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Synthesis of silica-like coatings containing metal-oxide nanoparticles by nitrogen-based dielectric barrier discharge

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Abstract: The aim of this work is to study the relationships between the parameters of an Atmospheric Pressure Townsend Discharge sustained in a gas mixture containing metal-oxide nanoparticles and the properties of the multiphase films produced.

Keywords: nanocomposite, dielectric barrier discharge, colloidal solution

1. Introduction

Plasma Enhanced Chemical Vapor Deposition has already demonstrated its ability for the realization of nanocomposite thin films. In most cases, low-pressure plasma processes are used. However, recent works show the usage of atmospheric pressure processes to deposit such thin films with catalytic [1], optical and/or anticorrosive properties [2]. Furthermore, deposition of thin films at atmospheric pressure opens the way to low-cost and eco-friendly industrial developments [3].

In this work, we use colloidal solutions of metal-oxide nanoparticles (TiO_2 or ZnO) dispersed in an organosilicon monomer (hexamethyldisiloxane), atomized in an dielectric barrier discharge (DBD) working in the Townsend mode, to deposit silica-like layer containing nanoparticles.

The aim of this paper is to study the relationship between the deposition process and the characteristics of the obtained coatings.

2. Experimental details

The DBD is ignited at atmospheric pressure between two parallel electrodes ($3\times3cm^2$) made of metalized paint deposited on 635µm thick alumina plates, with 1mm gas gap. In this paper, the discharge is sustained using sinusoidal voltage with amplitude ranging from 11 kV_{pk-pk} to 17 kV_{pk-pk} and excitation frequency ranging from 0,3 to 8 kHz sinusoidal voltage. A 3 slm gas flow is injected from one side of the discharge (longitudinal gas injection). Such a configuration has been chosen as it allows studying the deposit properties as a function of the equivalent gas residence time in the discharge area. The main gas is nitrogen. In order to deposit a silica-like matrix, hexamethyldisiloxane (HMDSO) as monomer and nitrous oxide (N_2O) as the oxidizing gas have been chosen.

The strategy used to get nanocomposite thin films is based on the atomization of a stable colloidal solution in the plasma phase. Briefly, ex-situ synthesized metal-oxide nanoparticles are functionalized and mixed with HMDSO in order to get a stable colloidal solution (3 wt%). This solution is injected in the gas mixture using a pneumatic injector (LEGATO 110 Fischer) coupled to a nebulizer (Burgener Mira Mist CE). The obtained colloidal aerosol is then evaporated (1 meter long heated line at 70°C) before reaching the discharge chamber. This allows to avoid the presence of liquid droplets during the deposition process. Finally, the ignition of an Atmospheric Pressure Townsend Discharge in this gas mixture (N_2/N_2O/HMDSO + NPs) leads to a nanocomposite coating on the substrate.

Two types of nanoparticles were used: Titanium dioxide nanoparticles (TiO_2 NPs), anatase phase, 20 nm in diameter, and Zinc oxide nanoparticles (ZnO NPs), 5 nm in diameter.

The discharge is characterized mainly by electrical measurements. The voltage applied to the electrodes is followed by means of a high voltage probe, and the total discharge current is measured through a 50Ω resistor in series with the cell discharge. In order to measure the evolution of the current as a function of the position along the gas flow, some measurements were also done using a ground electrode divided in four disconnected strips (see Fig. 1), each strip being connected to a 200 Ω resistor (total equivalent resistor = 50 Ω), and the 4 channels being acquired simultaneously using a data acquisition board. It has been checked that the splitting of the ground electrode does not perturb the discharge homogeneity, nor the total discharge current. The presence of particles is checked thanks to the following of the amplitude of the harmonics of the discharge current as a function of the gas residence time [4].

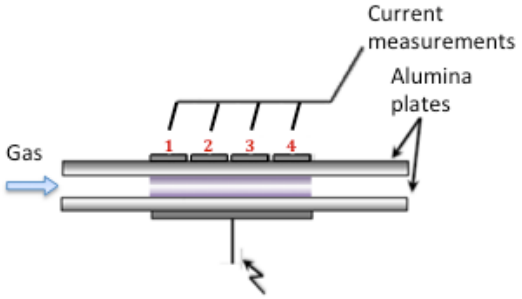

Fig. 1. Schematic of the split electrode.

The thin film properties are studied using spectroscopic ellipsometry, profilometry, atomic force microscopy (AFM), scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDS), X-ray Photoelectron Spectroscopy (XPS) and Fourier Transform Infrared Spectroscopy (FTIR) in transmission and ATR (Attenuated Total Reflectance) modes. Raman and SEM analyses confirm the presence of nanoparticles.

3. Study of the colloidal solutions

The colloidal solutions have been analysed previous to the atomisation process: the hydrodynamic radius of agglomerates present in the solution is obtained by the Dynamic Light Scattering analysis (DLS) by a Zetasizer, and size distributions of nanoparticles are measured through transmission electron microscopy (TEM). Fig. 2 shows an example of such measurements in the case of a solution with 3 weight% of ZnO in pure HMDSO. Besides single particles also collectives were observed. By using a higher magnification of 500 000 the crystalline structure is clearly visible (Fig. 2B).

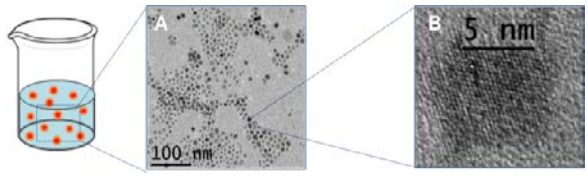

Fig. 2. TEM analysis of 3 weight% of ZnO in HMDSO. A: 25 000X magnification, B: 500 000X magnification.

The size distribution, shown in Fig. 3, is deduced from these TEM measurements. The mean diameter amounts to about 5-9 nm.

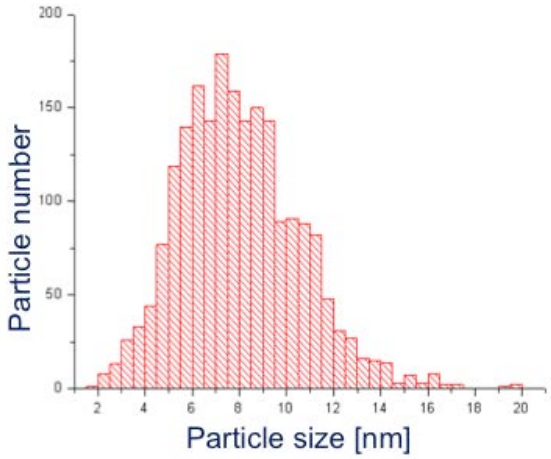

Fig. 3. Size distribution of ZnO particles in HMDSO calculated from TEM analysis.

The studies done by DLS have shown that the stability of the solution increases if HMDSO is not used pure: hence, the adding of ethanol (TiO_2 case) or pentane (ZnO case) leads to better dispersed solutions.

4. Study of the coatings containing metal-oxide NPs

First we check the influence of adding either ethanol or pentane on the discharge working domain and on the silica coatings. Fig. 4 shows FTIR spectra of coatings realized with 7 ppm of HMDSO, 170 ppm of N_2O, and an increasing amount of pentane (0, 7, and 14 ppm), keeping a fixed discharge power (0.25 W/cm^2). These measurements, and associated XPS analyses, confirm that the pentane does not strongly influence the SiO_x layer, neither its composition. No additional carbon is detected.

On the other hand, the adding of pentane leads to a decrease of the SiOx growth rate, as shown by the absorption intensity of SiO band in Fig. 3, and confirmed by ellipsometric measurements (8.7 nm/min; 7,8 nm/min and 6 nm/min with respectively 0, 7, and 14 ppm of pentane). The amount of HMDSO injected in the discharge being always identical (7 ppm), and the discharge power being kept constant, this leads to the conclusion that the reactive species (mainly N_2 metastable states) reacts strongly with pentane. This loss of energetic species decreases the fragmentation of HMDSO and lowers the number of HMDSO radicals necessary for the coating leading to lower growth rates.

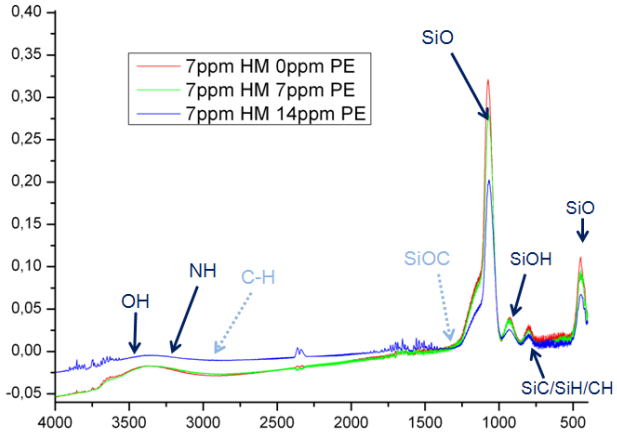

Fig. 4. FTIR measurements of silica-like coatings.

When adding TiO_2 or ZnO NPs in the gas phase, the first interesting point is that these NPs do not influence the discharge regime, the DBD remaining stable in the Atmospheric pressure Townsend mode.

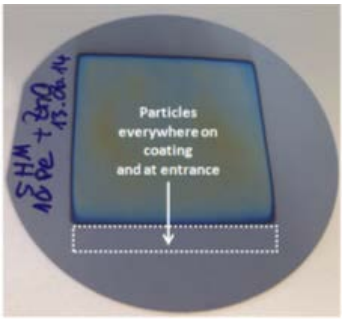

Fig. 5. Example of a silica coating with ZnO NPs

Fig. 5 shows an example of coating realized on a silicon wafer with ZnO NPs: the visual analysis of the coating clearly shows that particles are present everywhere on the coatings, and preferably at the entrance of the discharge (and even before). This can be explained looking at the main forces acting on the NPs (hydrodynamic force and electrostatic force).

FTIR analysis does not show any additional peak of ZnO compared to coatings deposited without NPs (Fig. 4). This is probably due to the fact that ZnO related vibration peaks are located at around 500 cm^{-1}, which is at the same location as the as the second Si-O band and is thereby not recognized.

However, SEM analyses confirm the presence of nanoparticles dispersed over the matrix (Fig. 6A). Taking a closer look at single particles by scanning the topography, we saw that they are well embedded inside the matrix (Fig. 6C). Besides single particles also agglomerates have been identified (Fig. 6B). However, first EDS measurements seem to indicate a rather low percentage of Zn in the coating (around 1%).

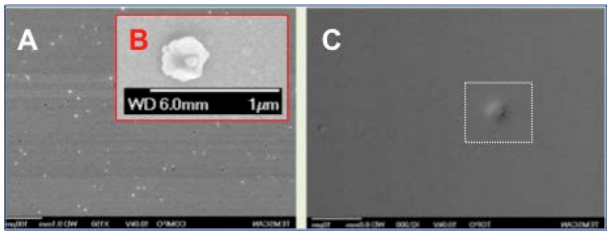

Fig. 6. SEM analysis. SEM analysis. A: ZnO particle distribution inside SiOx matrix (backscattering mode)
B: Agglomerate on the surface C: Topography image of embedded ZnO particle inside SiOx matrix

5. Conclusion

Townsend dielectric barrier discharge can be used for the deposition of nano-composite coating at atmospheric pressure. Both TiO_2 NPs and ZnO NPs have been successfully used, dispersed in a silica-like layer.

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7. References

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