Effects of hydrogen addition in nitrogen atmospheric pressure plasma on its optical and electrical properties and silicon-based deposits compositions

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Abstract. Si-based coatings were deposited with a cold plasma jet (Plasmabrush® PB1 from Reinhausen Plasma) at atmospheric pressure with nitrogen as main carrier gas and hexamethyldisilazane (HMDSN) as precursor. Effects of hydrogen addition on the plasma characteristics and the coatings compositions have been evidenced with optical emission spectroscopy (OES), power measurements and XPS in-depth analyses. The intensity evolution of the nitrogen line (at 315.9 nm) with the applied voltage has a sigmoid shape for the pure nitrogen plasma but a quite linear one with hydrogen addition (up to 3%). Based on OES spectra, the presence of the NH specie in the nitrogen-hydrogen plasmas has been evidenced (around 336.0 nm) but not in the pure nitrogen plasmas. Although the plasma power is similar for both gases, the nitrogen atomic concentrations in the films as evidenced by XPS were lower with the nitrogen-hydrogen plasmas than with the pure nitrogen plasmas indicating a chemical effect of the presence of hydrogen in the plasma.

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) \cite{1}, plasma enhanced CVD (PECVD) at low pressures \cite{2}, PECVD at atmospheric pressure \cite{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 \cite{5-6}. Furthermore, atmospheric pressure PECVD exempts from maintaining vacuum in a chamber and allows treating large surface areas in continuous processes \cite{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 \cite{2-4, 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 \cite{1, 3-4}, hexamethyldisiloxane \cite{2}, hexamethyldisilazane \cite{3, 5-6, 8}, tetramethylsilane \cite{9}, tetramethyldisiloxane \cite{3}, tetramethylecyclothetrasiloxane \cite{3}, hexamethylecycloisilazane \cite{8}, bis(trimethylsilyl)carbodiimide \cite{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.
effect of hydrogen additions on the plasma characteristics was investigated by optical emission spectroscopy (OES) and power measurements. XPS in-depth analyses were used to characterize the coatings obtained by pure nitrogen and nitrogen-hydrogen mixture plasmas.

2. Experimental details
The cold plasma jet used in this work is the commercial Plasmabrush® PB1 system from Reinhausen Plasma (figure 1). This system consists in a central powered electrode surrounded by a grounded electrode with a dielectric between them. It was operated in a chamber filled with nitrogen at atmospheric pressure. The main plasma gas is nitrogen (with a 20 l/min flow rate) or nitrogen (with the same flow rate) with a 3% volume concentration of hydrogen. The precursor used for the deposition is hexamethyldisilazane (HMDSN 98.5% from ABCR). This liquid precursor (with a 56 g/h flow rate) is vaporized and mixed with a separate nitrogen flow (3 l/min) before being introduced in the plasma post-discharge. A new plasma source head in polyoxymethylene was made for this purpose (figure 2) and was used only for the deposition process (not for the plasma OES and electrical measurements performed without any precursor). Precursor mixture is injected at the end of the new plasma source head (figure 3). The aluminum substrate (cut in a 36 µm thickness Reynolds aluminum foil) is put at a distance of 5 mm from the new plasma source head.

![Figure 1. Commercial Plasmabrush system.](image1)

![Figure 2. New plasma source head for the precursor injection.](image2)

![Figure 3. Design of the new plasma source head.](image3)

The plasma is characterized by optical emission spectrometry with the HR4000CG spectrometer from Ocean Optics. The wavelength range is 200-1100 nm with a 0.75 nm resolution. The optical fiber is placed vertically below the plasma (looking inside the plasma source). Each spectrum is recorded with a 1 second exposure time (except when specified).

The power delivered to the system is calculated from current and voltage measurements (average over 10 ms). The current sensor is the CWT015B/2.5/700 sensor from Powertek. It is composed of a Rogowski coil and an integrator. Its work principle is described in [10]. Its frequency bandwidth ranges from 150 Hz to 2.2 MHz. The coil is wrapped 3 times around the cable placed between the grounded electrode and the ground. The applied voltage is measured using a high voltage probe (TESTEC HVP 15HF, bandwidth: 50 MHz). Both measurements are recorded (one record every 200 ns) with the Tektronix TDS5052 oscilloscope (bandwidth: 500 MHz, maximum sample rate: 2.5 GS/s).

The coatings are analyzed by XPS depth profiles with a PHI-Quantum 2000 spectrometer. The spectrometer is characterized by a monochromatized Al Kα primary X-ray beam and a photoelectron take-off angle of 45 degrees against the sample normal direction. Analysis quantification is based on sensitivity coefficients proposed by the equipment manufacturer. In-depth profiles are obtained by alternating 4 keV-1µA ion sputtering steps and analysis sequences. Sputtering rate is evaluated on iron at 8nm/min.

3. Plasma optical characterization
The evolution of the optical emission spectra of the plasma is studied as a function of the gas composition (N₂ and N₂-H₂ mixture) and the applied voltage varied between 3.0 and 4.5 kV.
The main optical emission lines observed in the optical emission spectra of pure nitrogen (figure 4) and nitrogen-hydrogen (figure 5) plasmas are the nitrogen second positive system bands [11-12]. CN violet system bands (around 385 and 388 nm [11]) are also visible on the pure nitrogen plasma spectra but disappear with hydrogen addition in the plasma. The carbon may come from the atmosphere pollutants or from the plasma source head. Although the main atomic hydrogen lines (at 486.1 and 656.3 nm [11]) were not observed in the nitrogen-hydrogen plasmas spectra, the presence of hydrogen in the plasma can be evidenced by the shoulder to lower wavelengths in the nitrogen band at 337.1 nm (figure 6). This shoulder corresponds with the NH band at 336.0 nm [11].

Figure 4. OES spectrum of pure nitrogen plasma at 4.5 kV (exposure time: 0.5 second).

Figure 5. OES spectrum of nitrogen-3% hydrogen plasma at 4.5 kV.

Figure 6. OES spectra of nitrogen with and without hydrogen plasmas at 3.6 kV showing the presence of the NH band for the nitrogen-3% hydrogen plasma.

The figure 7 describes the variation of the nitrogen line (at 315.9 nm) optical emission intensity with the applied voltage for nitrogen with and without hydrogen plasmas. The curve observed for pure nitrogen plasmas (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 3.7 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. This nitrogen line at 315.9 nm is representative of the OES spectrum area called brightness in this paper (figure 8).
4. Plasma electrical characterization

The applied voltage and current are measured for nitrogen and nitrogen-hydrogen plasmas at applied voltages ranging from 3.0 to 4.5 kV. The voltage lags the current by about 85 degrees (figures 9 to 12) which corresponds with a capacitive system such as in a dielectric barrier discharge (DBD). A lot of peaks can be observed on the current signal indicating the discharge is filamentary. When the applied voltage is increased more peaks can be seen. Hydrogen enhances the plasma filamentary behavior and therefore helps the plasma activation at lower voltages.

Figure 7. Nitrogen line (315.9 nm) intensity vs. applied voltage for pure nitrogen and nitrogen-3% hydrogen plasmas.

Figure 8. Brightness (spectrum area) and nitrogen line (315.9 nm) intensity vs. applied voltage for nitrogen-3% hydrogen plasma.

Figure 9. Current and voltage vs. time for pure nitrogen plasma at 3.3 kV.

Figure 10. Current and voltage vs. time for nitrogen-3% hydrogen plasma at 3.3 kV.

Figure 11. Current and voltage vs. time for pure nitrogen plasma at 4.5 kV.

Figure 12. Current and voltage vs. time for nitrogen-3% hydrogen plasma at 4.5 kV.
As for the nitrogen line optical emission intensity, the evolution of the power was studied as a function of the applied plasma voltage. This evolution is quite linear for nitrogen-hydrogen plasmas but has a sigmoid shape for pure nitrogen plasmas (figure 13). Therefore it partially explains the nitrogen line optical emission intensity evolution with the applied voltage. As the power is in similar range for both gases (except for applied voltages from 3.2 to 3.6 kV), there is also a chemical effect of hydrogen addition in nitrogen plasma.

5. Si-based coatings

Si-based coatings were deposited on aluminum substrates by nitrogen and nitrogen-hydrogen (with a hydrogen volume concentration of 3%) plasmas. The coatings were characterized by XPS depth profiles. The figure 14 shows a XPS depth profile of a coating obtained by pure nitrogen plasma (without hydrogen) with the new plasma source head (figure 2). In that case the film contained not only silicon but also significant levels of oxygen, nitrogen and carbon.

When hydrogen was added in the plasma (figure 15) the carbon and nitrogen atomic concentrations in the film decreased. It has already been observed that the hydrogen presence in the plasma reduces the carbon content in coatings obtained with organosilicon precursors [8].

6. Conclusions

The addition of a small quantity of hydrogen (3%) in nitrogen plasma has a large influence on the plasma properties as it has been evidenced by optical emission spectroscopy and electrical measurements as well as on the composition of Si-based films deposited with HMDSN.

Based on OES spectra the hydrogen addition (3% volume concentration) in the plasma produces the NH specie. It also “linearizes” the evolutions of the nitrogen line (at 315.9 nm) optical emission
intensity (representative of the OES spectrum area) and of the power with the applied voltage whereas these evolutions have a sigmoid shape for pure nitrogen plasmas. As a matter of fact, the total power is similar for both gases when the applied voltage ranges from 3.7 to 4.5 kV and at 3.0 kV but the nitrogen line optical emission intensity is different. Therefore there are chemical and electrical effects of hydrogen addition in nitrogen plasma.

Hydrogen addition in nitrogen atmospheric plasma changes the films composition. The coatings deposited with pure nitrogen plasma are SiO$_x$C$_y$N$_z$ but those deposited with nitrogen-hydrogen plasma are close to SiO$_2$.

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