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SPECTROSCOPIC MONITORING OF PLASMA DEPOSITION OF SILANE AND SILOXANE BASED THIN FILMS *

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The main part of this work is focused on the identification of the spectra measured during the plasma deposition using the vinyltriethoxysilane. The deposition process was carried out in a continual regime as well as in a pulsed regime with the varied relative pulse duration. The vinyltriethoxysilane was mixed in various ratios with oxygen. The oxygen to vinyltriethoxysilane flow rate ratios varied in the range from 0 to 73. We observed a decrease of the relative intensity of C_2 spectral bands with increasing pulse duration and a decrease of this spectral band with increasing flow rate of oxygen.

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1 Introduction

In the last years the plasma deposition of various thin films has been a subject of many studies. The special focus is on the layers based on organic molecules and organo-silicon molecules. The main objective of our experimental work was the monitoring of the RF low-pressure discharge by optical emission spectroscopy during the deposition process. The discharge was studied in two different regimes. The first regime was continual the second one was pulsed with the relative pulse duration varied between 0.005 and 0.5 at the repeating frequency between 10 and 500 Hz. The main part of this work was focused on the identification of the spectra observed during the plasma deposition using vinyltriethoxysilane. In Fig. 1 is given the structure of monomer used for deposition.

2 Experimental part

A schematic diagram of the device for low-pressure plasma deposition is given in Fig. 2. Inductively coupled RF discharge was used as the plasma source. During the whole experiment the working pressure was in the range from 1 – 1.1 Pa. Argon and oxygen lines were connected to the device. Argon was used only for cleaning of the reactor. The monomer was kept in the thermostat box what enabled obtain defined monomer pressure and keep flow rate constant. For optical emission spectra measurement the spectrometer Jobin Yvon Triax 550 was used.

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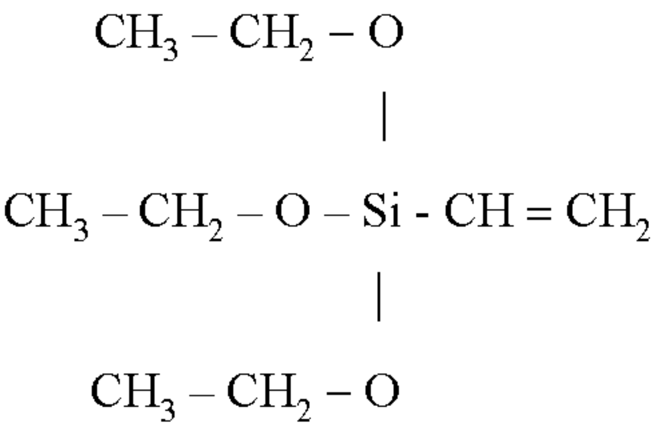

$$\begin{array}{c} CH_3-CH_2-O \\ | \\ CH_3-CH_2-O-Si-CH=CH_2 \\ | \\ CH_3-CH_2-O \end{array}$$

Fig. 1. Monomer structure

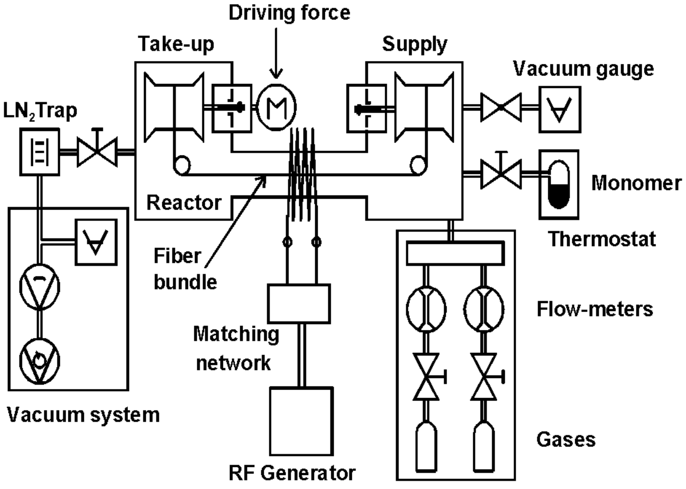

Fig. 2. Experimental device

3 Results

Initially, a small amount of nitrogen was added into the discharge to estimate the neutral gas temperature as a function of the total discharge power in the continual regime. Due to the low resolution of the nitrogen second positive spectra, our program Simul was applied [1]. The rotational temperature of (400 ± 50) K was obtained. Its value was more or less independent of the

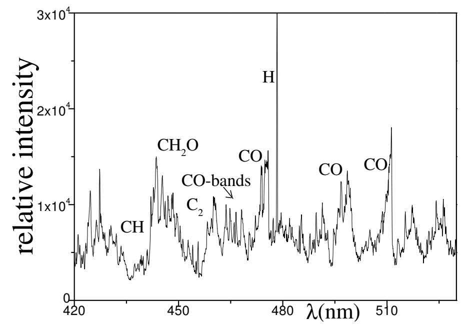

Fig. 3. Optical emission spectrum obtained during measurement of plasma deposition in a continual regime

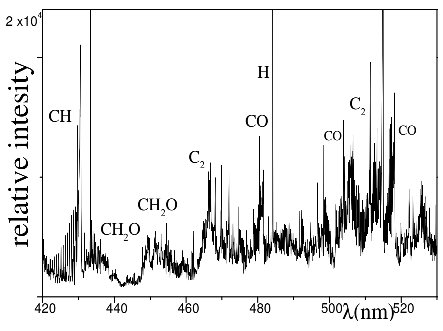

Fig. 4. Optical emission spectrum obtained during measurement of plasma deposition in the pulsed regime (pulse duration 1:9)

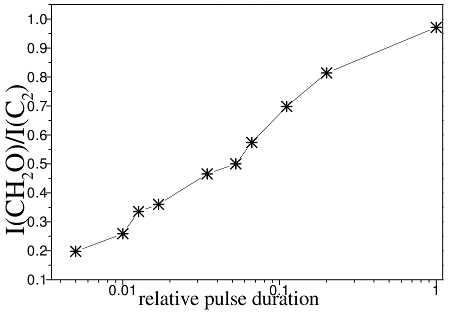

Fig. 5. Dependence of the CH_2O band intensity related to the C_2 band intensity as a function of the pulse duration

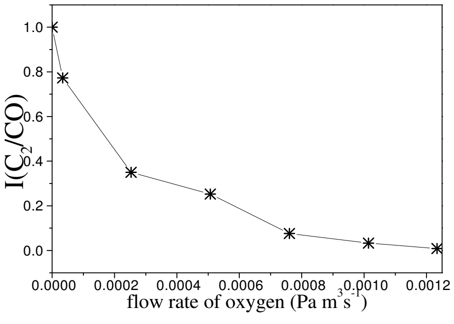

Fig. 6. Dependence of the C_2 band intensity related to the CO band intensity as a function of the oxygen flow rate

total discharge power. Additionally, the same spectral system as mentioned above, was used for calculation of the vibrational temperature. This quantity was established at (2850 ± 150) K and it was independent of the RF power, too. In the first set of experiments pure vinyltriethoxysilane was used. First of all, the plasma composition was studied initially in the continual regime under the following experimental conditions: the power was changed from 10 to 100 W, the gas pressure was about 1Pa, the monomer flow rate was 8.45×10^{-4} Pa m^3s^{-1}. The emission of the hydrogen lines and molecular hydrogen bands was remarkably high each time. Furthermore, many bands with very complex structure originating from the same spectral system were observed (see Fig. 3). Some of them were identified as the radiation of the CH_2O molecule [2]. The bands of CH_2O were observed in the zone from 380 to 522 nm. Some bands were observed at shorter wavelengths under 380 nm, no reference for them has been found up to now. Moreover, the CO bands (Angström system $B^1\Sigma$ - $A^1\Pi$ as well as and much weaker Herzberg system $C^1\Sigma$ - $A^1\Pi$) were observed.

The second part of our work concerned the pulse mode. The pulse duration was changed in the region from 1:1 to 1:999. The other experimental condition e.g. pressure, flow rates, were the same as in the first part. The spectrum obtained in the pulse regime is shown in Fig. 4. It appears to be completely different from the non pulsed plasma which was analysed as the first one. The presence of the very intensive hydrogen lines and molecular bands was characteristic for both regimes. Among the bands corresponding to the $\mathrm{CH_2O}$ molecule could be recognised only some bands with very low intensity. On the other hand, a strong emission of the $\mathrm{C_2}$ Swan system ($\mathrm{A}^3\Pi_g$ - $\mathrm{X}^3\Pi_u$) was observed. The intensities of both these bands are strongly dependent on the pulse duration. These results led to the idea to measure the dependence of the $\mathrm{C_2}$ and $\mathrm{CH_2O}$ band intensities as a function of the pulse duration. The results of these observations are shown in Fig. 5. The next part of this work was focused on spectroscopic observation during deposition using the vinyltriethoxysilane monomer with various oxygen to vinyltriethoxysilane flow rate ratio. This deposition was carried out in the pulsed regime (with pulses 1:9) with gas pressure of about 1.1 Pa. Oxygen flow rate was changed from 3.38×10^{-4} Pa $\mathrm{m^3 s^{-1}}$ (partial pressure of oxygen was 0.093 Pa) to 1.234×10^{-3} Pa $\mathrm{m^3 s^{-1}}$. The same spectral bands were identified during this experiment but the intensity of the CO spectral bands was stronger. Thus, this bands can be observed in more regions than before. In accordance with our estimations, the CO band intensities increased with increasing oxygen addition, whereas the intensities of $\mathrm{CH_2O}$ and $\mathrm{C_2}$ spectral bands were decreasing with the increase of the amount of oxygen.

4 Conclusion

In the present work, the plasma deposition process of the organosilicon thin layers by the emission spectroscopy was investigated. The dependencies of the $\mathrm{CH_2O}$ band intensity related to $\mathrm{C_2}$ as a function of pulse duration show highlighted that the character of optical spectrum approaches the continual regime with increasing energy (increasing relative pulse duration). More intensive $\mathrm{C_2}$ bands in higher intensity appear in spectrum with the shorter pulse duration. It is probably caused by the elimination of the vinyl group from molecule of monomer. Intensities of the $\mathrm{CH_2O}$ and CO bands grow much slower. In the case of long pulse duration we can suppose the preferential elimination of the ethoxy group. From the optical emission spectra measured during the plasma deposition using vinyltriethoxysilane with various amount of oxygen, a significant oxidation of all the components can be observed. The results obtained by the emission spectroscopy correspond with the physical properties of the prepared layers [3]. The dependence of the layer properties on the plasma conditions as well as the creation the appropriate kinetic model of the plasma processes during plasma depositions will be a subject of further experiments.

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