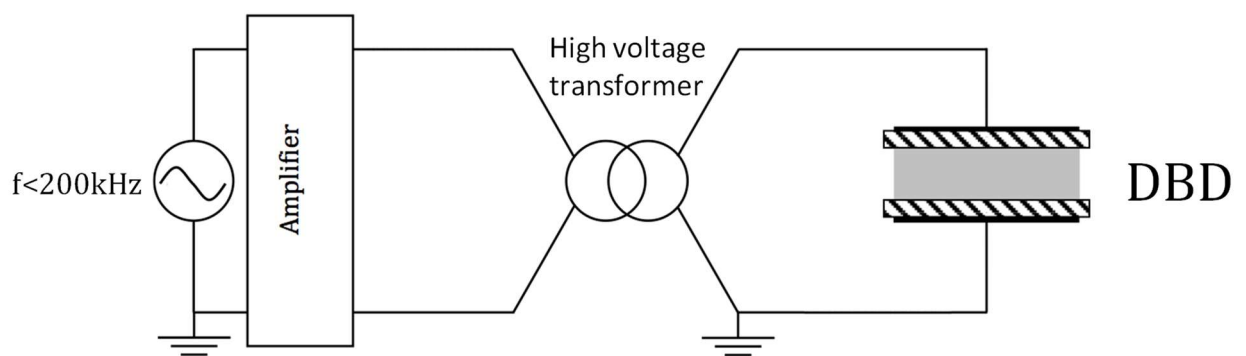
Figure 1. Electron temperature and electron density of the various types of discharge: TDBD, GDBD, FDBD, RFGD (<sup>m</sup> exponents relates to metastables). Data taken from<sup>[17,21,31,48,49,54-57]</sup>.



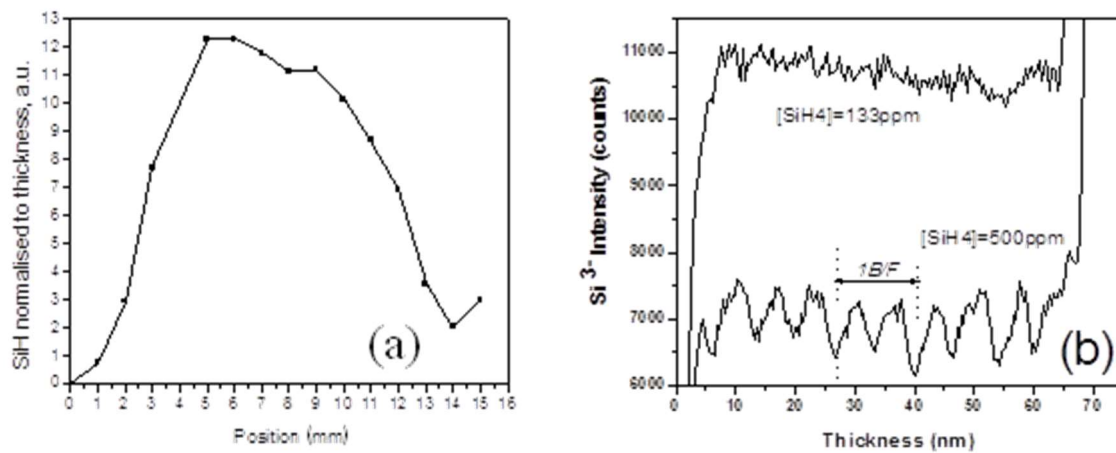
*Figure 2* Examples of cold atmospheric pressure direct plasma gas injection configuration, (a) lateral, (b) central (i.e. T-configuration), (c) through electrode (i.e. showerhead).



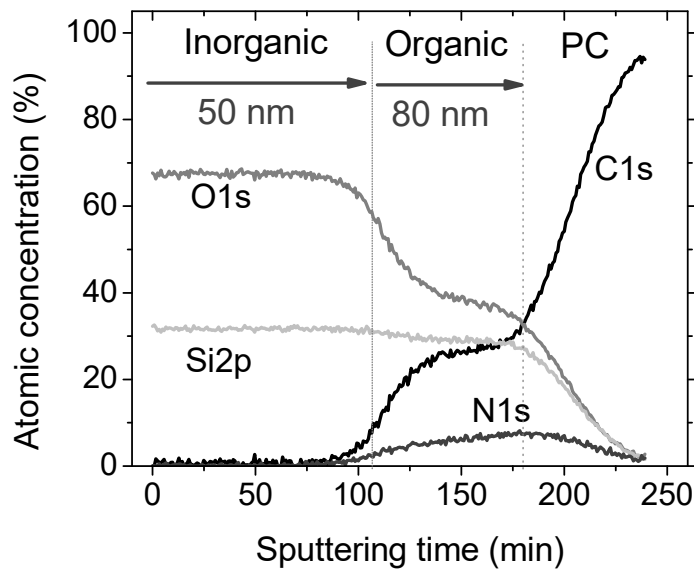
*Figure 3.* Photographs of SiO<sub>x</sub> layer deposited by a Townsend DBD, (a) with and (b) without recirculations in the gas injection, all other experimental conditions being kept constant. The arrows indicate the gas flow direction.<sup>[125]</sup>



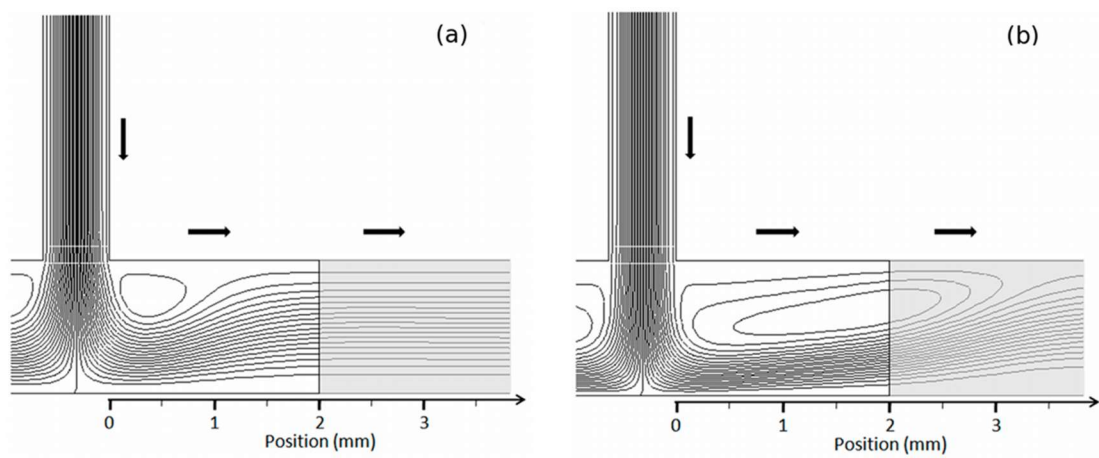
*Figure 4.* Schematic diagram of a low frequency DBD power supply using a linear amplifier and a transformer to get the high voltage necessary to turn on the discharge. This low cost solution allows to choose the waveform and to adjust independently the frequency and the amplitude of the voltage.



*Figure 5.* Chemical composition of an AP-PECVD SiN:H thin film a) SiH absorbance normalized to the thickness as a function of the position in the plasma (i.e. the residence time) measured by FTIR on a static substrate b) Si content as a function of the sample thickness measured by SIMS on substrate moving back and forth in the plasma. The chemical composition oscillations are correlated to the sample displacement.



*Figure 6.* XPS depth profile measurements of a multilayer deposited on a polymer substrate. Taken from [171]. The organic layer is deposited from  $N_2/HMDSO$  in a TDBD, the web rolling in the opposite direction of the gas flow. The inorganic layer is deposited from  $N_2/N_2O/HMDSO$  in a TDBD. Note the gradual decrease of the C from the polymer substrate (polycarbonate, PC) to the inorganic layer, and the correlated increase of the O.



*Figure 7.* Calculated flow streamlines at 1 slm (a) and 6 slm (b). Only one side of the discharge cell is presented. The discharge zone is shaded in grey.<sup>[125]</sup>

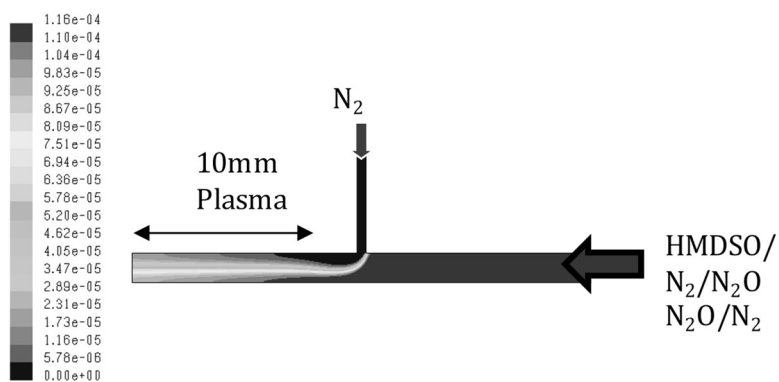


Figure 8. Calculated profile of the mass fraction of HMDSO in case of a double injection. The plasma is not taken into account (no consumption of HMDSO). Taken from<sup>[174]</sup>.

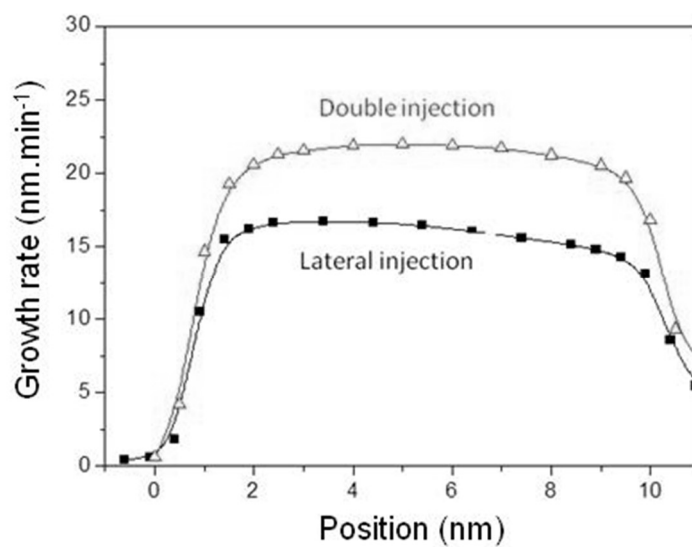


Figure 8. Experimental growth rate in case of a simple injection (lateral) and a double injection (all other parameters being kept constant). Taken from<sup>[174]</sup>.

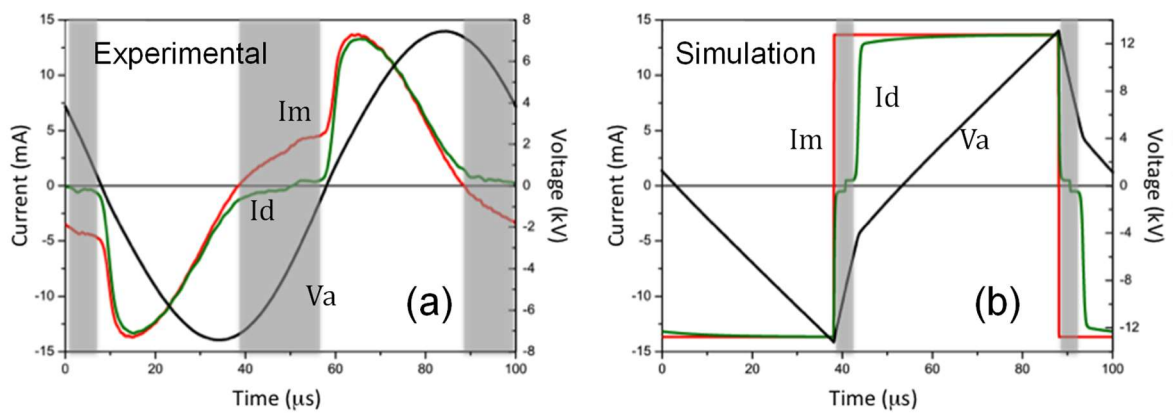


Figure 9. Comparison between sinusoidal voltage source (a) and square-wave current source (b) for the same discharge current amplitude: applied voltage ( $V_a$ ), measured current ( $I_m$ ) and discharge current ( $I_d$ ) (the discharge is off in shaded areas).

*Table 1.* Characteristics and energetic species densities for different AP discharges

<b>Discharge</b>	<b>Discharge duration</b>	<b>Max current density [A·cm<sup>-2</sup>]</b>	<b>Max power density [W·cm<sup>-2</sup>]</b>	<b>Max electron density [cm<sup>-3</sup>]</b>	<b>Max metastable density [cm<sup>-3</sup>]</b>	<b>Max ion density [cm<sup>-3</sup>]</b>
<b>FDBD</b>	10-100 ns	1-10 A·cm <sup>-2</sup>	10	10 <sup>14</sup>	10 <sup>13</sup>	10 <sup>14</sup>
<b>GLDBD</b>	200 ns	0.1-1 A·cm <sup>-2</sup>	5	not available	not available	not available
<b>GDBD (APGD)</b>	1-5 μs	1-10 mA·cm <sup>-2</sup>	1	10 <sup>10</sup> -10 <sup>11</sup>	10 <sup>11</sup>	10 <sup>11</sup>
<b>TDBD (APTD)</b>	half of the period	0.1-5 mA·cm <sup>-2</sup>	5	10 <sup>7</sup> -10 <sup>8</sup>	10 <sup>13</sup>	10 <sup>11</sup>
<b>RFGD</b>	always ON	50 mA·cm <sup>-2</sup>	5	10 <sup>12</sup>	10 <sup>12</sup>	10 <sup>11</sup> -10 <sup>12</sup>

*Table 2.* Comparison of different dilution gases characteristics including the possible type of discharge (Data taken from<sup>[21,32,79,80]</sup>)

<b>Gas</b>	<b>Cost</b>	<b>Breakdown field at AP</b> <b>[kV·cm<sup>-1</sup>]</b>	<b>Discharge</b>
He	€€€€	9 – 4 <sup>a)</sup>	FDBD, GLDBD, GDBD, RFGD
Ar	€€€	2,7 – 1,4 <sup>a)</sup>	FDBD, GLDBD, GDBD <sup>a)</sup> ,RFGD
N <sub>2</sub>	€€	35	FDBD, GLDBD, TDBD
Air	€	30	FDBD, GLDBD, TDBD

<sup>a)</sup> In Penning mixtures like He-impurities, He-N<sub>2</sub>, Ar-NH<sub>3</sub> or Ar-ketone

Table 3. List of published works on direct AP-PECVD with lateral gas injection

Type of discharge	Electrical excitation	Power [W·cm <sup>-2</sup> ]	Precursor and additives	[Precursor] and [Additive]	Dilution gas	Dilution gas flow rate [slm]	Max deposition rate [nm·s <sup>-1</sup> ]	Ref.
GDBD	μs Pulsed – 100-800 Hz	0.003	CH <sub>2</sub> =CH <sub>2</sub>	0.2-3.7%	He	0.001-0.02	0.2	[43]
GDBD	3 kHz	?	CH <sub>2</sub> =CH <sub>2</sub> CF <sub>2</sub> =CF <sub>2</sub>	0.03-0.13% (C <sub>2</sub> H <sub>4</sub> ), 0.04-0.18% (C <sub>2</sub> F <sub>4</sub> )	He	4.5	0.28	[124]
FDBD	10μs Pulsed – 1 kHz	?	CH <sub>2</sub> =CH <sub>2</sub>	100%	-	0.5	0.01	[44]
FDBD	50μs Pulsed – 1 kHz	?	CH <sub>4</sub>	100%	-	0.5	0.56	[45]
GDBD	1-4 kHz	?	CH <sub>2</sub> =CH <sub>2</sub>	5%	He, Ar	10	1.67	[155]
RFGD	27.12 MHz	5.6-33.3	CH≡CH	< 1.5%	He	?	166.67	[150]
GDBD	0.5-10 kHz	?	CH=CH CH <sub>2</sub> =CH <sub>2</sub>	0.02-0.08%	He	4.5	1.38	[156]
GDBD	10-30 kHz	0.14-0.49	CH <sub>2</sub> =CH <sub>2</sub>	0.1-0.5%	He	2-5	1.33	[83]
FDBD	9 kHz	?	CH≡CH	100%	-	5	70	[151]
RFGD	13.56 MHz	3.57-4.76	CH <sub>4</sub> /H <sub>2</sub>	0.2% (CH <sub>4</sub> ), 0.4-0.8% (H <sub>2</sub> )	He	1	3.33	[70]
GDBD	50 kHz	0.75-2.23	CH <sub>2</sub> =CHCOOH	0.8-2.5 ppm	Ar	1-10	3.14	[157]
GDBD	Unipolar squared – 2kHz	?	C <sub>6</sub> H <sub>5</sub> -CH=CH <sub>2</sub>	He bubbler flow = 0.05 -0.3slm	He	0.5-7	1-1.5	[158]
GDBD FDBD	50 kHz	1.37 GDBD 1.85 FDBD	(CH <sub>3</sub> ) <sub>3</sub> SiOSi(CH <sub>3</sub> ) <sub>3</sub>	2.86 ppm	Ar, Ar/O <sub>2</sub>	3	5.93 (Ar), 1.95 (Ar/O <sub>2</sub> )	[159]

GDBD	50 kHz	0.45-1.21	$(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$	1.3-4 ppm	He	3	4.82	[160]
FDBD	Modulated 10 kHz	0.93	$(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$	0.1%	$\text{N}_2$	19.5	8	[107]
TDBD	$\leq 6$ kHz	$\leq 2$	$\text{SiH}_4/\text{N}_2\text{O}$ $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3/\text{N}_2\text{O}$	$\leq 5$ ppm ( $\text{SiH}_4$ ), 4 ppm $((\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3)$ , 96-100 ppm ( $\text{N}_2\text{O}$ )	$\text{N}_2$	5	0.33 ( $\text{SiH}_4$ ), 0.2 $((\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3)$	[90]
GDBD	30 kHz	1	$\text{Al}(\text{C}_2\text{H}_5)_3$	Bubbler flow = 0.4-1.5 slm	He	9	0.77	[161]
FDBD	5 kHz	?	$\text{TiCl}_4/\text{O}_2$	0.015% ( $\text{TiCl}_4$ ), 2500 ( $\text{O}_2$ )	Ar	4	0.23	[162]
FDBD	1 $\mu\text{s}$ Pulsed - 0-20 kHz	?	$\text{TiCl}_4/\text{N}_2\text{O}$	$\text{TiCl}_4:\text{N}_2\text{O} = 0.2$ - 0.8:1 (~40 sccm)	He	?	1	[47]
TDBD	3 kHz	0.4	$\text{CH}_2=\text{CH}_2$	10 ppm	$\text{N}_2$	1-6	0.12	[163]
FDBD	10 kHz	?	$\text{CH}_2=\text{CH}_2$	0.05-0.6%	$\text{N}_2$	10	9	[94]
GDBD	15-30 kHz	0.25-0.57	$\text{CF}_2=\text{CFCF}_3$ $\text{CF}_3\text{CF}_2\text{CF}_3/\text{H}_2$	0.01% $(\text{CF}_2=\text{CFCF}_3)$ , 0.025% $(\text{CF}_3\text{CF}_2\text{CF}_3)$ , $\leq 0.02\%$ ( $\text{H}_2$ )	He	4	0.6	[67]
GLDBD	130-150 kHz Pulse mode (pulse duration 200 $\mu\text{s}$ , DC = 2-40%)	0.25 - 4	$(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$ $\text{O}_2$	80 ppm $((\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3)$ , 1.5% ( $\text{O}_2$ )	Ar / $\text{N}_2$	13 (80:20)	3.83	[28]
GDBD	35 kHz	0.83-2	$[(\text{CH}_3)_2\text{SiO}]_4$ $\text{CH}_2=\text{CHCOOH}$	0.05-0.1 $\text{ml}\cdot\text{min}^{-1}$ Aerosol	He	10-20	?	[99]
DBD	20 kHz	$\leq 2.08$	$\text{CH}_3[(\text{CH}_3)_2\text{SiO}]_n\text{CH}_3$ $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$ $(\text{CH}_3)_2\text{HSiOSi}(\text{CH}_3)_2$ H $\text{O}_2$	15-50 $\mu\text{l}\cdot\text{min}^{-1}$ aerosol, 0.5% ( $\text{O}_2$ )	He	20	0.2	[100]
DBD	15 kHz	?	$\text{C}_6\text{H}_5\text{-CH=CH}_2/$ $\text{CF}_3\text{SO}_3\text{H}$	?	He Ar	?	21	[164]
DBD	4 kHz		$\text{CH=CH}$ $\text{C}_4\text{H}_4\text{NH}$ Protein solution	5% ( $\text{CH}\equiv\text{CH}$ ), $\text{C}_4\text{H}_4\text{NH/Aerosol?}$ , 5 $\text{ml}\cdot\text{h}^{-1}$ Protein solution aerosol	He	6	3 ( $\text{CH}\equiv\text{CH}$ )	[101]

*Table 4.* List of published works on direct AP-PECVD atmospheric with central gas injection (i.e. T-configuration)

Type of discharge	Electrical excitation	Power [W·cm <sup>-2</sup> ]	Precursor and additives	[Precursor] and [Additive]	Dilution gas	Dilution gas flow rate [slm]	Max deposition rate [nm·s <sup>-1</sup> ]	Ref.
FDBD	20-50 kHz	?	CH <sub>4</sub> , CH=CH, CH=CCH <sub>2</sub> OH, Si(CH <sub>3</sub> ) <sub>4</sub> , Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> , CF <sub>2</sub> =CF <sub>2</sub>	~0.1%	Ar, N <sub>2</sub> , O <sub>2</sub>	?	0.17 (a-C:H), 3.33 (a-C:F), 1.67 (SiOx), 33.33 (a-SiC:H)	[71]
FDBD	Modulated sine of 1 ms	?	CH <sub>2</sub> =C(CH <sub>3</sub> )CO <sub>2</sub> -C <sub>3</sub> H <sub>5</sub> O	0.07%	N <sub>2</sub>	1-15	4	[153]
FDBD	40 kHz	?	c-C <sub>4</sub> F <sub>8</sub> , CF <sub>3</sub> CF <sub>2</sub> CF <sub>2</sub> H	9%	Ar	?	1.46	[165]
FDBD	1.5 kHz	0.5-0.85	C <sub>4</sub> H <sub>9</sub> NH <sub>2</sub>	0.74 ppm	N <sub>2</sub> , Air	5	0.6	[166]
GDBD	30 kHz	?	(CH <sub>3</sub> ) <sub>3</sub> SiNHSi(CH <sub>3</sub> ) <sub>3</sub>	0.45-1.36%	He/Ar/O <sub>2</sub>	5 (He), 3 (Ar), 14 (O <sub>2</sub> )	0.91	[166]
GDBD	50 kHz	1.7 W/cm <sup>3</sup> 2mm of gas gap?	SiH <sub>4</sub> /NH <sub>3</sub>	??	Ar	??	??	[84,85]

Table 5: List of published works on direct AP-PECVD with gas injection through the upper electrode (i.e. showerhead) or other designs

Type of discharge	Electrical excitation	Power [W·cm <sup>-2</sup> ]	Precursor and additives	[Precursor] and [Additive]	Dilution gas	Dilution gas flow rate [slm]	Max deposition rate [nm·s <sup>-1</sup> ]	Ref.
RFGD	RF (13.56 MHz)	33.1-49.6	CH <sub>4</sub> , CH≡CH	5% (CH <sub>4</sub> ), 2% (C <sub>2</sub> H <sub>2</sub> )	He	0.2	5	[167]
GDBD	100 kHz	2.68	CH <sub>2</sub> =CH <sub>2</sub> , CF <sub>2</sub> =CF <sub>2</sub>	0.06-0.4%	He	20	1.5	[168]
GDBD	20-100 kHz	?	CH <sub>2</sub> =CH <sub>2</sub> , CH <sub>2</sub> =CH <sub>2</sub> /N <sub>2</sub> or NH <sub>3</sub>	1.5% (C <sub>2</sub> H <sub>2</sub> ), 1% (N <sub>2</sub> or NH <sub>3</sub> )	He	6	~3.33	[69]
GDBD	100 kHz	0.08-0.33	(CH <sub>3</sub> ) <sub>3</sub> SiOSi(CH <sub>3</sub> ) <sub>3</sub>	0.025%	He	0.03	2	[31]
GDBD	15 kHz	?	[(CH <sub>3</sub> ) <sub>2</sub> SiO] <sub>3</sub> , [(CH <sub>3</sub> )HSiO] <sub>4</sub>	0.12 mL/h Aerosol	He, He-1% O <sub>2</sub>	1.9	0.5 ([(CH <sub>3</sub> ) <sub>2</sub> SiO] <sub>3</sub> ), 4 ([(CH <sub>3</sub> )HSiO] <sub>4</sub> )	[4]
GDBD	15 kHz	?	CH <sub>2</sub> =CHCOOH	0.1 ml/h Aerosol	He	1.9	3.8	[95]
GDBD	50 kHz	1.15-3.7	CH <sub>2</sub> =CCH <sub>3</sub> COOCH <sub>3</sub>	0.09%	He	3	3.35	[123]
RFGD	RF (13.56 MHz)	0.85-1.98	Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> /O <sub>2</sub>	Ar bubbler flow = 5 slm (SiC <sub>8</sub> H <sub>20</sub> O <sub>4</sub> ), 0-0.25 slm (O <sub>2</sub> )	Ar	5	0.5	[111]
GDBD	Pulsed, 20 Hz	?	Zn(O <sub>2</sub> C <sub>11</sub> H <sub>19</sub> ) <sub>2</sub>	Vaporized in 300 sccm He (C <sub>22</sub> H <sub>38</sub> O <sub>4</sub> Zn), 0.2-2% (O <sub>2</sub> )	He/O <sub>2</sub>	2	0.6	[40]
DBD	25 kHz	?	(CH <sub>3</sub> ) <sub>3</sub> SiNHSi(CH <sub>3</sub> ) <sub>3</sub> O <sub>2</sub>	≤ 1.5% ((CH <sub>3</sub> ) <sub>3</sub> SiNHSi(CH <sub>3</sub> ) <sub>3</sub> ) ≤ 20% (O <sub>2</sub> )		2		[169]

Table 6. Advantages and drawback of the different AP-PECVD discharge regime

Discharge	Advantage	Drawback	Restrictive conditions		
			Power supply	Gas	Electrode
<b>FDBD</b>	Easy to set-up	- Discharge localization - Limited uniformity of the coating - No dense layer	No conditions	No conditions	Dielectric at least on one electrode
<b>TDBD</b>	-Homogeneity -Stability	- Restricted conditions - Current limitation	< 20 kHz	N <sub>2</sub> , Air	Dielectric on both electrodes
<b>GDBD</b>	Homogeneity	- Restricted conditions - Sensitivity to surface conductivity - Power limited	>= 10 kHz	Noble gases, penning mixtures	Dielectric on both electrodes
<b>GLDBD</b>	Homogeneous coating	- Not available	Very specific	No conditions	Not available
<b>RFGBD</b>	-Homogeneity - No substrate effect	- Current limited - Gas heating - Impedance adaptation	> Mhz	He, Ar	No conditions

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**The aim of this review is to contribute to find a solution for AP-PECVD of dense film at a growth rate suitable for industrial applications.** It compares the different plasma sources, the different reactor configurations, power supplies, precursors nature to try to point out advantages and drawbacks and converge to the best solution.

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**Atmospheric pressure low temperature direct plasma technology: status and challenges for thin film deposition**

