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Nano-particle size-dependant charging and electro-deposition in Dielectric Barrier Discharges at Atmospheric Pressure for thin SiO_x film deposition

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Abstract. This paper focuses on charging and electro-deposition of nano-particles produced in a mixture of Silane and nitrous oxide diluted in N₂, by Dielectric Barrier Discharge (DBD) at atmospheric pressure for SiO_x film deposition. Townsend Discharge (TD) and Filamentary Discharge (FD) are compared with and without SiH₄. Without SiH₄, particles are produced by filament-surface interaction. Both filament-surface and plasma-Silane interactions lead to bimodal particle size distributions from nucleation and agglomeration. With SiH₄, particle formation and growth imply the same mechanisms in TD and FD. Faster dynamics in FD are related to higher local volume energy density than in TD. From scanning electron microscope images of the film and measurements downstream of the DBD reactor, the diameter of the particle produced is below 50 nm. An analytical model of electro-collection in ac electric field is used to investigate nano-particle charging. To account for the selective electro-deposition leading to particles smaller than 50 nm being included in the layer and to the particle size distribution measured downstream of the DBD, the same size-dependent charging and electro-deposition of particle are involved, with different charging dynamics in TD and FD.

1. Introduction

SiO₂ thin films can be used for microelectronic applications, barrier layers and hard or anti-reflective coatings. Mixtures of Silane (SiH₄) and nitrous oxide are used for thin SiO_x films deposition in low pressure plasmas [1] and at atmospheric pressure using Dielectric Barrier Discharge (DBD) [2-3]. At low pressure, nano/micro-particle formation is observed and has been studied in most of the reactive plasmas used for industrial applications [4-6]. When SiH₄ is used in DBD at atmospheric pressure, the layer also includes nano-particles [2], but their formation and charging occur in quite different conditions in terms of spatial and temporal evolutions of reactive and charged species densities than at low pressure.

Nano-particles in plasmas at atmospheric pressure are formed by gas-to-particle conversion (i.e. nucleation of condensable species). The condensable species are produced by (i) vaporization at the interface of Filamentary Discharges (FD) with surfaces in carefully conditioned gas [7-9] as well as (ii) by gas-phase reactions between a gaseous precursor and reactive species produced in the discharge [2, 10-12]. These processes will be referred to as physical nucleation and reactive nucleation respectively.

In spark generators, the interaction of a spark filament on a surface with a high energy per filament (from few mJ up to few J) leads to large particle diameter and high concentration (above 100 nm and 10⁷ cm⁻³ respectively) [8]. Indeed high particle concentration leads to particle growth by Brownian agglomeration so that the initial concentration of nucleated nano-particles and agglomeration time lead to the final particle diameter of the unimodal self preserving size distribution [12-15]. Despite smaller energy per filament in DBD (~ μJ) than in spark, shorter duration (~ nanosecond) and smaller surface (~ 10⁻⁵ cm²) imply high surface power density (~ 10¹² W.m⁻²), thus fluence threshold for vaporisation (0.1 J.cm⁻²) is reached enabling the nucleation of the hot vapour around these filamentary discharges. Particles are also formed by filament-surface interaction in DBD but lead to smaller particles than with

spark and at concentrations below 10^7 cm^{-3} , as excepted from the smaller vapour fluxes than with more energetic spark [12].

Particle charging by FD has been demonstrated in plane to plane DBD in air, by the collection on the dielectric surface of initially neutral particles between 20 and 70 nm injected in the DBD reactor [16]. Ions remaining in the gap a few microseconds after the filament lead to diffusion charging of the particles. The excess of positive ions in the discharge gap, due to the higher mobility of electrons, leads to positive net charge of the nano-particles. For such an ultra fine aerosol, the final number of charges per particle depends on particle size and on the charging conditions including $Ni \cdot \tau$ product, with Ni , the ion density, and τ , the transit time of the particle in the ion cloud [13]. The mechanism of field charging, for which the ions drift along the electric field lines ending on the particle, is negligible compared to diffusion charging if the particles size is below 100 nm.

At Atmospheric Pressure, in plane-to-plane DBD in nitrogen, the two discharge regimes are: Filamentary Discharge (FD) and Townsend Discharge (TD) [17]. In FD, thin and brief streamer-like filaments (duration: a few 10's of ns, diameter a few 10's of μm) are homogeneously distributed over the dielectric surface [18]. In TD, streamer formation is not observed, but a larger homogeneous discharge occurs with respect to the more confined FD. Both regimes are used to create silicon-based films at atmospheric pressure from diluted Silane (SiH_4 with nitrous oxide in nitrogen), leading to Chemical Vapour Deposition (CVD) of condensable species and radicals, as well as SiO_x particles [2, 3].

Electrical characterization of the different plasma regimes, related to applied voltage, frequency and Silane concentration is first depicted in this paper. Then, physical nucleation of particles produced by filament-surface interaction in an N_2/O_2 mixture without a Silane precursor is presented. The dynamics of particle formation and growth are then depicted from the size distribution of the particles measured downstream of the DBD.. Finally, with a Silane precursor, the reactive nucleation and the particle deposition are analysed through SEM images of the layer and particle number-size distributions measured downstream of the DBD for both discharge regimes (TD and FD) according to local and mean volume energy densities of the discharges. As diffusion and thermophoresis are negligible, one can assume that particle deposition is only due to electro-collection. So an analytical model of charged particle trajectory is presented and validated in controlled conditions with monodispersed singly charged particles injected in the discharge. The efficiency of electro-collection is computed from the model for different conditions of diffusion charging to account for the particle size distributions. Special attention is paid to charging of the nano-particles to account for the fact that deposited nano-particles found both in the film as well as in suspension are smaller than 50 nm.

2. Experimental setup

Two parallel plates of alumina (thickness 0.5 mm), separated by 1 mm, were polarized by 3 cm long and 2 cm wide brass electrodes supplied by a 1-5 kHz sinusoidal power supply (cf. figure 1). Current and voltage were measured with an oscilloscope and treated as described in [19].

Figure 1: Experimental setup

The gas flow rate between the plates was adjusted between 2 and 4 L/min by mass flow controllers, leading to transit time and gas velocity in the reactor between 9, 18 ms and 1.6, 3.3 m.s^{-1} respectively. The experimental setup is detailed in [2].

The aerosol particle concentrations downstream of the DBD reactor were measured using a Condensation Particle Counter (CPC). The CPC counts particles from 0.005 to 3 μm using the principle of light scattering after growth by heterogeneous condensation of butanol. The size distributions of the particles were obtained by counting with the CPC after two size-selective devices (a diffusion battery and a Scanning Mobility Particle Sizer -SMPS-). The diffusion battery separates aerosol particles into ten stages from 0.002 to 0.2 μm . Each stage consists of a grid collecting a

fraction of the particles by diffusion. At $0.9 \text{ L}\cdot\text{min}^{-1}$, the SMPS classifies particles with an electrostatic classifier from 8 to 350 nm into 128 stages. Before classification particles are neutralized by a radioactive source (Kr 85) leading to a Boltzmann charge distribution of the particles centred at zero (at 10 and 50 nm more than 99 % and 60 % of the particles are neutral, respectively).

3. Experimental results in plane-plane AC DBD at atmospheric pressure

3.1 Electrical characterisation

Depending on the voltage frequency, applied voltage and Silane concentration, one can generate either FD or TD. TD in N_2 requires seed electrons provided by secondary emissions due to metastable impact and quenching on the dielectric surface [20].

Figure 2 (a) shows the operating voltage and Silane concentration required for TD or FD at 4 kHz. TD occurs for a given voltage range depending on the Silane concentration, SiH_4 being involved in the quenching of metastables required for Penning ionization. Conversely, for a given Silane concentration, TD only exists at intermediate voltages. At higher voltage, electric field and ionization rate, Meek's criterion is fulfilled and FD develop, as shown in figure 2 (b). At lower voltage, FD arise from insufficient secondary electron emissions from the cathode due to the small metastable flux. The two FD regimes will be referred to as the low and high power FD.

Figure 2 : Electrical characterization of plane-plane AC DBD at atmospheric pressure at 4 kHz.

TD produces lower densities of electrons, ions and metastables, which are more homogeneously distributed through the gap than in FD where these species are concentrated in transient and local streamer-like FD [12]. This enables comparison of the formation, charging and electro-deposition of nucleated particles involved in thin film deposition in both cases.

3.2 Physical nucleation by FD-surface interaction in nitrogen

The dynamics of formation by nucleation and growth by agglomeration of particles formed by filament-surface interaction in N_2 without Silane precursor (already detailed in [12]) is used to depict the mechanisms associated with production and transport of nano-particles.

Townsend discharge (TD)

No aerosol is detected except when volatile organic compounds (from a silicon paste used for sealing) produce condensable species by plasma-gas interactions in the bulk gas leading to nucleated ultra-fine particles ($d_p < 10 \text{ nm}$). Aerosol formation stops with desorption of the silicon paste solvent.

Filamentary discharge (FD)

In pure nitrogen as well as in N_2/O_2 mixtures (with only a few percent of oxygen), particles are counted downstream of the plane-to-plane AC DBD reactor whatever the voltage amplitude and frequency are. Number-size distributions in pure N_2 for different gas flow rate (the 10 s duration at 1 lpm is due to an additional volume in the outlet gas line) and in N_2/O_2 mixtures (99.5 % N_2 , 0.25 % O_2) are shown in Figure 3 (a) and (b) respectively. It should be emphasized that gas composition and dielectric surface roughness modify the size distributions.

Figure 3: Size distribution of the particles produced by FD in dielectric barrier discharge measured (a) with SMPS in pure N_2 , $V_{pp}=20 \text{ kV}$, $P=4 \text{ W}$, $F=1 \text{ kHz}$, for different gas flow rates and (b) with the diffusion battery in N_2/O_2 mixture, $Q_{N_2}=3 \text{ L.min}^{-1}$, $Q_{air}=0.4 \text{ L.min}^{-1}$, $V_{pp}=18.4 \text{ kV}$, $F=1.5 \text{ kHz}$ and $P=4.5 \text{ W}$

In Figure 3 (a), with decreasing gas flow rate, the number-size distributions of the particles evolve from monodisperse ultra-fine ($< 20 \text{ nm}$) to bimodal size distribution. Ultra fine particles are produced by nucleation of vapour arising from the cathode plane (cf. section 1.). Once the particles are formed, they grow by Brownian agglomeration. From Figure 3 (b) and Figure 3 (a) for 1 L.min^{-1} , the particle size distributions are bimodal and similar for different tools, validating the measurements. The larger size of particles measured with the SMPS than with the diffusion battery arises from the 10 s and 100 μs duration before measurement respectively.

Growth dynamics

The size distribution measured after a few hundred milliseconds is bimodal as expected for nucleated aerosol (e.g. with spark discharge [8], flame [21], or DBD [12]). Indeed, the initial unimodal size distribution evolves to transitory bimodal size distributions and finally turns into unimodal self preserving particle size distribution related to particle agglomeration [12, 15]. The self preserving size distributions are not reached in this case due to moderate particle concentration that would require longer growth times. The dynamics of particle growth depends on particle concentration, particle size and gas temperature.

The resulting transitory size distribution depends on radial distributions of condensable species and primary nano-particles around the source, related to characteristic times of cloud expansion, nucleation, condensation and agglomeration [12]. The transitory size distributions are composed of two modes.

The first mode, from a few to tens of nanometres, is related to nucleation and fast agglomeration of primary nucleated nano-particles in the production zone close to the vapour source.

As decreasing gas flow rate in Figure 3 (a) induces both (i) the increase of primary particle concentration and (ii) the increasing duration between DBD reactor and SMPS measurement favouring agglomeration, the second mode is related to Brownian agglomeration of particles from the first mode. Brownian agglomeration of particles from the first mode requires particle concentration above 10^8 cm^{-3} to be noticeable within the 100 ms transit time from the entrance of the reactor to the CPC [13]. The related total particle concentrations measured downstream of the DBD depend on gas flow rate, particle size and particle production rate (nucleation frequency). Except for 4 L.min^{-1} , where the particle below 8 nm are not detected leading to an under-estimation of the total particle concentration, the mass flux downstream of the DBD is constant, showing that particles only grow by agglomeration during the post production transit (the $3 \cdot 10^6$ and 10^4 cm^{-3} concentration measured at 1 and 2 L.min^{-1} are related to a mass detected per minute of 10 ng). In pure N_2 and N_2/O_2 mixtures, the absence of particles larger than 60 nm shows that particles do not have the time ($\leq 100 \text{ ms}$) to grow above 60 nm due to moderate particle concentration.

Finally, such ultra-fine aerosol ($< 60 \text{ nm}$) can only arise from nucleation and pure agglomeration. The aim of the following section is to show that the same processes occur on the particles produced by reactive nucleation when a Silane precursor is injected in the discharge.

3.3 Reactive nucleation from plasma-Silane interaction for thin film deposition

This section deals with SiO_x layer formation focuses on the mechanism of particle charging and electro-deposition. When a few ppmv of SiH_4 are injected with N_2 and few 100 ppmv of N_2O in the plasma reactor, a SiO_x layer is formed on the dielectric materials. Chemical pathways from Silane to SiO_x have been identified and modelled in low pressure rf-plasmas [10] and are similar at atmospheric pressure [2].

With SiH_4 , aerosol concentration downstream of the DBD ($\sim 10^8 \text{ cm}^{-3}$) is higher than for physical nucleation alone, proving that a portion of the particles detected arises from reactive nucleation. The 100 ms duration between DBD reactor and particle measurement is short enough to keep the size distribution unchanged according to dynamics growth, the size distributions are related to the mechanisms occurring in the DBD reactor. A special attention is paid to charging of the nano-particles to account for the fact that deposited nano-particles included in the film as well as suspended are smaller than 50 nm. The efficiency of electro-collection is computed from the model of electro-collection for different diffusion charging conditions to highlight an eventual additional mechanism involved in the charging of particles and/or size dependant charging condition seen by particles.

Mechanisms of SiO_x layer formation

Figure 4 shows relative Silane density, particle concentration and typical layer formed along the reactor in a TD.

Figure 4: SiO_x film formation in $\text{N}_2/\text{SiH}_4/\text{N}_2\text{O}$ side and upper SEM image by TD

The SiO_x film at the surface is formed, near the inlet of the reactor by a radical flux, followed by a combined deposition of radicals and particles and ending with particles only near the reactor outlet [2]. The Silicon mass balance shows that aerosol downstream of the DBD reactor contains only 0.1 % (from 1 up to $20 \text{ ng} \cdot \text{min}^{-1}$) of the incoming Silicon, so that most of the precursor is deposited in the film.

The radical flux leads to a dense SiO_x layer formed by Chemical Vapour Deposition (CVD). The combined deposition of radical and particle leads to adherent coatings of agglomerated nano- SiO_x particles with a cauliflower structure (as in low pressure plasmas [22]); radicals enable strong covalent bonds between nano-particles in the film and between the film and the substrate. Lastly, nucleated nano-particles formed in the gas are deposited on the surface. This final unadherent film probably arises from the deep decrease in the radical concentration limiting surface radical and cohesion of agglomerated nano-particles.

Nano-particle diameter included in the film is smaller than 50 nm. This confirms that particles are formed by reactive nucleation, from reactant injection up to a few centimetres, when no more reactant is available after a transit of a few milliseconds, according to local volume energy density, input power, SiH_4 concentration and gas flow rate, as detailed below.

Layer profile according to local and mean volume energy densities

Figure 5 shows the typical profiles of the layer versus the position along the direction of the gas flow in both FD and TD for a given SiH_4 concentration. The structures of the layers formed at the surface

are similar whatever the discharge regime is (dense SiO_x layer, agglomerated nano- SiO_x and unadherent nano- SiO_x). The term Max in the figure 5 represents the position of the maximal thickness of the layer. The mean energy density is computed from the ratio of the input power, P and the gas flow rate, Q; $\langle J_E \rangle = P/Q$. The local volume energy density is computed either from the ratio of the energy per filament, E and the volume of the filament, V ($J_{E\text{max}} = E/V$) for FD or from the ratio of the maximum energy yield and the volume of the discharge zone for TD.

Figure 5: Typical upper views of a coating along the direction of the gas flow in TD and low and high energy FD

The radical flux stops when no more SiH_4 is available. At first approximation, it coincides with the end of the dense SiO_x layer (i.e. the beginning of the unadherent nano- SiO_x particles) and is related to both local and mean volume energy density. Indeed, the CVD ends faster in FD than TD, due to faster reactions expected from the higher local volume energy density in FD leading to higher active species densities in FD than in TD. Moreover, CVD stops faster in high power FD than in the low power FD, which is related to a faster consumption of the reactants induced by higher mean volume energy density due to more numerous filaments per unit time and surface. It should be emphasized that the characteristics of the filaments evolve along the reactor according to the structure of the layer.

The mean formation time of the particles (≥ 3.8 ms), the size of agglomerated nano- SiO_x and the maximal thickness of the film depend on the mean volume energy density [2]. The local volume energy density defines the minimal formation time of the particles (about 0.7 ms for DF and 2.3 ms for DT).

Despite similar structures, the agglomerated nano- SiO_x particles are formed closer to the precursor injection in FD than in TD, implying a faster formation and growth of nucleated nano-particles with FD, as required to account for the faster electro-deposition. Indeed, faster particle formation in FD than in TD is due to higher local volume energy density leading to higher reactive species concentration implying faster formation kinetics of condensable species resulting in higher nucleation frequency. Higher local primary nano-particle concentration in FD than TD leads to higher agglomeration rate and faster particle growth. Moreover, the extra-source of nano-particle from FD-surface interaction triggers the nucleation of condensable SiO_x particles increasing the nucleation frequency.

In the case of high power FD, for high mean volume energy density (for instance $J_E = 0.36$ J.cm⁻³ in Figure 5), there are no more nano-particles produced by reactive nucleation at the end of the reactor, as all the SiO_x has already been deposited. Only particles produced by physical nucleation are detected downstream of the DBD as already described in section 3.2. The mean volume energy density threshold depends on SiH_4 concentration. Then, to measure the size of nano-particles produced by reactive nucleation, the mean volume energy density is adjusted below the threshold.

Mechanisms of charging and analytical model of electro-collection

The charging of nano-particles can occur via one or two steps: (i) during the formation by eventual ion-induced nucleation and (ii) after the production during the transit in the DBD. In this part, only the post-production charging by ion diffusion is considered; eventual additional photo-charging will then be discussed (cf. paragraph entitled particle charging related to size distribution).

Due to the lack of experimental and theoretical data in highly heterogeneous ion densities in space and time, classical diffusion charging laws, validated in quasi-homogeneous ion densities, are used to investigate particle charging and electro-collection of nucleated nano-particles with an analytical

model of electro-collection developed previously [16]. The mean charging condition (product of ion density and transit time in the ion cloud) is estimated using various assumptions. Then, the particle charge is calculated from theoretical laws for each particle diameter. Finally, the efficiency of electro-collection is computed from the model to account for the size selective deposition mechanism in agreement with the size of the particles smaller than 50 nm both included in the layer and measured downstream of the DBD.

The model of charged particle trajectory in an AC electrical field without discharge only accounts for electrical and viscous drag forces, assuming a parabolic gas velocity profile. Moreover, as the working frequency is below 5 kHz, the increase of gas and surface temperatures is only a few Kelvin; thermophoresis force can thus be neglected. Besides, diffusion losses are negligible within the few ms transit time in the DBD reactor, whatever the particle size is.

The electro-collection of initially monodispersed and singly-charged particles (20, 30, 50 and 70 nm) has been investigated in air. In a laminar flow regime, the collected fraction of the particles depends on the amplitude of motion of the particle which is related to the particle electrical mobility, the peak-to-peak applied voltage (V_{pp}) and the frequency (F) of the applied voltage. Indeed, resolving Newton's second law of motion with electrical and viscous drag forces, the amplitude of the particle motion, z_p can be approximated, for particles smaller than 100 nm and frequency below 60 kHz by:

$$z_p \approx \frac{\mu_p \cdot E}{2\pi \cdot F} \quad (1)$$

Where E is the amplitude of the electrical field in the gap, F is the frequency of the applied voltage and μ_p is the particle mobility.

$$\mu_p = \frac{n_p \cdot e \cdot Cu(d_p)}{3\pi \cdot \eta \cdot d_p} \quad (2)$$

Where n_p is the number of charges, e is the charge of an electron, Cu is the Cunningham correction factor, η is the air viscosity and d_p the particle diameter.

For residence time longer than a voltage period, the collection efficiency of charged particles is independent of the gas velocity. Total collection in the DBD occurs only for particles with electrical mobilities higher than the critical mobility (μ_c) whatever their positions in the gap are. μ_c can be written as,

$$\mu_c = \left(1 + \frac{2e}{\epsilon_r \cdot d}\right) \frac{2\pi \cdot F \cdot d^2}{V_{pp}}, \quad (3)$$

where d is the distance between the dielectrics (i.e. the gap width), e is the dielectric plate thickness and ϵ_r is the relative dielectric constant of alumina. To account for the proportionality between the amplitude of the electrical field and the applied voltage leading to equation (2) it has to be mentioned that surface polarization by FD does not modify the collection efficiency as demonstrated for 20 nm singly charged nano-particles (cf. Figure 6). Thus the amplitude of homogeneous electric field in the gas or Laplace field is used to describe electro-collection. For the experimental conditions in this work ($F=4$ kHz, $d=1$ mm and $11 < V_{pp} < 18$ kV), the critical mobility is about $2 \cdot 10^{-6} \text{ V} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$.

The collection efficiency η is defined as $\square (C_{po} - C_p)/C_{po}$ where C_{po} is the initial output concentration without applied voltage and C_p is the output concentration. The amplitude of the particle movement z_p defined in equation (1) defines the two collection volumes of the particles above the dielectrics; collection efficiency is calculated by integration of the particle flux in those volumes [16].

$$\eta = \frac{3}{d} \left(z_p - \frac{d}{6} - \frac{4(z_p - \frac{d}{2})^3}{3d^2} \right) \quad \text{if } z_p < d/2 \quad (4)$$

$$\eta = 1 \quad \text{if } z_p \geq d/2$$

Figure 6 shows theoretical and measured collection efficiencies of initially singly charged particles of 20 and 30 nm diameters injected in the gap versus the homogeneous electric field at 1 kHz.

Figure 6: Collection efficiencies versus electric field in 1 kHz DBD for singly charged particles of (a) 20 nm and (b) 30 nm diameters, V_t is the discharge voltage threshold

As collection efficiencies of singly charged particles injected in the gap are consistent with the model for the singly-charged 20 nm particles, charging during the transit can be neglected, as expected from low charging efficiency for this particle size (cf. Figure 8). Moreover transient field modifications by surface polarization at the feet of FD can be neglected to assume a sinusoidal homogeneous field for ac electro-collection [16].

For 30 nm and bigger singly-charged particles, the model is also relevant. Higher electro-collection efficiencies than those calculated for singly charged particle are caused by additional charging during the transit in the DBD reactor. The initially singly charged 30 nm particles reach a mean charge of 1.8, as described in the paragraph entitled charging conditions.

Particle size distribution downstream of the DBD for both FD and TD

With 2.4 ppmv of SiH_4 and 190 ppmv of N_2O in N_2 , for a gas flow rate of 2.4 L/min, an attempt has been made to detect particles in suspension after the deposition reactor using either FD or TD.

At 4 kHz, the discharge regime depends on the peak-to-peak applied voltage (cf. Figure 2). For $V_1=11.9$ kV, the discharge is considered as TD like as it is an homogeneous TD discharge with only 1 micro-discharge every three half periods. For $V_2=15.5$ kV, there are approximately 20 micro-discharges per half period per cm^2 , superimposed on a TD. The discharge obtained for V_2 is therefore a mix between TD and FD. The power dissipated in the discharge for V_1 and V_2 are respectively 1.3 W and 10 W and the mean volume energy densities are 0.032 and 0.25 $\text{J}\cdot\text{cm}^{-3}$, below the threshold required to prevent from total collection of the SiO_x nano-particles in the deposit reactor, as described above (cf. Figure 5).

The total concentration of particles is approximately 10^8 cm^{-3} for V_1 and V_2 . This is one order of magnitude higher than the maximum value found without SiH_4 (Figure 2), so that at least 90 % of the detected particle arise from nucleation of condensable SiO_x species.

The number-size distributions of the particles for V_1 and V_2 are shown in Figure 7. As already observed on MEB images of the film [2], these measurements confirm that both TD and FD induce gas-to-particle conversion (nucleation) when SiH_4 is used to produce thin SiO_2 films for both discharge regimes, contrary to pure physical nucleation only reported for filament surface interaction. Numbers from 1 to 5 will be used to depict the particle size distributions with respect to growth dynamics and electro-collection.

Figure 7: Size distributions of particles produced by DBD in $N_2/SiH_4/N_2O$ mixture, frequency of 4 kHz, voltage amplitude of a) $V_1=11.8$ kV leading to a TD b) $V_2=15.5$ kV leading to a mix of FD and TD.

As for pure physical nucleation with filament-surface interaction, reactive nucleation leads to bimodal size distributions for both discharge regimes. It can be reasonably assumed that nucleation and particle growth dynamics by Brownian agglomeration account for the bimodal size distribution whatever the origin of the condensable species is, from the brief and localized cathode spot on the surface at the base of the discharge filament or from gas-phase reactions with a Silane precursor in FD or in TD as described in section 3.2.

Moreover, to account for the fact that no particle above 50 nm are included in the layer and for the particle size distribution (99 % of particles smaller than 50 nm), the same size-dependent particle charging is involved in both regimes; even if production rate, growth and charging dynamics are faster in FD as described above for production and growth and detailed in the paragraph below for charging. Indeed, as the charging of particles depends on their size, the electrostatic collection (implying an efficient charging during formation and growth) probably plays a major role in this size selective deposition mechanism as discussed below.

Charging conditions

The competition between particle extraction and collection is depicted here for different sizes using the electro-collection model, depending on the particle charge. The charging conditions used for the diffusion charging theories are $Ni \cdot \tau$ products of 10^9 and 10^7 s.cm⁻³ to be compared to the standard 10^7 s.cm⁻³ in corona charger ($10^7 < Ni < 10^9$ cm⁻³ and $0.01 < \tau < 1$ s).

The $Ni \cdot \tau$ products are estimated by the time-integration of the ion density along the 10 ms particle trajectory considering a linear trajectory. For FD, the maximum ion density in a filamentary discharge channel is about 10^{16} ions per cm⁻³ and some ions remain in the gas for a few μ s due to dielectric surface polarization with a spatial extension of a few hundred μ m [23]. Assuming 20 filaments per half period per cm² homogeneously distributed on the surface, the particle moves across about 10 ion clouds with an average ion density of 10^{11-13} per cm⁻³ in each cloud, and spend only 0.1 ms in each of those clouds (0.1 % of its transit time), leading to a mean $Ni \cdot \tau$ product between 10^7 and 10^9 s.cm⁻³.

Besides, the range of $Ni \cdot \tau$ products is validated by partial charging laws related to the fraction of neutral particles. It concerns the smallest particle below a few tens of nm. The neutral fraction, f_n can be estimated from:

$$f_n = \exp\left(-\frac{\pi}{4} d_p^2 \cdot \overline{c_i} \cdot Ni \cdot \tau\right), \quad (5)$$

where $\overline{c_i}$ is the mean thermal ion velocity (m.s⁻¹) [24].

From Figure 7, particle of 10 nm are detected and, according to the electro-collection model, charged 10 nm particles are collected, thus a portion of the 10 nm particles is neutral. According to relation (5), the mean $Ni \cdot \tau$ product is thus below 10^9 s.cm⁻³.

For TD, the maximum ion density in the gap is lower (about 10^{11} cm^{-3}) but more homogeneously distributed in time and space and for a longer duration than within the filament (about $80 \mu\text{s}$ in each half period of $150 \mu\text{s}$). The spatial distribution of successive positive ions clouds, with a brief transient electron density at the field inversion leads to particles charged in both polarities with a higher probability for positive charge. The mean $Ni.\tau$ products are lower than for FD about $10^{6-7} \text{ s.cm}^{-3}$.

Figure 8 shows the number of charges per particle required to reach the critical mobility at 4 kHz for an amplitude of the Laplace field of $7 \cdot 10^6 \text{ V.m}^{-1}$ at an applied voltage of 15.5 kV (solid line), as well as the charge number acquired by diffusion charging according to Fuchs's theory [25] (dotted lines) versus particle diameter.

Figure 8: Number of charges per particle required for total collection and acquired by diffusion charging

The number of charges required for total collection (solid line) related to electrical mobility of $2 \cdot 10^{-6} \text{ V.m}^{-1}.\text{s}^{-1}$ (cf. critical mobility from the model of electro-collection) corresponds to singly-charged particles of 10 nm diameter. Thus, if formed, initially singly charged clusters are collected. As expected, the number of charges per particle required for total collection increases with particle diameter (14 charges for a 40 nm particle).

Particle charging related to size distribution

From Figure 8, the computed numbers of charges per particle acquired by diffusion charging in both charging conditions are far below the required value for total collection, which is in agreement with the fact that particles are detected downstream of the DBD.

The mean charge calculated for particle below 20 nm is less than one due to partial charging. A portion of the particles smaller than 20 nm is neutral and exits the DBD reactor.

Moreover, above 10 nm, the discrepancy between the charge numbers, required to reach the critical mobility and acquired by diffusion charging increases with particle diameter so that smaller particles are better collected than larger ones.

The first and the second modes (cf. Figure 7) are thus the consequences of both the growth and charge dynamics and the electro-collection (partial charging and decreasing electro-collection with particle size respectively) as detailed below.

Figure 9 shows the penetration of a particle, P ($P=1-\eta=C_p/C_{po}$) calculated from equation (4) versus particle diameter for different mean $Ni.\tau$ products taking into account the mean charge per particle and the charged fraction presented above. The particle penetration would correspond to particle size distribution downstream of the DBD if an aerosol containing an iso-concentration of all particle size was injected in the DBD and charged only by diffusion, without taking into account particle growth dynamics. These calculations can be used to depict the size distributions presented in Figure 7.

Figure 9: Calculated electro-collection efficiency according to particle charging with $10^7 < \text{Ni} \cdot \tau < 5 \cdot 10^{12} \text{ s} \cdot \text{cm}^{-3}$

The high penetrations are related to partial charging for ultra fine particles and to low electrical mobilities for larger particles. Maximum collection is reached for 10 nm particles. If the calculated penetrations are compared with the measured particle size distributions, the shapes of the curves are similar in the intermediate particle size. The minimum penetration (10 nm) is different from the minimum of the size distributions around 20 nm, different assumptions to deal with this shift are discussed below. Only the particle growth dynamics can account for the boundaries below 10 nm and above 30 nm.

To sum up, the particle size distributions of the particles (cf. Figure 7 and numbers from 1 to 5) are related to both particle growth and charge dynamics and electro-collection:

There are few particles under 6 nm (1) due to fast agglomeration consuming primary nano-particles and to eventual initial electro-collection of the high electrical mobility nano-particles formed by ion-induced nucleation.

The first mode around 10 nm (2) is related to nucleation of condensable SiO_x species and partial charging; some of these particles are not charged and thus not collected.

Few particles are detected around 20 nm (3), which corresponds to particles growth dynamics and high particle electro-collection efficiencies.

The second mode around 30 nm (4) is related to Brownian agglomeration of particles from the first mode. All the particles are charged but weaker electrical motilities of particles leads to weaker electro-collection than for smaller particles.

There are no particles larger than 50 nm (5), due to moderate particle concentration and a transit time shorter than characteristic agglomeration time for the 20-50 nm particles preventing growth by Brownian agglomeration.

To account for the discrepancy between the results of the electro-collection model and particle size measurements electric field, particle charge and particle transit time could be involved. The calculated electric field is valid, as the model has been validated by injection in the discharge of particle in well-controlled conditions. In the model, the particles are supposed to get charged only by diffusion with a linear trajectory. Three additional effects should be taken into account to deal with particle charging.

Energetic photons emitted by the excited molecules may lead to particle charging by photo-emission increasing mean charge per particle and probably modifying the charge-diameter relation.

Particles can be trapped in potential wells between space charges left by the FD increasing the transit time and the probability of electro-collection.

At last, the effect of particle trajectory on charging should be considered. Indeed, particle charging rate and subsequent kinematics influence the ion density seen by a particle according to its size, probably leading to a different charge-diameter relation than the ones established in quasi-stationary ion density profile.

4. Conclusions

Without a precursor, particles are only detected downstream of the DBD when filament-surface interactions occur. With a Silane precursor, plasma-volume interaction leads to the formation of nano-particles in both Filamentary Discharge (FD) and Townsend Discharge (TD).

Both filament-surface interaction in N_2 and plasma-volume interaction with Silane lead to bimodal particle number size distributions corresponding to nucleation and agglomeration modes. The dynamics of particle formation by nucleation and of size evolution by agglomeration are similar whatever the origin of the condensable species is (from the brief and localized cathode spot on the surface at the base of the discharge filament or from gas-phase reactions with a Silane precursor in FD or in TD).

With respect to thin SiO_x film growth mechanisms, when a Silane precursor is used, these measurements prove that nano-particle production and electro-deposition are involved in the film formation. To account for the particles below 50 nm being included in the layer (confirmed by characterization of particles downstream of this deposition reactor), a similar selective size-dependent particle charging and electro-collection mechanism is involved in both TD and FD, even if the charging conditions are very different due to different charge dynamics coupled to particle trajectory. Despite similar structures, the layer is formed closer to the precursor injection in FD than in TD, implying faster formation, growth and charging of particles in FD compared to TD. Indeed, the higher local volume energy density in FD than in TD leads to higher local concentrations of both active species involved in chemical reactions to form nano-particles, and of ions involved in particle charging.

These mechanisms may also arise when a different gaseous organo-silicon precursor is used such as tetraethoxysilane (TEOS) or tetramethylsilane (TMS). Nano-particles of defined structure and size could be used to reach specific properties of the film as far as electro-deposition is controlled versus the dynamics of formation and growth and the charging conditions related to applied voltage and frequency.

The charge per particle reached in plane-to-plane FD is higher than in quasi-stationary ions density profiles of DC corona. Transient charging conditions i.e. in varying electrical field and charge densities seems favourable, additional charging mechanisms and charging conditions leading to the higher charge require further investigations.

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