Synthesis of SiO_x thin films on glass substrate: a comparison between atmospheric and low-pressure plasma processes

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Abstract: Atmospheric pressure dielectric barrier discharges (AP-DBD) and low-pressure plasma (RF sputtering) were used to synthesize SiO_x coatings on glass surfaces. In the AP-DBD operated in helium with HMDSO for PECVD, current-voltage characteristics revealed homogeneous glow discharge regime. Plasma-deposited thin films were then analyzed by FTIR and water contact angle to link their surface chemistry with their wetting properties. Micro-scratch analysis were also performed to assess the mechanical properties of the films. Both thin films exhibit alike properties, a positive outcome for the AP-DBD process.

Keywords: AP-DBD, Intelligent glass, HMDSO, FTIR, Water contact angle, Micro-scratch

1. Introduction

The glass industry has been expanding its market with the increase of highly valuable intelligent glass products. Active commodities such as electrochromic [1], photochromic [2] or thermochromic [3] glasses reveal changes of the glass optical properties as a reaction to applied forces. On the other hand, passive products do not require to be under constraint to act, opening the way to more eco-responsible intelligent glass products by limiting maintenance and energy spending. These solutions are often the results of nanostructured thin films with diverse properties, such as self-cleaning [4] or anti-reflective [5], deposited on glass surfaces.

By modifying the wetting properties of a surface by thin film deposition, it is possible to create optical coatings presenting hydrophobic or hydrophilic characteristics [6]. The functional groups responsible for these chemicals characteristics can be used to improve the efficiency of a wide array of technological applications such as analytical instruments [7], surgical procedures [8], energy production [9], transportation [10], and food packaging [11].

The industrial viability of optical coatings greatly depends on their mechanical properties, such as adherence to the substrate and resistance to wear and tear. In this context, wet chemical solutions can give access to a variety of new properties. However, such processes based on the surface application of either cream, oil, or spray often present poor adherence to glass substrates. This greatly limits the durability of such treatments and thus significantly increases glass maintenance costs.

Due to their dry chemical nature, thin films deposited by plasma processes are generally more adhesive to the surface than their wet counterparts. In many cases, this leads to a better longevity of the coatings and therefore greatly reduces the need for maintenance. Plasmas can also give place to eco-friendly processes as they eliminate the need for solvents and require low consumption of chemicals and energy.

In the last years, non-thermal plasmas at atmospheric pressure, for example dielectric barrier discharges (DBDs), have been proposed as an alternative to low-pressure plasma processes for continuous, in-line deposition of thin films over large area substrates [12]. This aspect is particularly interesting for the glass industry that often requires large-area deposition of functional, nanostructured coatings with very high throughputs.

In this study, hydrophilic coatings are synthesized on glass substrates using a dielectric barrier discharge at atmospheric pressure with helium as working gas, hexamethyldisiloxane (HMDSO) as precursor, and oxygen as oxidant gas. The chemical and mechanical properties of these plasma-deposited coatings are compared to those obtained by the well-established RF sputtering technique in a low-pressure plasma.

2. Experimental procedure

The experiments were conducted with a plane-to-plane DBD cell contained in a vacuum chamber. The cell is comprised of two electrodes made from metallic paint deposited on alumina plates. A schematic of the DBD cell is shown in *figure 1*.

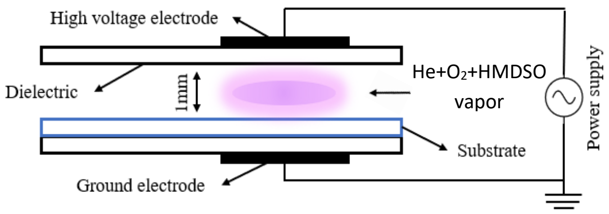

Fig. 1. Schematic of the dielectric barrier discharge cell for plasma deposition of functional coatings in non-thermal plasmas at atmospheric pressure.

Glass substrates were cleaned for 30 minutes. A 3 steps bathing cycle using ethanol, acetone and distilled water in a sonic bath was performed. Substrates were rinsed with distilled water between each 10 minutes step. Once dried with pressurized air, a substrate was placed on the ground electrode. The gaseous gap between the glass substrate and the high-voltage electrode is set to 1 mm using two glass slides placed on the side; these glass slides also force the flow of gas along the substrate surface.

Gases, helium as carrier gas, HMDSO as precursor vapor (after evaporation), and oxygen as oxidant gas, were injected in the gap using a diffuser located at one end of the high-voltage electrode. Discharges were produced by applying a sinusoidal voltage (12 kHz) to inject and maintain a power of 1 mW/cm^2 into the plasma. Electrical measurements were recorded by a high voltage probe (Tektronix P6015A) and a wide-band terminated current transformer (LILCO Ltd. 13W5000), both signals were displayed on an oscilloscope (Tektronix DPO5204B).

An FTIR spectrometer (Vertex 70, Bruker) was used to perform the measurements of coating's chemistry at the beginning, centre and end of the deposit zone on the glass substrate. Measurements were normalized using the Si-OH peak corresponding to the bending vibration mode of the bond [13], at 909 cm^{-1}, dominating all spectrums.

A contact angle goniometer (OneAttension Theta, Biolon Scientific) was used to measure the static contact angle with the software (Attension) controlling the camera and sessile drop process. A droplet of 15µL in volume is deposited on the surface at the beginning, centre and end of the deposit zone on the glass substrate.

A micro-scratch tester (CSM) was used to assess the adhesion and scratch resistance of the coating [14, 15]. The tests were performed with a Rockwell type C tip of 100 µm radius, a starting load of 0.03 N and a final load of 15 N over a 2 mm distance at a speed of 4 mm/min.

3. Results and discussion

On *figure 2*, electrical measurements are shown for a power of 1 mW/cm^2 in the presence of glass substrate. The applied voltage (V_a) appears as coloured dots while the discharge current (I_m) are coloured lines. Each discharge current curve presents typical characteristics of homogenous discharges with current pulses lasting between 5 to 10 µs [16]. In addition, the shape of the peaks is characteristic of glow discharges in helium gas at atmospheric pressure [17]. Hence, coatings were deposited under homogenous glow discharges.

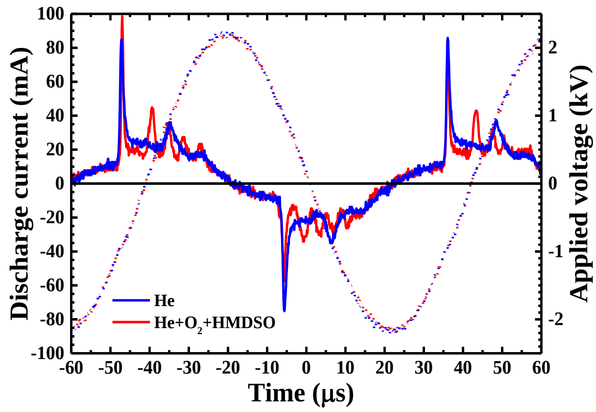

Fig. 2. Current-voltage characteristic of homogenous discharges with or without precursor and oxidant gas for 1 mW/cm^2 power.

The glass samples were under vacuum for 15 minutes before treatment to minimize the impurities in the discharges. Atmospheric pressure treatment lasted for 35 minutes, with 1.5 sccm oxidant gas, 0.04 sccm of precursor and 3 L/min helium carrier gas.

Fourier-transform infrared spectroscopy was performed on the treated surface to analyze the chemical composition of the coatings. Results are shown on *figure 3*. In both atmospheric-pressure and low-pressure made samples, hydroxyl Si-OH groups are noticed with the large band from 2800 to 3650 cm^{-1}; this is a typical feature during deposition of hydrophilic coatings. The atmospheric pressure coating also reveal a peak at 1025 cm^{-1}, associated to the asymmetric vibration mode of the Si-O-Si bond [13]. This indicates that the silica-like lattice is more disordered than the one obtained in low-pressure plasmas.

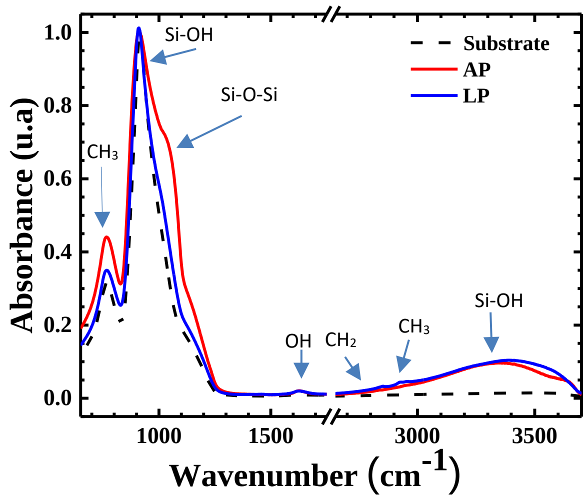

Fig. 3. FTIR measurements of coatings at atmospheric (red) and low (blue) pressure.

While their impact is certainly minimal, the low-pressure coating contains trace amounts of organic impurities with CH_2 and CH_3 small blobs at 2854 cm^{-1} and 2971 cm^{-1} respectively, which can be attributed to undesired carbon residues in the reactor. Additional measurements are currently underway to optimize the obtained coatings and their chemistry.

Table 1. Peak Assignments.

CH_3	767cm^{-1}
Si-OH	909cm^{-1}
Si-O-Si	1025cm^{-1}
OH	1626cm^{-1}
CH_2	2854cm^{-1}
CH_3	2971cm^{-1}
Si-OH	2800-3650cm^{-1}

Contact angle measurements were done to characterize the wetting properties of the coatings. *Figure 4* shows that the static contact angle on the low-pressure coating was 50°. As for the atmospheric pressure coating, it was 51.3±1.4°, representing the mean value obtained from measurements at beginning, centre and end of the deposit zone on the glass substrate. These values are characteristic of hydrophilic coatings [18].

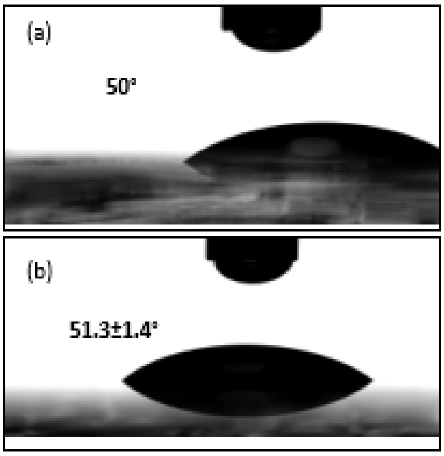

Fig. 4. Contact angle measurements.
(a) Low Pressure (b) Atmospheric Pressure

Micro-scratch testing was performed on the coatings to assess their mechanical properties. *Figure 5* shows no delamination of the coatings, which testifies for their good adherence to the glass substrate. Both coatings present plastic deformation (circles) resulting from the compression and tension of the layer under moving stress. The observed cracks are attributed to the glass substrate under the coatings breaking down violently once the scratch test was completed. In-situ observations during the tests, with a video camera mounted on the scratch tester, were also made to understand the complex formation mechanisms of defects in both the thin films and at the interface with the glass substrate.

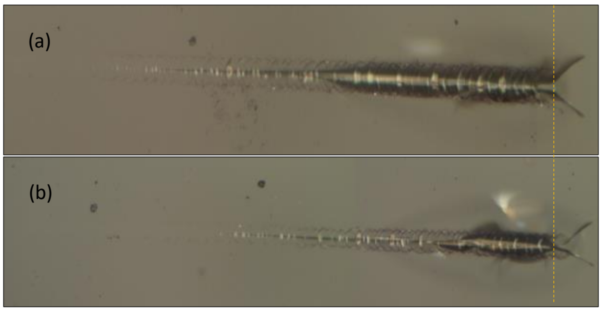

Fig. 5. Optical microscope pictures of micro-scratch performed on coatings (a) Low Pressure (b) Atmospheric Pressure. Maximum load of 15N (orange dashes).

This demonstrates that both low-pressure and atmospheric-pressure coatings possess adequate adherence and scratch resistance properties, which is promising as we would have expected low-pressure coatings to possess much better mechanical properties due to their highly ordered silica lattice.

4. Conclusion

Electrical properties of non-thermal DBD at atmospheric pressure have been shown for the admixture O_2+ HMDSO added to the nominally pure He plasma. All coatings were produced in the homogenous glow discharge regime. The chemical structure of the coatings was analyzed by FTIR. It was shown that the coatings presented an important quantity of hydroxyl hydrophilic groups. Contact angle measurements confirmed the hydrophilic properties of the coatings with contact angles in the 0-65° range depending on the experimental conditions. Micro-scratch testing assessed the adherence of the coatings on the glass substrate and their resistance to stress.

This demonstrates that atmospheric pressure plasma processes can mimic very well the properties of silica coatings obtained in low-pressure plasmas, a very promising result for applications requiring continuous, in-line deposition of coatings over large area substrates.

5. References

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