Chemistry and mechanisms of powder formation in the afterglow plasma polymerization of silicon-organic precursors with a cold atmospheric plasma jet

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Abstract: The particle formation was studied by an electrical low pressure impactor as a function of precursor flow rate and total gas flow rate. It is found that the substrate position is affecting the particle measurement. A SEM analysis of an embedded particle in the coating indicates that heterogeneous reactions contribute to the powder formation.

Keywords: atmospheric plasma, thin film deposition, particle, powders.

1. General

The deposition of functional coatings by atmospheric pressure (AP) plasma jets is of great interest to industry. The attractiveness of the technology arises from good compatibility with in-line production processes, and from high deposition rates resulting in short process times. One of the main limitations for industrial use, however, can be the formation of particles. The particles can become incorporated inside the coating usually degrading its performance, can be emitted into the atmosphere posing a health risk, and lead to a high consumption of precursor associated with high deposition cost. To understand particle/powder formation and to develop strategies for its reduction is therefore essential for a full breakthrough of AP plasma jets for thin film deposition, although first industrial installations exist [1,2].

For this paper we studied the mechanisms of particle formation when plasma-polymerizing HMDSO in the afterglow of an AP plasma with a strong energy gradient. The influence of different process parameters on particle formation is studied. The coating is analyzed by electron microscopy and the particle formation in the gas phase by using an electrical low pressure impactor.

2. Experimental

A commercial cold plasma jet source modified by us for thin film deposition was used [3-5]. For plasma excitation the center electrode is driven by an excitation frequency between 17 and 22 kHz, with pulse peak heights of approx. 5 kV. The flow rate of the compressed air gas for plasma operation is 29 slm. For thin film deposition a precursor injection was integrated into the plasma system at the exit of the plasma nozzle. In this region the plasma transits from the excitation volume to the relaxing afterglow plasma jet (plume). As precursor in the PE-CVD process hexamethyldisiloxane (HMDSO) was used. The precursor was mixed with nitrogen and vaporized in an oven at 85 °C before feeding into the plasma. Monomer mass flow was varied between 3 and 40 g h⁻¹. Fig.1 shows a drawing of the plasma jet. For SEM analysis of the coatings an Dual Beam FEI Helios Nanolab 600 with FIB unit was used. Gas phase particle analysis was accomplished by an electrical low pressure impactor (ELPI+, Dekati, Finland) classifying particle sizes from 6 nm to 10 µm in 14 size ranges (“boxcars”). In the graphs the average aerodynamic particle size in spherical approximation of each “boxcar” is given. Particles were collected at a horizontal distance \( l = 0 \) mm from the plasma jet and the tube length \( L \) between particle collection and the actual measurement device was typically 2 m.

3. Results and Discussion

A typical particle size distribution observed in the gas phase in the direct vicinity of the plasma jet exit is displayed in Fig.2. The smallest particle size detectable by our analyzer is around 6 nm and in this size range we also observe the largest number of particles. We did not find evidence for a significant formation of particle sizes larger than 5 µm.
Fig. 2. Particle size distribution at a monomer flow rate of 40 g/h and at an analyzer-plasma jet distance D = 0 cm and substrate - plasma jet distance d = 21 cm.

Fig. 3 presents the number of particles and their sizes as a function of the mass flow rate of the precursor. We observe the highest densities for the smallest particle sizes at all flow rates investigated. It can be also seen that with increasing precursor flow rate the formation of larger particles (> 500 nm) is induced. This can be related to a higher gas phase concentration of the monomer leading to an increased probability of particle-forming collisions of the monomer molecules and its fragments.

An additional route for the formation of particles are heterogeneous reactions at the exit of the plasma jet housing or at the substrate surface. To study the influence of the substrate we varied the vertical distance D between plasma jet exit and particle collector at a fixed distance d between plasma jet and substrate. As can be seen from Fig. 5 the number of particles increases when the particle collector is moved away in downstream direction from the plasma jet exit (except for the largest particle size detected at around 760 nm).

To better understand the particle formation mechanism(s) we measured the particle sizes as a function of the gas flow rate that is used for plasma operation. Fig. 4 shows the particle densities for two different flow rates. Except for the smallest particle size the number of particles is smaller for the higher flow rate. This could be attributed to the higher gas speed that is reducing the transit time of the monomer molecules in the plasma region at the nozzle exit. Since less time is available for reactive particle-forming collisions the number of particles generated is smaller. This could indicate that particles are formed mostly by homogeneous gas phase reactions. In addition, by increasing the gas flow rate the relative concentration of the precursor in the gas flow as well as the energy/molecule is reduced. This can also contribute to the generation of fewer particle (c.f. Fig. 3).

Fig. 4. Particle numbers and sizes as a function of two different gas flow rates of 29 and 50 standard litre per minute (slm). Measurement at an analyzer-plasma jet distance D = 0 cm and a substrate - plasma jet distance d = 21 cm.
The substrate was at a distance $d = 21$ cm from the plasma jet exit for these measurements. The behavior in Fig. 5 could be explained by a similar argument as for Fig. 4. At a location further downstream the protoparticles and monomer molecules have more time for additional particle-forming reactions. As a consequence this may lead to the formation of larger and more particles. However, another argument can be evoked that can also explain the observations in Figs. 4 and 5 in a different way. The gas flow exiting from the plasma jet is predominantly flowing downstream until it hits the substrate surface. There the gas flow is diverted and partially reflected. In this process it is possible that particles are moving upwards again and only after this reflection are collected from the particle analyzer. The results in Fig. 6 seem to indicate that this latter explanation cannot be ruled out. Fig. 6 compares the particle densities in the gas phase for three distances of plasma jet exit and substrate.

Fig. 6 Particle numbers and sizes as a function of the distance $d$ between plasma nozzle and substrate. Measurement at an analyzer-plasma jet distance $D = 0$ cm and a HMDSO flow rate of 40 g/h.

It can be seen from Fig. 6 that for nearly all particle sizes the number of particles decreases when the substrate is further relocated from the plasma jet exit. This shows that the substrate location clearly influences the number of particles in the gas phase. This might be due to the induction of heterogeneous particle formation or the above mentioned gas diversion affecting the particle measurement. In the latter case the likelihood of particles entering the analyzer is significantly reduced when the substrate is far away from the nozzle exit. Likewise the results in Fig. 5 could be affected by the rising diverged gas flow leading to an increased number of particles when the analyzer is closer to the substrate.

An additional experiment (not shown) where we measured the time between turning on the precursor flow and the onset of the increase in the particle number signal seem also to support this explanation. This time delay is getting larger with increasing distance of the substrate from the jet exit. It is therefore likely that the diversion of the gas flow is affecting the measurements.

Fig. 7 shows an SEM image of a coating obtained under particle-generating conditions. The particle sizes in the coating are mostly below 5 μm and therefore correspond to the particles sizes found in the gas phase. However, occasionally also larger particles are found. Since a very small number of particles ($< 100$/cm$^3$) is not reliably detected by the analyzer we assume that most particles embedded in the coating were already formed in the gas phase.

Fig. 7 SEM image with embedded particles in the coating

It is very interesting to have a look at the cross section of such particles inside the coating by using fast ion beam (FIB) preparation.

Fig. 8 Two cross sections of an embedded particle by FIB preparation at different cut planes
Fig. 8 shows two cross sections of such a particle embedded in the coating. It can be seen in the cross sections that the particle has not a spherical geometry. Instead its irregular shape indicates a heterogeneous origin. This could be caused for example by a substrate-surface reaction or a particle sputtering/release reaction from the nozzle exit. A gas phase reaction under very fast non-equilibrium conditions might be also an explanation, but seems not very likely. It has to be pointed out that analysis of further particles is necessary to check if this observation is true for all particles.

An EDX analysis of the particles shows that the particle are composed of Si and O only. Typically there is no carbon found, which seems to indicate that the particle growth does not favor the inclusion of carbon and/or the reaction of carbon-containing fragment in the particle formation steps.

In summary the gas phase analysis gives indication that particle growth occurs in the gas phase and is affected by the effective residence time and the monomer concentration in the jet exit zone. It is also found that the substrate and its location is affecting the number and sizes of particles that are detected by the analyzer. The corresponding gas flow diverging effects can affect the particle measurement. This effect should be not neglected when interpreting the gas phase particle measurements. SEM measurements in combination with FIB preparation indicate that at least some particles are of heterogeneous origin.

5. References


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