

Plasma based aerosol processes for nanocomposite thin film deposition at low temperature and atmospheric pressure

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The aim of this work is to develop a new method to coat thermosensitive materials with a nanocomposite thin film. It is based on the coupling of an atmospheric pressure plasma and of an aerosol formed from a suspension of nanoparticles (Nps) in a liquid. The plasma dissociates the liquid molecules to create reactive species which interact with the NPs in the gas bulk or at the surface to make a nanostructured thin film. This method could work in roll to roll configuration and be therefore useful for inline coating of large two-dimensional substrates like polymer films.

The atmospheric pressure plasma is a low temperature plasma generated in argon at atmospheric pressure by a dielectric barrier discharge i.e. by applying an AC high voltage on electrodes separated by a gas gap and covered by a solid dielectric. It has been developed to create dense thin films by AP-PECVD (Atmospheric Pressure- Plasma Enhanced Chemical Vapor Deposition). High quality thin films like water or oxygen barriers [1] or antireflective and passivating layers of silicon crystalline solar cells [2] are obtained with this method. Usual precursors are gases or liquid vapour. The low temperature plasma activates these precursors which polymerize at the surface to form the thin film. The coating is uniform, dense but usually amorphous. Recently, the idea of using NPs as precursors came up [3]. One interest of NPs is that their large size as compared to that of liquid or gas molecules leads to high growth rate. Moreover, NPs synthesized by a method like sol-gel have well defined and controlled characteristics which cannot be so easily achieved using PECVD. If NPs and liquid are simultaneously introduced in the plasma, a nanocomposite thin film is obtained.

The aim of this work is to improve the properties of the nanocomposite thin film through the control of the process parameters including the discharge voltage waveform. NPs in the plasma were characterized using laser scattering. Thin film were characterized by SEM, AFM, XRD, IRTF, XPS, and wettability. Calculation of NPs trajectories and numerical modelling of both gas flow and NPs transport in the gas were developed. The results were obtained as a function of the process parameters like gas flow, discharge voltage amplitude and frequency, NPs or NPs aggregate size, charge and sticking coefficient to the substrate. These results allow to better understand the experimental measurements and to optimise the process parameters required to achieve specific nanocomposite thin film characteristics.

The NPs are TiO₂ NPs of 20 nm diameter. A percentage of 1% of weight is dispersed in isopropanol. The aerosol is made with a nebulizer or an atomizer. The

liquid of the droplets is evaporated before entering the plasma. All the NPs are included in a droplet aggregates. Isopropanol vapours and NPs aggregates having a size between 100 nm and 2 µm are injected in the plasma using an argon stream.

The observation of the thin film shows NPs aggregates stucked together or inserted in a carbon matrix. Porosity can be significantly changed. Depending on conditions, NPs aggregates are more or less coated by a carbon film. This was previously observed in the case of ZnO NPs in octane or octadienne, the hierarchical roughness leading to super hydrophobic organic-inorganic nanocomposite thin film [3]. Our contribution deals with the explanation and control of the thin film characteristics.

According to XPS measurements, up to 17% of TiO₂ is included in the carbon matrix made from isopropanol polymerization [4]. An original method to independently enhance the NPs transport to the surface and the dissociation rate of the vapour is found. It is based on the design of a special voltage waveform. The use of a given frequency enables to first control the TiO₂ percentage while a second frequency allows to control the NPs aggregates coating and the porosity of the nanocomposite thin film. The higher is the discharge frequency and thus the discharge power, the larger is the liquid dissociation rate. In addition, the NPs aggregates become rapidly negatively charged in the plasma and the electrostatic force controls their transport to the surface as far as the frequency is low enough. If the frequency gets too high, the electrical field oscillation traps the NPS aggregates in the plasma. Consequently, there exists a threshold frequency above which NPs are trapped.

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