Analysis of the deposition of Si-based coatings by a cold plasma jet at atmospheric pressure

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Abstract: Si-based coatings were deposited on aluminum substrates by a cold plasma jet at atmospheric pressure. The plasma has been characterized by optical emission spectroscopy, while the coatings have undergone XPS in-depth analysis. The effect of hydrogen additions on the plasma characteristics and the coatings compositions has been evidenced. The influence of the precursor inlet design on the coatings properties has also been examined.

Keywords: PECVD, atmospheric pressure, Si-based coatings, OES, XPS

1. Introduction
Barrier coatings are widely used in the industry. In particular, silicon oxide films have a good oxidation resistance. These films can be deposited using different methods: thermal chemical vapor deposition (CVD) [1], plasma enhanced CVD (PECVD) at low pressures [2], PECVD at atmospheric pressure [3-4]… CVD processes require high temperatures. For the PECVD processes the thermal energy is replaced by electrical energy. This allows treating the substrates at lower temperatures [5-6]. Furthermore, PECVD at atmospheric pressure exempts from maintaining vacuum in a chamber and allows treating large surface areas in continuous processes [3, 4, 7]. While using PECVD for deposition processes, some authors inject the precursor in the afterglow region and place their substrates downstream from the plasma [2, 3, 4, 7]. In this remote PECVD system, the substrate is not damaged by energetic ions.

A lot of precursors are used for the deposition of silicon-based coatings: tetraethoxysilane [1, 3, 4], hexamethyldisiloxane [2], hexamethyldisilazane [3, 5, 6, 8], tetramethylsilane [9], tetramethyldisiloxane [3], tetramethylocyclotetrasiloxane [3], hexamethylocyclotrisilazane [8], bis(trimethylsilyl)carbodiimide [5]… In this work, Si-based coatings were deposited on aluminum substrates by a commercial cold plasma jet at atmospheric pressure and by introducing hexamethyldisilazane in the post-discharge. The effect of hydrogen additions on the plasma characteristics was investigated by optical emission spectroscopy. XPS in-depth analyses were used to characterize the coatings obtained by a pure nitrogen plasma and a nitrogen-hydrogen mixture plasma with two different precursor inlet designs.

2. Experimental details
The cold plasma jet used in this work was the commercial Plasmabrush® PB1 system. It was operated in a chamber filled with nitrogen at atmospheric pressure. The main plasma gas was nitrogen. A small amount of hydrogen was added to nitrogen in some cases. The precursor used for the deposition was hexamethyldisilazane (HMDSN). This liquid precursor was vaporized and mixed with a separate nitrogen flow before being introduced in the plasma post-discharge. Two precursor inlet designs were used as shown on Fig.1. The first one was a horizontal inlet perpendicular to the plasma jet and parallel to the substrate. With the second one the precursor is injected vertically inside the plasma and towards the substrate.

![Fig.1 Precursor inlet designs.](image)

The plasma has been characterized by optical emission spectrometry. The coatings have been characterized by XPS depth profiles.

3. Plasma characterization by OES
The evolution of the optical emission spectra of the plasma as a function of the gas composition and the applied voltage was studied. The applied voltage was varied between 3 and 4.5 kV. The plasma gas was nitrogen or nitrogen with a hydrogen concentration ranging from 1 to 3%. Fig.2 describes the variation of the nitrogen optical emission intensity (315.9 nm) as a function of the applied voltage for different hydrogen concentrations in the plasma with a nitrogen flow rate of 20 l/min. It shows that the curve observed for a pure nitrogen plasma (without hydrogen) can be divided in 3 parts. The first part is nearly horizontal at low voltages. The second part is a transition between 3.3 kV and 3.6 kV. The third part shows a nearly linear increase of the emission intensity with the applied...
voltage. When hydrogen was added in the plasma the transition was not observed. The evolution of the intensity was nearly linear with the applied voltage. Increasing the hydrogen concentration decreased the optical emission intensity for the recorded line.

This effect of the hydrogen addition in the plasma is observed at small hydrogen concentrations. For a 0.2% hydrogen concentration in the plasma, the transition has almost disappeared (Fig.3). Above 0.4%, no more transition is seen.

Fig.3 Variation of the nitrogen optical emission intensity (315.9 nm) as a function of the applied voltage for various low hydrogen concentrations in the plasma (with a 20 l/min nitrogen flow rate).

Fig.4 presents the same results but as a function of the hydrogen concentration in the plasma instead of the applied voltage. The optical emission intensity of this nitrogen line is maximum for a small concentration of hydrogen in the plasma. This concentration depends on the applied voltage used. It increases by decreasing the applied voltage.

As shown on Fig.5, for a smaller nitrogen flow rate (10 l/min instead of 20 l/min), the transition appears at lower voltages (between 3.2 kV and 3.5 kV).

Although the plasma source producer does not consider the addition of hydrogen in the plasma in its operating manual, these results show that it stabilizes the plasma.

Fig.5 Variation of the nitrogen optical emission intensity (315.9 nm) as a function of the hydrogen concentration in the plasma for different applied voltages (with a 20 l/min nitrogen flow rate).

4. Si-based coatings

Si-based coatings were deposited on aluminum substrates by nitrogen and nitrogen-hydrogen (with a hydrogen concentration of 3%) mixture plasmas. The coatings were characterized by XPS depth profiles. Fig.6 shows a XPS depth profile of a coating obtained by a pure nitrogen

Fig.6 XPS depth profile of a coating deposited on aluminum by a pure nitrogen plasma with the horizontal precursor inlet design.
plasma (without hydrogen) with the horizontal precursor inlet design. In that case the film contained non only silicon but also significant levels of oxygen, and carbon. Aluminum from the substrate was also observed.

When hydrogen was added in the plasma (Fig.7) the carbon and nitrogen atomic concentrations in the film decreased. It has already been observed that the presence of hydrogen in the plasma tends to reduce the carbon content in a coating obtained with organosilicon precursors [5]. The film obtained in this work is thin and aluminum is observed at the surface of the coating.

These results suggest that the precursor doesn’t mix well with the plasma and is therefore misused for the deposition process. For this reason a new precursor inlet design was used. With this design the precursor is injected vertically inside the plasma and towards the substrate. Fig.8 shows a XPS depth profile of a coating obtained by a pure nitrogen plasma (without hydrogen) with the vertical precursor inlet design. Comparing this profile with the one of Fig.6 it is clearly seen that the thickness of the film is increased when the vertical precursor inlet design is used instead of the horizontal one. The film composition has also changed. The oxygen atomic concentration is increased but the nitrogen and carbon atomic concentrations are decreased with the new precursor inlet design.

As it was observed with the horizontal precursor inlet design, when hydrogen was added in the plasma (Fig.9) the carbon and nitrogen atomic concentrations in the film decreased. It became nearly silicon dioxide. As for the coating obtained by a pure nitrogen plasma the thickness of the film is increased when the vertical precursor inlet design is used instead of the horizontal one (comparing this profile with the one of Fig.7).

5. Conclusion

The addition of a small quantity of hydrogen (less than 3%) in a nitrogen plasma has a large influence on the plasma stability as it has been evidenced by its optical emission properties and on the composition of the Si-based films deposited. The precursor inlet design influences the composition and the thickness of the coatings.

Acknowledgements

The authors would like to thank the Walloon Region for financial support.

References
