Deposition of SiO$_x$ thin films using hexamethyldisiloxane in atmospheric pressure plasma enhanced chemical vapor deposition

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Abstract. The atmospheric pressure plasma enhanced chemical vapor deposition method was used to study the enhancement of the particle growth and thin layer deposition. For this purpose, an atmospheric pressure plasma jet was used to deposit silicon oxide compounds on a (100)-silicon wafer substrate. In this parametric study, hexamethyldisiloxane (HMDSO) was dissociated under different plasma jet parameters. It was found that by varying the working gas, the treatment time and jet parameters, such as nozzle-to-substrate distance and input energy, it is possible to influence the particles size and the morphology of the thin film. The choice of the working gas plays a major role in the formation of nanoparticles and the surface texture. This study was focused on the particles growth and how the growth can be controlled by tuning the parameters mentioned. Particles size of up to 100 nm was achieved under optimized conditions.

1. Introduction

Atmospheric pressure plasmas offer wide opportunities for industrial and biomedical applications. Unlike the chemical vapor deposition (CVD) and the plasma enhanced chemical vapor deposition (PECVD) methods, the atmospheric pressure plasma chemical vapor deposition (APECVD) is easy to integrate into in-line processes making expensive and complicated vacuum techniques obsolete [1, 2]. In particular, atmospheric pressure plasma jets (APPJ) are widely used for APECVD. Depending on the jet-system, the plasma discharge between the electrodes can be realized by either a DC or an AC power supply. In thermal jets, the power supply is realized by a continuous or pulsed DC voltage, where in most non-thermal jets the power is mainly supplied in a pulsed mode with an AC voltage in a frequency range from several kHz to GHz [3]. It is possible to induce a plasma through many different discharge methods. The most common discharge types in jets are dielectric barrier discharges, RF or MW discharges, corona discharges and arc discharges. Plasmas contain numerous types of particles, like charged electrons and ions, excited and neutral species.

The discharge can be used for different types of surface treatments, e.g. surface cleaning, surface activation, nanoparticle production and deposition of thin films of different materials by using precursors [4, 5, 6, 7]. In the last case, the plasma is used to dissociate the precursors through collisions with charged particles, which break the bonds of the precursor molecules. This leaves

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behind an additional number of particles, as electrons, ions, precursor fragments and radicals. These radicals are unstable molecules containing an unpaired valence electron, which makes them highly chemically reactive and, thus, important for formation of particles and growth of thin films, since they spontaneously dimerize by reducing the energy level of forming new stable compounds [8]. Organic molecules can produce radicals by absorbing ionizing photons. In addition to the introduced particle species, the plasma also produces UV radiation as a result of radiative recombination processes between electrons and ions. [9]. Radicals are therefore not only produced within the ionized working gas and in the plasma reaction with the precursor, but also on the substrate surface, creating gaps and open bonds on which newly formed molecules can attach.

In this study, we used an APPJ to dissociate hexamethyldisiloxane (HMDSO, C\textsubscript{6}H\textsubscript{18}OSi\textsubscript{3}), a monomeric substance consisting of a Si-O-Si core, where each silicon atom is linked to three additional methyl groups.

The works of Creatore et al. [10] and Benedikt et al. [11] have shown that the dissociation of HMDSO is initiated by charge-exchange reactions with plasma ions followed by dissociative recombination reactions with electrons [10]. As a product of the dissociation process, low molecular radicals (Si, O, SiO, CH, OH, CO, CO\textsubscript{2}) and molecules of higher mass (including hydrocarbons, aldehydes, carboxylic acids and oligomers) are produced. The products of the dissociation process are then transported outwards of the reaction zone creating the opportunity to start the polymerization process. The detailed mechanisms of particle growth and thin film deposition under atmospheric pressure conditions are not well understood [12]. However, it is agreed that the formation of nanoparticles takes place in several stages. Identified as the first stage, a nucleation process leads to the formation of clusters of a critical size, at which the particles are as likely to grow as to decay [13]. The main process for nucleation in a thermal plasma reaction is rather unclear, since it can be driven by physical conditions of a super-saturated vapor, where there is no need for the presence of ions as nucleation sites. But it can also be driven by chemical conditions, where nucleation starts from sub-critical clusters which grow to critical size by undergoing a sequence of chemical reactions rather than by physical condensation [14]. In a second stage, where coalescent coagulation takes place, the particles randomly attach to each other via mutual collisions due to the collection of electrostatic charges. This charge effect is also known in relation with space plasma, e.g. taking place in pre-solar nebula, circumstellar, circumplanetary and cometary environments described in more detail by Horanyi et al. [15]. In the stage of coalescence, the growth process continues and is strongly dependent on the temperature, the primary particle size and the precursor used [16, 17]. A detailed assessment of particle nucleation and growth in thermal plasma was given by Girshick et al. [13].

2. Experimental setup

In this experiment, a common type of thermal APPJ was used, namely, FG5001 [18, 19] (Plasmatreat GmbH, Steinhagen, Germany). It consists of a cylindrical discharge chamber containing a center electrode surrounded by a ring electrode located on the outer wall. The inside of the outer wall is partially covered with a dielectric layer, in order to realize a sufficiently long discharge to generate the plasma. The working gas supply is connected to an additional pre-chamber above the central electrode. Both chambers are connected through a turbulence grid that contains diagonally drilled holes providing a rotational drift motion of the gas. This ensures a rotation of the discharge minimizing the erosion of the electrodes. The FG5001 is operated in a pulsed mode, whereby a square wave signal is adjusted by the plasma cycle time (PCT). The pulse duration at 100% PCT equals the pause duration for a given frequency range from 17 kHz up to 25 kHz [20].

A pure (100)-silicon wafer of a size of 1 cm\textsuperscript{2} was rinsed with isopropanol and dried with compressed air to serve as a substrate. The substrate was attached to a sample holder and then placed on a moving table, on which the substrate travels across the effluent of the plasma jet. Figure 1 shows the setup of the APPJ, which was used for sample processing with HMDSO.

The plasma was generated at a frequency of 19 kHz, with 100% PCT and a constant working gas of flow rate of 30 slm. The flow rate was controlled by a MKS MF1 mass flow controller. The liquid
HMDSO was heated up to 343 K and then introduced into the nozzle region by bubbling nitrogen (N₂) at a constant rate of 1 slm through the liquid.

The sample was then moved at different speeds across the effluent of the jet, thus varying the treatment time. The nozzle-to-substrate distance was also varied in order to change the particle growth time in the effluent and the substrate surface temperature; the working gas was switched between nitrogen and air. Additionally, the initial power for plasma generation was varied by changing the generator's voltage in the range 240 V up to 320 V. In order to optimize the particles growth for this system, the following variation plan was systematically carried out:

- The nozzle-to-substrate distance was adjusted to 3 mm, 5 mm, 6 mm and 8 mm.
- The substrate treatment time was varied by changing the traversing velocity in steps of 5 m/min from a minimum velocity of 5 m/min to a maximum of 30 m/min.
- The plasma generator's voltage was changed in steps of 20 V.
- The working gas was changed from nitrogen to air and all previous adjustments were repeated.

SEM imaging was used to analyze the surface structure and the particle size of the deposited films on a ZEISS Ultra Plus 55 scanning electron microscope. The resulting images were examined using ImageJ [22]. The deposited particles were counted and their corresponding diameters were determined.

3. Results and discussion

The parameters varied, namely, nozzle-to-substrate distance, treatment time and working gas type, had a significant effect on the size of the particles and the surface structure of the thin film. The observations confirmed the recent results on the same plasma source proposed in [20]. However, varying the input power in the range quoted did not produce any observable changes. This is due to the high kinetic energy of the plasma species exceeding the binding energies by several orders of magnitude [23]. Thus, plasma generation by itself was sufficient to split the precursor.

Figures 2a and 2b show that using the best possible parameters for particle growth (nozzle-to-substrate distance of 6 mm, power of 300 V, and traversing velocity of 5 m/min) and nitrogen as a working gas produced cauliflower-like nanoparticles forming a particle-laced film with a rough surface structure.
If the nozzle-to-substrate distance is small, the path and, hence, the time for particle production in the gas phase are reduced, preventing the production of big nanoparticles. By increasing this distance, the time for particle growth and agglomeration in the gas phase of the effluent is extended, which is observed by a shift of the average particle size to bigger structures, as shown in figure 3. The histograms show the particle size by superposing the histograms of the two distances.

The treatment time variation results in adjusting the particle sizes in the range from 50 nm up to 100 nm. The treatment time, which is controlled by adjusting the traversing speed, had a considerable effect on the resulting thin film. Figure 4 shows a superposition of the velocity variation histograms, illustrating that an increase of the traversing speed reduces the time for particle formation on the surface. This is a good indication that the particles growth takes place not only in the gas phase of effluent, but also on the substrate surface. With a shorter time of substrate treatment, the time for particle formation and chemical reactions on the substrate surface is reduced. Thus, only small particles are allowed to adhere and connect to the surface structure.

![Figure 3. Overlay of particle size histograms for nozzle-to-substrate distance for a sample treated by nitrogen plasma.](image3)

![Figure 4. Overlay of particle size histograms of treatment time (by varying the traversing speed) for a sample treated by nitrogen plasma.](image4)

Changing the working gas from nitrogen to air increases the oxygen content in the reaction phase. This results in a complete change of the thin film structure. Instead of a cauliflower-like structure built from nanoparticles as shown in figure 2a, a quartz-like consistent thin film with a few embedded nanoparticles was found (figure 5a). The significant difference compared to the nitrogen plasma is caused by the higher reactivity due to the oxygen radical content and the additional oxygen atoms, leading to a stronger fragmentation of HMDSO, inhibition of particle formation, all this favoring the growth of a SiO$_2$ film [11]. The plasma reaction in combination with a higher oxygen content leads to a stronger oxidation of the methyl groups and in an increase in the formation rate of smaller molecules [24]. In addition to the increase of oxygen in the plasma reaction, Reuter et al. [25] have observed that the presence of UV radiation in the effluent originating from the discharge region produces atomic oxygen by dissociating molecular oxygen and ozone in the substrate region. As suggested by Ellerweg et al. [9] and Sonnenfeld et al. [26], this leads to an additional increase in the oxygen concentration favoring the production of trimethylsilanol (C3H10OSi), hexamethyldisilane (Si2C6H18), pentamethyldisiloxane (C5H16OSi2), heptamethytrisiloxane (C7H21O2Si3), and octamethyltrisiloxane (C8H24O2Si3), which release methyl groups in the subsequent electron impact ionization reaction. Additionally, it is assumed that oxygen can directly react with the silicon atoms [12, 9, 25]. Moreover, these reactions, due to the increased presence of oxygen, probably cause the observed smooth structure the thin film. Compared to the pure nitrogen plasma, there is no significant particle formation, leaving a quartz-like thin film on the substrate. Only locally are there some small nanoparticles embedded within the thin film, as seen in figure 5b.
investigations should focus in the film thickness and confirm the effect on the growth rate and the surface texture, since an increase in the oxygen content due to the use of air as a working gas leads to a bigger supply of atomic oxygen, favoring the formation of SiO$_2$. To confirm the above explanatory approaches and unveil the chemical reaction pathways, further investigations should focus in the film thickness and its chemical composition.

4. Conclusions
The investigation of a SiO$_2$ thin film and particle growth using an APPJ and HMDSO as a precursor showed that nitrogen plasma with well-chosen setup parameters can lead to a customized particle size distribution, favoring a faster film growth with a rough surface structure due to bigger particles compared to air as a working gas. Parameters such as nozzle- to-substrate distance and treatment time have a significant effect on the surface structure of the films, whereas the variation of the generator voltage has only small effects in the particular setup used. In particular, the working gas has a major effect on the growth rate and the surface texture, since an increase in the oxygen content due to the use of air as a working gas leads to a bigger supply of atomic oxygen, favoring the formation of SiO$_2$. To confirm the above explanatory approaches and unveil the chemical reaction pathways, further investigations should focus in the film thickness and its chemical composition.

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