Spectroscopic Observation of Low Pressure Plasma Deposition of Thin Silane and Siloxane Based Films

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Abstract

The main part of this work is focused on the identification of the spectra measured during the plasma deposition using the vinyltriethoxysilane in a continual regime and also in a pulsed regime with the varied relative pulse duration and during deposition with an amount of oxygen added in various ratios. The next part is focused on spectroscopic observation during the plasma deposition using the hexamethyldisiloxane and γ-metacryloxyprophyltrimethoxysilane.

Introduction

The plasma deposition of various thin films has been a subject of many studies during last years. The special focus is on the layers based on organic molecules and organo-silicone molecules. The study of the deposition process is currently at the first stage. Our experimental work focuses on the optical emission spectroscopy during the RF low-pressure discharge deposition of the organosilicone thin films. The discharge was studied in two different regimes. The first of them was continual, the other 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 the vinyltriethoxysilane, in the following section the focus was on spectroscopic observation during plasma deposition using the hexamethyldisiloxane and γ-metacryloxyprophyltrimethoxysilane. Monomer structures as given in Fig.1.

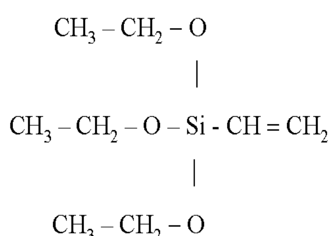

Fig.1a: Vinyltriethoxysilane (VTEO)

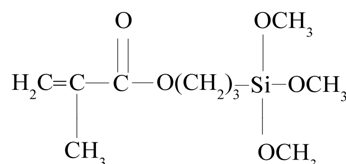

Fig. 1b: γ-metacryloxyprophyltrimethoxysilane

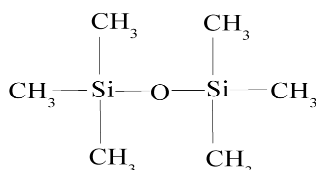

Fig.1c: Hexamethyldisiloxane (HMDSO)

Experimental part

A schematic diagram of the device for low-pressure plasma deposition is given in Fig. 2. As a plasma source the RF inductively coupled discharge was used. During the whole experiment gas pressure of 1-1,1 Pa was used. Argon and oxygen pipes are connected to the device. Argon is used only for purification of the reactor. The monomer is kept in the thermostat box so that the defined monomer pressure and its constant flow rate during the deposition process could be obtained. For optical emission spectra measurement a spectrometer Jobin Yvon Triax 550 with CCD detector was used.

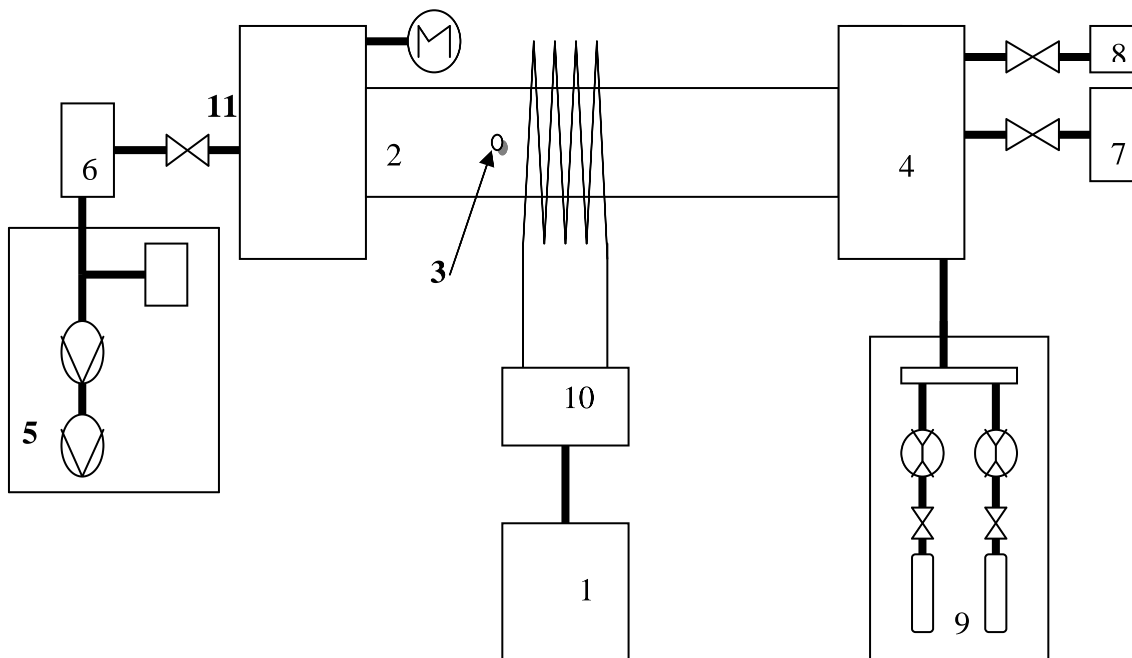

Fig.2: Scheme of the experimental device: 1-RF generator, 2-reactor, 3-point of the spectroscopic measurement, 4-supply, 5-vacuum system, 6-LN_2 trap, 7-monomer, 8-vacuum gauge, 9-gases (Ar, O_2), 10-matching network, 11-driving force.

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 results show the rotational temperature of

(400 ± 50) K, more or less independent of the total discharge power. Simultaneously the spectral system mentioned above was used for the vibrational temperature calculation.

This quantity was established at (2850 ± 150) K, also independent of the RF power.

The pure vinyltriethoxysilane was used in the first set of the experiments. The plasma composition was studied initially in the continual regime under the following experimental conditions: power was changed from 10 to 100 W, gas pressure was about 1Pa, monomer flow rate 0,5 sccm. The emission of the hydrogen lines and molecular hydrogen bands was remarkably high each time. Besides, many bands with very complex structure originating from the same spectral system were observed, see Fig 3a. Some of them were identified [2] as the radiation of the CH_2O molecule. The bands of CH_2O were observed in the region 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 much weaker Herzberg system $C^1\,\Sigma$ - $A^1\,\Pi$) were observed.

For the second part of our work the same experimental conditions were used and the pulse duration was changed from 1:1 to 1:999.

The spectrum obtained in the pulsed regime is shown in Fig 3a. It appears to be completely different from the non pulsed plasma, which was analysed as the first one. Among the bands corresponding to the CH_2O molecule could be recognised only some bands with very low intensity. On the other hand, a strong emission of the C_2 Swan system ($A^3\,\Pi g$ – $X\ ^3\Pi\ _u$) was also observed. The intensities of both these bands are strongly dependent on the pulse duration. The hydrogen lines and molecular bands were also present in the other regime.

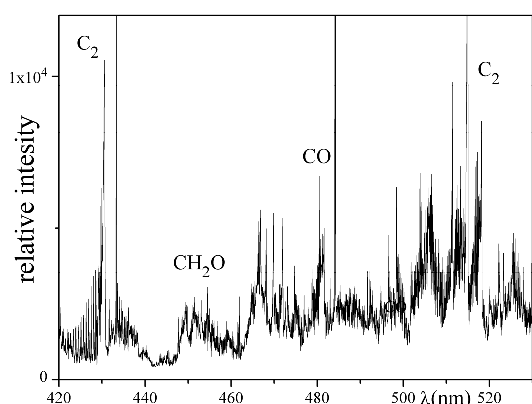

Fig. 3a: Optical emission spectrum obtained during measurement of plasma deposition using VTEO in pulsed regime (pulse duration 1:9)

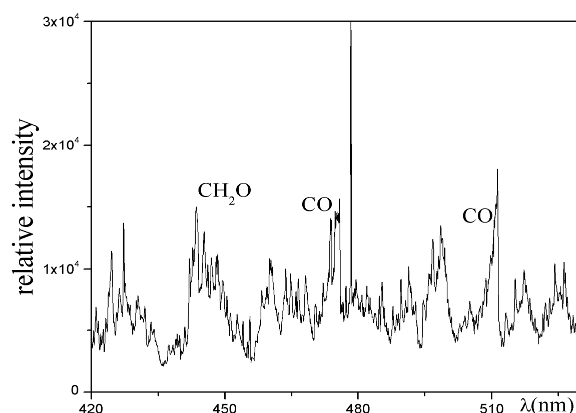

Fig.3b: Optical emission spectrum obtained during measurement of plasma deposition using VTEO in continual regime.

These results led to the idea to measure the dependence of the C_2 and CH_2O band intensities as a function of the pulse duration. The results of these observations are shown in Fig. 4.

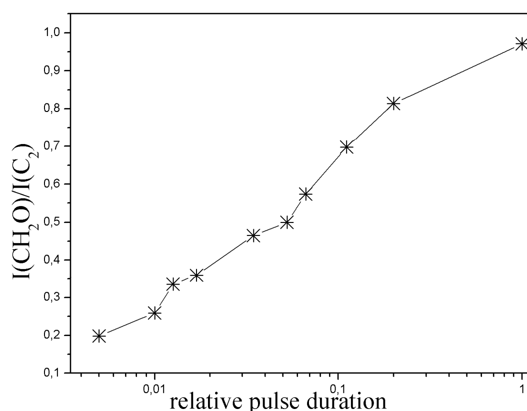

Fig. 4: Dependence of the CH_2O band intensity related to the C_2 band intensity as a function of the relative pulse duration.

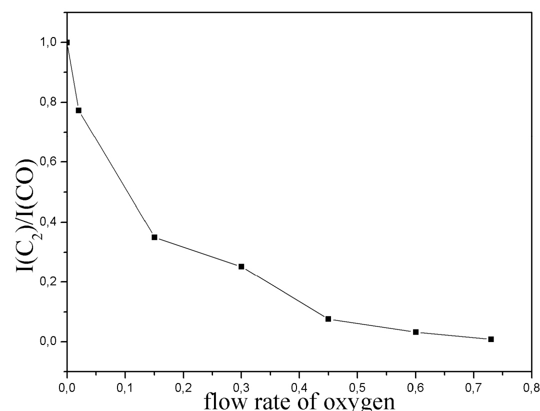

Fig.5: Dependence of the C_2 band intensity related to the CO band intensity as a function of the oxygen flow rate.

The second part of this work was focused on spectroscopic observations during the plasma deposition using the vinyltriethoxysilane monomer with various oxygen additions. This deposition was carried out in the pulsed regime (with pulses 1:9) and under the gas pressure of about 1,1 Pa. Oxygen flow rate was changed from 0,02 sccm (partial pressure of oxygen was 0,093 Pa) to 0,73 sccm.

The same spectral bands were identified during this experiment but the intensity of the spectral bands of CO was stronger. Thus, these bands can be observed in many other spectral regions than before. The CO band intensities, in accordance with our estimations, increase with the increase of oxygen addition, whereas the intensities of CH_2O and C_2 spectral bands were decreasing with the increase of the amount of oxygen.

Furthermore, hexamethyldisiloxane and γ-metacryloxyprophyltrimethoxysilane were used for plasma deposition in the continual regime and especially in the pulsed regime. Experimental conditions were the same as during the first part of the experiment. During the spectroscopic observations we have found out that lines and bands of hydrogen (H, H_2) and CH band (Angström system $A^2\Delta$ - $X^2\Pi$) were the most intensive ones in both regimes. In the spectra measured during the plasma deposition using hexamethyldisiloxane in pulsed regime, bands of CO^+ (first negative system $B^2\ \Sigma$ - $X^2\ \Sigma$) and bands of CO in the region of 450 – 500 nm the bands appeared in considerable intensities. The ratio of the relative intensity of CO^+ to total intensity of the spectrum increased with the decreasing pulse duration (Fig.6).

When using γ-metacryloxyprophyltrimethoxysilane for plasma deposition, besides hydrogen (H, H_2) and CH bands, many bands of CO (Angström system $B^1\Sigma$ - $A^1\Pi$ and triplet bands ($d^3\Delta$ - $a^3\Pi$) and bands of C_3 ($^1\Pi_u$ - $^1\Sigma_g^+$) were observed.

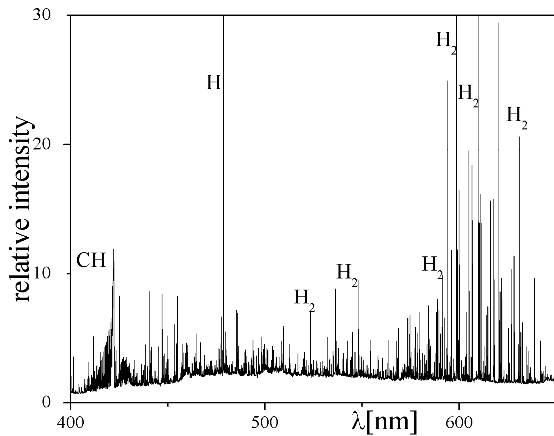

Fig.5a: Optical emission spectrum obtained during measurement of plasma deposition using HMDSO in continual regime.

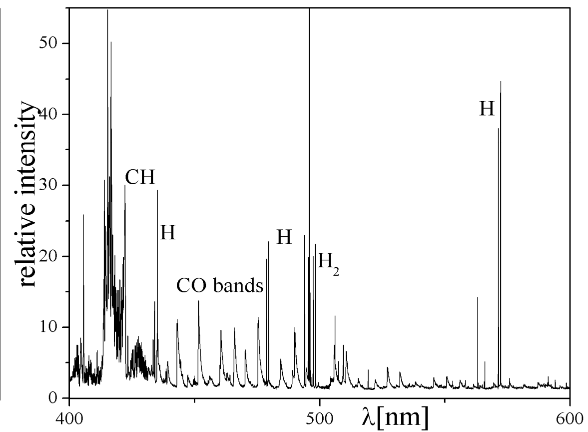

Fig.5b: Optical emission spectrum obtained during measurement of plasma deposition using HMDSO in pulsed regime.

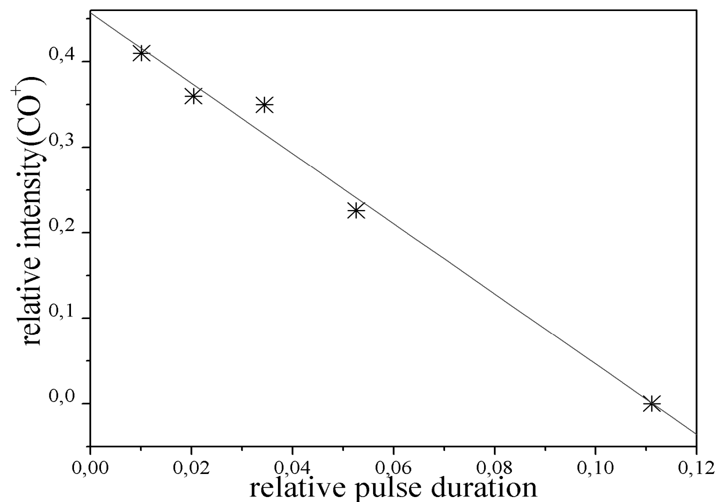

Fig.6: Dependence of the CO^+ band intensity as a function of relative pulse duration.

Conclusions

In our work we studied the plasma deposition process of the organosilicone thin layers by the emission spectroscopy. A dependence of the CH_2O band intensity related to C_2 as a function of the pulse duration shows that the character of optical spectrum approaches to the continual regime with increasing energy (increasing relative pulse duration). On the other hand, more C_2 bands in higher intensity appear in the spectrum with the shorter pulse duration. It is probably caused by the elimination of the vinyl group from the molecule of monomer. Intensities of the CH_2O and CO bands grow much weaker with shorter pulse duration. In the case of the long pulse duration it is possible to expect 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 through the increase of the CO band intensity and decrease of the CH_2O and C_2 spectral bands. Spectroscopic observations of plasma deposition using hexamethyldisiloxane show strong increase of the relative intensity of the CO bands and CO^+ bands in case of pulsed regime.

Oxygen could be eliminated from Si-O-Si bonds. Collisions and combination with carbon from CH_3 groups are probable and growth of the Si-H and CO bonds is presumable in the plasma. Due to the appearance of C_2 and C_3 bands in the emission spectrum, we can suppose also CH_2 and CH_3 or Si-CH_3 groups in primary state.

As for spectroscopic measurements during deposition using γ-metacryloxyprophyltrimethoxy-silane, it was found out that there was not a considerable difference between continual regime and pulsed regime. The lines of hydrogen, CH_2O, C_3 bands and CO bands were very intensive in the spectrum.

The results obtained by the emission spectroscopy correspond with physical properties of the prepared layers [3]. The dependence of the layer properties on the plasma conditions will be a subject of further experiments as well as creating the appropriate kinetic model of the plasma processes during plasma depositions.

Acknowledgements

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