INFRARED FIBRE BASED IN SITU EVANESCENT WAVE SPECTROSCOPY ON THIN FILMS DEPOSITED IN HMDSO-CONTAINING PLASMAS OF RF DISCHARGE.

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Abstract

The molecular structure of the plasma polymers as well as its time evolution during the deposition in the hexamethyldisiloxane-containing plasmas of rf discharge was investigated by means of in situ infrared evanescent wave spectroscopy (EWS) and infrared reflection absorption spectroscopy (IRRAS). The interface layer is formed between a Si wafer and a bulk plasma polymer. The structure of the interface reflects the initial steps of the monomer fragmentation in plasma. Admixture of O₂ allows one to deposit the films with the SiO₂-like structure. The rate of deposition is higher on the substrates at the rf potential than on the substrates at the floating potential due to the different ion bombardment.

1. Introduction

Hexamethyldisiloxane (HMDSO) is the simplest siloxane compound widely used for the deposition of Si-containing organic or SiO₂-like films which have found a wide range of applications as protective coatings [1], biomedical materials [2], permselective membranes [3], dielectric films [4], optical coatings [5]. The properties of deposited thin films are determined by their molecular structure and atomic composition. The knowledge of the influence of process parameters on the deposition mechanism and, hence, on the formation of structure and composition of plasma polymer films allows one to obtain the films of required quality.

Plasma chemical conversion of the monomer is characterised by a stepwise formation of several groups of new compounds with time [5, 6]. The HMDSO content decreases continuously. Concentration of oligomers, Si(CH₃)₃, groups grows in course of the time. These products are converted into low-molecular compounds (H₂, CₓHₓ). Low fragmentation regime characterised by small energy input provides the deposition of organic Si-containing plasma polymers. High fragmentation regime realised by enhanced energy input and/or oxygen admixture results in the intense building of Si, SiOₓ radicals which are the precursors for the growing inorganic film [7 – 11].

The aim of the work is to study the formation of molecular structure of thin films growing in the HMDSO-containing plasmas of an asymmetric rf (13.56 MHz) discharge. The film growth on the substrates at the floating and rf potentials was compared. The study complements the data on gas phase analysis known from the previously done works and literature [8, 9,11-14].

2. Experimental

The experimental arrangement is shown in figure 1. HMDSO or its mixture with oxygen was supplied to the cylindrical vacuum chamber (20 l) from the side feed line.
The asymmetric rf (13.56 MHz) discharge was maintained between the powered electrode and the grounded wall by ACG-5 generator (ENI, USA) coupled through an automatic impedance matching network. Film thickness and deposition rate were derived from in situ ellipsometric measurements at a wavelength of 632.8 nm.

The films deposited on the rf electrode were analysed by the IRRAS technique [15]. Chalcogenide (As-Se-Te) fibre

Figure 1. Schematic diagram of the experimental set-up (Amorphous Materials Co., USA) was used for infrared evanescent wave spectroscopy. The refraction index of the chalcogenide fibre $n_{core} = 2.82$ [16] is higher than that of protecting polymer coating or plasma polymer. The diameter of the fibre core (250 µm) is large compared to the wavelength λ of the transmitted infrared radiation (2 – 10 µm).

Part of the cladding-free fibre was treated with chloroform (99%, Merck KGaA, Germany) in order to remove the protecting polymer coating from the fibre surface. This bare part of the fibre, situated in the chamber, served as the internal reflection element (IRE) while the all fibre also serves as medium transmitting the IR radiation. The fibre was arranged from the Vector 22 IR spectrometer (Bruker, Germany) through the vacuum chamber to the external MCT-detector. The fibre was under the floating potential in the plasma. Because of the small fibre diameter it is possible to carry out axially resolved measurements. In the current arrangement the fibre was situated at the distance of about 18 mm from the rf electrode.

3. Evanescent wave spectroscopy

Evanescent wave spectroscopy is related to internal reflection spectroscopy (IRS) which is more widely known by the name attenuated total reflection (ATR) spectroscopy. ATR spectroscopy is carried out at a single fixed incidence angle at the surface between the IRE and the medium in question. Evanescent wave spectroscopy is based on the optical fibres which are illuminated by a collimated light beam. Thus, there is a random ensemble of angles at which the radiation propagates in the fibre core and, hence, a more complex description of the resulted spectrum is required. This technique has been successfully applied for the chemical analysis of gases and solids [17 – 19] and plasma polymer films [20].

The rays propagates in the fibre as a result of total internal reflection at the interface “core/polymer”. The radiation is totally reflected at the core/polymer interface if $\theta > \theta_c$, where $\theta$ is the angle of incidence in the fibre core and $\theta_c$ is the critical angle obeying $\sin \theta_c = n_{pp} / n_{core}$. When total internal reflection occurs, the electromagnetic field penetrates from the dense medium (fibre core) into the rarer medium (polymer film) where the electric field amplitude decays exponentially with distance from the core boundary:

$$E = E_0 \exp(-\gamma r)$$

(1)

where the absorption constant is determined in the following manner [21]:

$$\gamma = 2\pi n_{core} \left( \sin^2 \theta - n_{pp}^2 / n_{core}^2 \right) V / \lambda$$

(2)

This nonpropagating electromagnetic field, called an evanescent wave, penetrates into the analysed medium for the depth of about $3d_p$ [22] where $d_p$ is the depth of penetration, defined as the required distance for exponential drop of the evanescent wave amplitude:
\[ d_p = \frac{\lambda}{(2\pi n_{\text{core}}(\sin^2 \theta - n_{pp}^2/n_{\text{core}}^2)^{1/2})} \]  

The value of \( d_p \) is varied from 143 nm up to 15.8 \( \mu m \) in dependence on the allowed incidence angle \( \theta \) and wavelength \( \lambda \) in the chosen spectral range. It has been shown that the IR absorption spectrum is independent on the wavelength in the case of thin films, \( d << d_p \) [23]. In this case the electric field can be assumed to be constant over film thickness. According Snyder and Love [21] the absorption per unit length of the fibre \( \gamma_f \) relates to the bulk absorption coefficient \( \alpha \) of the sample in such a way:

\[ \gamma_f = \left( \frac{\alpha \theta_z^2}{V \theta_c^2} \right) / \left( 1 - \theta_z^2 \frac{\sin^2 \theta_\alpha}{\theta_c^2} \right)^{1/2}. \]  

Here \( V \) is the fibre parameter given by the following expression:

\[ V = \frac{2\pi \rho(n_{\text{core}}^2 - n_{pp}^2)^{1/2}}{\lambda}. \]  

As was shown by Driver et al [19] the effective evanescent wave absorption coefficient is a linear function of the bulk absorption coefficient of the sample in the weak absorption limit, i.e. \( \gamma_z << 1 \). This means that molecular absorption bands have the same lineshape in evanescent wave spectrum as in a straight absorption spectrum.

The critical angle \( \theta_c \) is the important parameter defining the total internal reflection. Well resolved absorption spectra can be obtained if the angle of incidence in the fibre is higher than the critical angle, \( \theta > \theta_c \). When the angle of incidence \( \theta \) is smaller than \( \theta_c \), the spectra become distorted, the signal-to-noise ratio is very high [22]. To avoid this problem the fibre endface should be smooth and illuminated by a collimated IR beam.

The increase of the reflection number along the active part of the fibre allows to enhance the sensitivity of the technique. Very small diameter of the fibre provides very high values of the reflection number in comparison with ordinary rectangular IRE plates.

4. Results and discussion

4.1. Pure HMDSO plasma

Mass spectrometric study of HMDSO-containing plasmas [5,6] revealed a stepwise character of the monomer conversion into the stable neutral gaseous products. Composition of the neutral gas component achieves a steady state after a characteristic time which is determined by the process parameters and can reach minutes [6], for example 3 min at the process conditions 10 Pa, 60 W, \( f_{\text{total}} \) 4 sccm, HMDSO:Ar 9:1 which are similar to those exploited here.

Because the neutral species are the main precursor for the growing film [1, 9, 24], one should expect the formation of an interface layer between the substrate and the plasma polymer film deposited in the steady state. Moreover the structure of this interface layer should vary with time during the monomer conversion.

The analysis of the molecular structure formed at the different stages of the monomer conversion can be realised by a pulsed plasma regime. The duration of the plasma ignition corresponds to the different stages of the monomer conversion. Infrared absorption spectra of the films obtained at the different plasma pulse times are shown in figures 2 and 3. Longer plasma pulse duration leads to stronger fragmentation of monomer molecules and building of dense polymer layer. The rate of the deposition on the substrates at the rf potential is considerably higher than that at the floating potential due to intense ion bombardment, see Table 1.
Figure 2.
Infrared absorption (IRRAS) spectra obtained at the different stages of the monomer conversion. The spectra for the plasma pulses 1–10 s are identical compared to the spectrum for a steady state. Process parameters: 15 Pa, 130 W, 5 sccm HMDSO, Si wafer on the rf electrode.

Figure 3.
Infrared absorption (EWS) spectra obtained at the different stages of the monomer conversion. Process parameters: 15 Pa, 130 W, 5 sccm HMDSO, Deposition on the chalcogenide fibre at the floating potential.

Table 1. The rate of film deposition in HMDSO-containing plasmas of the asymmetric rf (13.56 MHz) discharge on Si wafers at the different potentials.

<table>
<thead>
<tr>
<th>plasma pulse time, s</th>
<th>Deposition rate, nm/min</th>
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<tbody>
<tr>
<td></td>
<td>HMDSO</td>
</tr>
<tr>
<td></td>
<td>U₀₉</td>
</tr>
<tr>
<td>1</td>
<td>41</td>
</tr>
<tr>
<td>5</td>
<td>55</td>
</tr>
<tr>
<td>10</td>
<td>68</td>
</tr>
<tr>
<td>240</td>
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The ion bombardment effects in the more inorganic character of the molecular structure. Peculiar to the siloxane compounds lineshape of the absorption band in the spectral range 1150 - 1000 cm⁻¹ is transformed into that characteristic for SiO₂ groups.

3.2. HMDSO/O₂ plasma

The admixture of oxygen causes the drastic changes not only in the deposition kinetics but also in the molecular structure of prepared films, see figures 4 and 5. Comparing the molecular structure of the films deposited at the different potentials the same trends are seen for the HMDSO/0₂ plasma as for the pure HMDSO plasma.

The formation of complex SiOₓ structure is indicated by the shift in the short wavelength range absorption band in the region 1250 – 1100 cm⁻¹. This band is caused by mixed longitudinal and transverse modes (LO, TO) of SiO₂, SiOₓ and Si-O-Si units [25 – 28]. The transformation of the asymmetry of this band in the spectra obtained by various plasma pulse times shows how the film structure changes from that of interface up to the SiO₂-like structure. Moreover plasma polymer deposited in a steady state do not have the absorption bands pertaining to the organic
constituent of HMDSO: Si-C symmetric deformation vibration in Si-CH₃ group at the 1260 cm⁻¹; CH₃ symmetric deformation vibrations in Si-CH₃ group at the 850 cm⁻¹ and CH₃ rocking at the 800 cm⁻¹; C-H asymmetric and symmetric stretching vibration modes in methyl group in the spectral range 2970 – 2880 cm⁻¹.

![Figure 4. Infrared absorption (IRRAS) spectra obtained at the different stages of the monomer conversion. Process parameters: 15 Pa, 130 W, 3 sccm HMDSO, 17 sccm O₂. Si wafer on the rf electrode.](image)

![Figure 5. Infrared absorption (EWS) spectra obtained at the different stages of the monomer conversion. Process parameters: 15 Pa, 130 W, 3 sccm HMDSO, 17 sccm O₂. Deposition on the chalcogenide fibre at the floating potential.](image)

4. Conclusions

The study of the time evolution of the molecular structure showed the formation of the interface layer between a Si wafer and a bulk plasma polymer. The structure of the interface reflects the monomer conversion in plasma. Ion bombardment results in the enhanced deposition rate. Admixture of O₂ not only leads to the deposition of the films with the SiOₓ-like structure but also changes drastically the deposition kinetics.

References


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