Optical diagnostics of atmospheric pressure glow discharge in nitrogen with admixture of organosilicon

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The atmospheric pressure glow discharge in nitrogen with small admixture of different organosilicon compounds such as hexamethyldisilazane and hexamethyldisiloxane was studied by means of emission spectroscopy. The deposited films were studied by means of indentation techniques.

1. Introduction

In the industrial applications there is a great effort to develop techniques to control the surface properties of materials. There is a wide range of plasma enhanced chemical vapour deposition (PECVD) methods enabling to prepare coatings with well-defined wetting and sticking behaviour and good mechanical properties. The disadvantage of the low pressure PECVD techniques is that they demand expensive vacuum pumping systems. Moreover, there are difficulties to arrange the deposition system for large area depositions. Recently plasma deposition at atmospheric pressure becomes a promising technology due to its economical and ecological advantages. During last years there is a great interest in atmospheric pressure glow discharges (APGD) especially in the industrial applications. The glow discharge in different pure gases can be easily generated [1, 2, 3, 4], but in nitrogen which is from the technological point of view the most suitable gas the small admixture of oxygen to nitrogen can lead to the generation of filamentary dielectric barrier discharge instead of APGD [4]. The objective of the present work is to study the APGD in nitrogen with small admixture of different organosilicon compounds such as hexamethyldisilazane - C\textsubscript{6}H\textsubscript{19}Si\textsubscript{2}N and hexamethyldisiloxane - C\textsubscript{8}H\textsubscript{18}Si\textsubscript{2}O. These mixtures can be used for plasma deposition of thin films with desired surface and bulk properties.

2. Experimental

The deposition of thin films was carried out by atmospheric pressure glow discharges with the operation frequency of 5 kHz. The APGD was carried out between two electrodes covered with insulating glass plates. The type of discharge as concerns the filamentary or glow mode was determined from the current-voltage measurements. The films were deposited from different mixtures of organosilicon (hexamethyldisilazane - HMDSZ, hexamethyldisiloxane - HMDSO) with nitrogen on glass substrate put on the bottom electrode. The nitrogen was bubbled through liquid HMDSZ or HMDSO monomers to evaporate the monomer from the liquid to gaseous state. The nitrogen with organosilicon vapors was mixed with pure nitrogen. The flow rate of the pure nitrogen was 81/min, the electrode gap was 1 mm and the supplied power was 30 W in all cases. The emission spectra from the discharges were recorded with TRIAX550 spectrometer and some parameters such as vibration temperature of nitrogen were determined. The mechanical properties were studied by means of the depth sensing indentation technique using a Fischerscope H100 tester.

3. Results and discussion

Fig. 1 shows the typical emission spectra of the APGD discharge in nitrogen with a small admixture of monomer (hexamethyldisiloxane or hexamethyldisilazane). The spectra were recorded in the range of 300–800 nm. However, above 430 nm only second spectral order of grid was observed. Spectra consist of the molecular bands of second positive system of nitrogen (C\textsuperscript{3}Π\textsubscript{u} → B\textsuperscript{3}Π\textsubscript{g}) and in case of the APGD in nitrogen with monomer two CN bands of CN violet system (A\textsuperscript{3}Σ\textsuperscript{+} → B\textsuperscript{3}Σ\textsuperscript{-}) were observed. The first one at 388 nm was more intensive than the second one at 422 nm. Vibrational bands of nitrogen with a corresponding change of vibrational quantum number Δν = -2, -3 were used to calculate the vibrational temperature. De-
Table 1: Vibrational temperature of nitrogen determined for different flow rates of organosilicones.

<table>
<thead>
<tr>
<th>hexamethyldisiloxane</th>
<th>hexamethyldisilazane</th>
</tr>
</thead>
<tbody>
<tr>
<td>flow rate (l/min⁻¹)</td>
<td>T (K)</td>
</tr>
<tr>
<td>0.0</td>
<td>1883 ± 67</td>
</tr>
<tr>
<td>0.3</td>
<td>2011 ± 100</td>
</tr>
<tr>
<td>0.6</td>
<td>1967 ± 110</td>
</tr>
<tr>
<td>1.2</td>
<td>1962 ± 85</td>
</tr>
</tbody>
</table>

Table 4: Time variation of current and applied voltage of APG discharge.

![Figure 2](image)

Figure 2: Structure of CN band with position at 388.3 nm.

terminated values of vibrational temperature for different concentrations of organosilicones are listed in Table 1. The structure of the CN band with the position at 388 nm is plotted on the Fig. 2. This CN band was used for calculation of the integral intensity of the band. Fig. 3 shows the integrated intensity of the CN band vs. flow rate of organosilicon mixed to the pure nitrogen. The exponential increase of the integrated intensity was observed for both types of monomer, but in case of HMDSZ the integrated intensity was much higher. The measurement of the discharge voltage and current is presented in Fig. 4. Whereas applied voltage is sinusoidal, the current consists of two parts. The sinusoidal current course corresponds to capacitive current, the small peak represents the current of the APG discharge. Deposited films were homogeneous and microhardness was in the range from 0.2 to 0.3 GPa. The elastic modulus ranged from 10 to 25 GPa. The films showed high ductility and good adhesion to the substrate.

4. Conclusion

It was found that APGD can be generated not only in pure nitrogen but also in nitrogen with a small admixture of organosilicones. In case of higher concentration of HMDSO or HMDSZ the APG mode changes to filamentary mode. The APGD was studied by means of emission spectroscopy and the vibrational temperature of nitrogen was determined. The vibrational temperature varied from 1800 to 2000 K and only lightly depended on concentration of monomer added to the nitrogen. The properties of thin films were studied by means of the indentation technique, the hardness of films was about 0.2 – 0.3 GPa.

5. Acknowledgements

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6. References