Plasma Deposition from Hexamethyldisiloxane (HMDSO) and HMDSO/Oxygen Mixtures

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We deposited protective films on polycarbonates from HMDSO and HMDSO/O_2 mixtures by PECVD method. We studied especially deposition rates, optical parameters in UV-VIS and IR transmittance spectra in dependence on supplied rf power, oxygen percentage in gas feeds and the interelectrode distance. Polymer-like films showed good transparency in the visible and increased absorption in UV region. Although the optical parameters in UV-VIS of HMDSO/O_2 films were similar to the tabulated SiO_2 the infrared spectra showed organic impurities present in the films.

Introduction

Polycarbonates are well-known, commercially available materials possessing physical and chemical properties which are useful in a wide variety of applications (automobile headlamps, corrective lenses, plastics vessels, compact discs and the like). In recent years they have become a very attractive business article. The world production of polycarbonates increases every year by 8–10 % and it is expected that in the year 2000 it will be more than 1.35 million tonnes/yr. The most important are polycarbonates on the basis of bisphenol A (business labels Diflon, Macrolon, Lexan etc.) having an excellent breakage resistance and a good transparency. They are of low inflammability and good workability because even in liquid state resist an oxidation and a thermal degradation.

However, the polycarbonate low hardness, the low scratch resistance and the degradation by ultraviolet (UV) radiation restricted their full utilization. To remedy this limitation the methods for producing protective coatings on PCs are applied. Plasma technologies seem to be a very promising modern technique. Many of the plasma deposition methods are based on PECVD of silicon oxide thin films. Extremely wide range of monomers including organosilicons or organosilazanes mixed with several buffer gases (oxygen, argon, nitrogen etc.) can be used for hard coatings in glow discharges [1], [2]. The present work deals with the protection of polycarbonate surfaces by means of thin films, SiO_2-like and polymer-like ones, deposited in a radio frequency (rf) discharge using hexamethyldisiloxane (HMDSO) as a monomer.

Experimental

We deposited films from HMDSO and HMDSO/O_2 mixtures in a stainless steel parallel plate reactor. The bottom substrate electrode, 420 mm in diameter, was capacitively coupled to an rf generator working on the frequency of 13.56 MHz. The upper showerhead electrode, 380 mm in the diameter and 55 mm distant from the bottom electrode, was grounded. In some cases the upper stainless steel flange, 120 mm distant from the bottom electrode, was used as the upper grounded electrode. Then gases were fed into the chamber through a feedthrough in the center of the flange. On the bottom electrode a negative self-bias was developed due to the asymmetric coupling. Its value could be increased by an additional dc high voltage supply. RF power P was changed from 50 to 450 W. HMDSO flow rate Q_{HMDSO} was kept at 4.0 and 5.0 sccm. The flow rate of oxygen Q_{O2} varied from 0 to 80 sccm. Films were deposited on polycarbonates Lexan LS2 and on silicon substrates placed on PC.

Films were characterized by the UVISEL Jobin-Yvon phase modulated ellipsometer in the spectral range 240–830 nm at the incidence angles 55°–75°by the step of 5°. We used the model of a single homogeneous film on semi-infinite substrate to calculate film optical parameters and film thicknesses. In the whole spectral range, they could be described by simple analytical formulae:

$$n = a + b/\lambda^2 + c/\lambda^4, \qquad k = \alpha.e^{-\beta\lambda} \tag{1}$$

where λ is the wavelength.

The morphology of the film surfaces was studied with a optical stereo-microscope and a scanning electron microscope. The composition of the films was deduced from Fourier transform infrared measurements on films on silicon substrates. The microhardness measurements were made with a Hanneman (Vickers) microhardness tester.

Results and Discussion

We studied the dependence of the deposition rate on the supplied rf power for the distance of 55 mm between the bottom and upper showerhead electrodes and for the distance of 120 mm between the bottom electrode and the upper flange serving as the upper electrode (see Figures 1 and 2, respectively). For the oxygen flow rate up to 20 sccm the deposition rate increased with increasing rf power. In case of pure HMDSO (plasma polymerized HMDSO films) we observed a linear growth of the deposition rate in both interelectrode distances. It means that we are in an energy-deficient region of the typical plasma polymerization [3]. An oxygen addition in the amount of 10 and 20 sccm decreased the deposition rate at the rf powers from 100 to 300 W as can be seen from Figure 1 as well as from dependences of the deposition rate on the oxygen flow at 100 W given in Figure 3. Nevertheless, as for low oxygen flow rates the deposition rates are rapidly increasing with rf power their values exceeds at 450 W the value of the deposition rate for pure HMDSO. When the oxygen amount in the feeds is 45 sccm or even higher we observed a decrease in the rate at higher powers.

All the films deposited with an addition of oxygen had absorption index so low that it was fixed at zero for the whole spectral range. When the rf power was set to 100 W the refractive indices of all these films were equal or slightly lower than tabulated for SiO_2 (see Figure 4). The refractive index of plasma polymerized HMDSO films (PPHMDSO) at

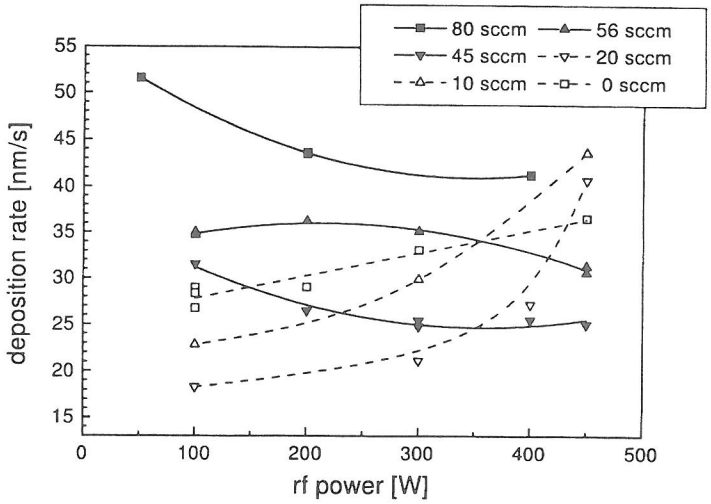

Figure 1: Dependence of deposition rate on supplied rf power for different oxygen flow rates. Distance between electrodes was 55 mm. HMDSO flow rate was 4.0 sccm.

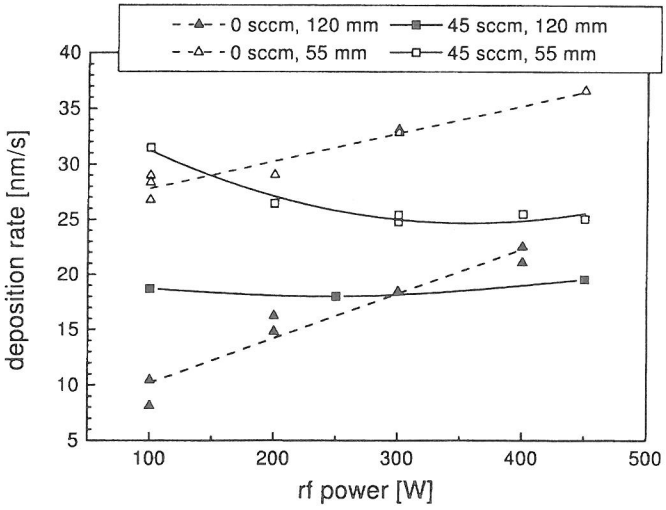

Figure 2: Dependence of deposition rate on supplied rf power for oxygen flow rates of 0 sccm and 45 sccm. Distance between electrodes was 55 mm or 120 mm. HMDSO flow rate was kept at 4.0 sccm.

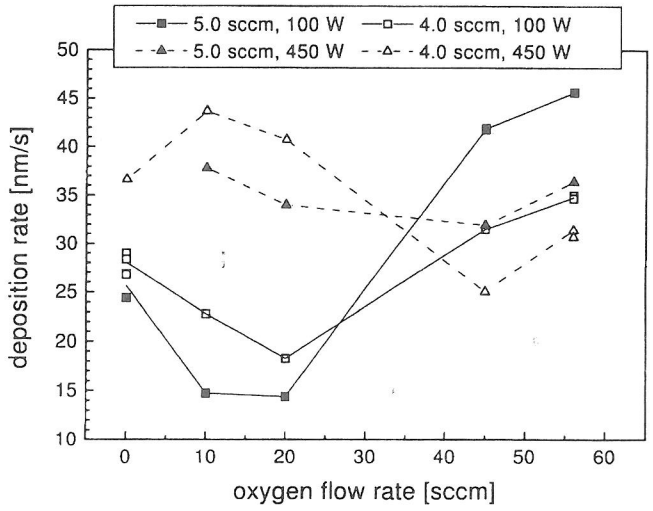

Figure 3: Dependence of deposition rate on oxygen flow rates for supplied rf power of 100 W and 450 W. Distance between electrodes was 55 mm. HMDSO flow rates were 4.0 and 5.0 sccm.

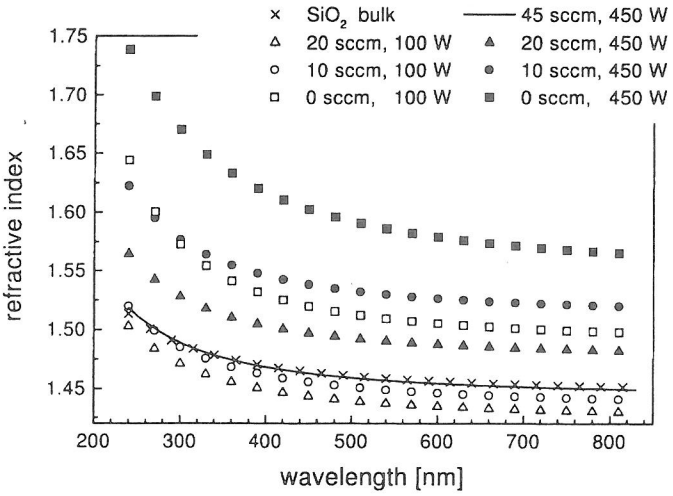

Figure 4: Dispersion of refractive index of films deposited in interelectrode distance of 55 mm. HMDSO flow rate was kept at 4.0 sccm. Oxygen flow rate changed from 0 to 45 sccm. Supplied rf power was 100 and 450 W.

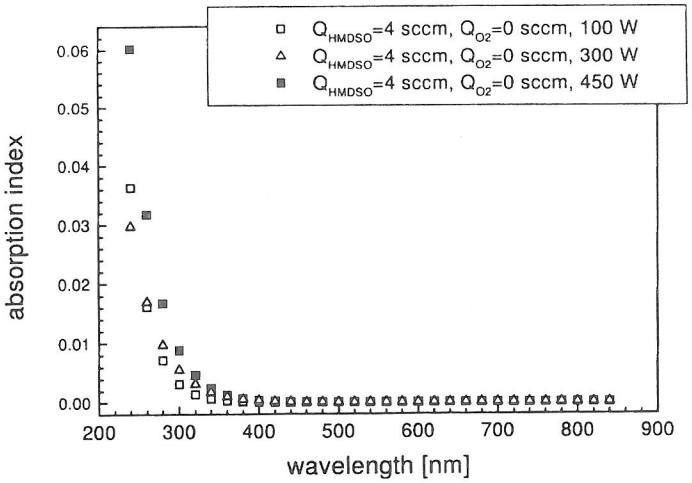

Figure 5: Dispersion of absorption index of films deposited in interelectrode distance of 55 mm from pure HMDSO feed. HMDSO flow rate was kept at 4.0 sccm. Supplied rf power changed from 100 to 450 W.

100 W was higher, 1.50 at 600 nm. At the highest rf power of 450 W the refractive indices of all the films deposited with low oxygen flow rates 0–20 sccm were shifted to higher values in monotonic dependence on the oxygen flow rate. The dispersions of absorption indices for PPHMDSO films is shown in Figure 5. In the ultraviolet region the refractive index achieved values as high as 0.030, 0.036 and 0.060 for films deposited at 100, 300 and 450 W, respectively. Therefore such films could be utilized to protect PC against the UV radiation.

Although from the refractive and absorption indices of the films deposited at 100 W with an addition of oxygen we could expect that these films are SiO_2-like the infrared transmittance showed that it is not the case (see Figure 6). Three absorption peaks characteristic of silicon oxide films [4] were identified around 1070 cm^{-1} (Si-O-Si stretching), 810 cm^{-1} (Si-O-Si bending), and 450 cm^{-1} (Si-O-Si rocking). Nevertheless, besides two broad bands centered at 3450 cm^{-1} and 3650 cm^{-1} (H-OH or Si-OH, respectively [5]) observed often in IR spetra of SiO_2-like films we found other impurities which differed in type and percentage for low oxygen flow rates, 10 and 20 sccm, and oxygen flow rates equal or higher than 45 sccm. For higher oxygen percentage there is a relatively strong peak at 921 cm^{-1} that can be associated with Si-OH stretch [4], a narrow peak at 1265 cm^{-1} (Si-$(CH_3)_3$ symmetric deformation) and two very weak peaks at 1413 cm^{-1} and 2970 cm^{-1} related to the Si-CH_3 asymmetric deformation and CH_3 asymmetric stretching, respectively [6]. Two additional peaks at 845 cm^{-1} (Si-CH_2 symmetric rocking) and 2908 cm^{-1} (CH_2 stretching) appeared for films with low oxygen flow rate. Moreover, the characteristic SiO_2 peaks were overlapped probably by a Si-$(CH_3)_3$ deformation 760–860 cm^{-1} and

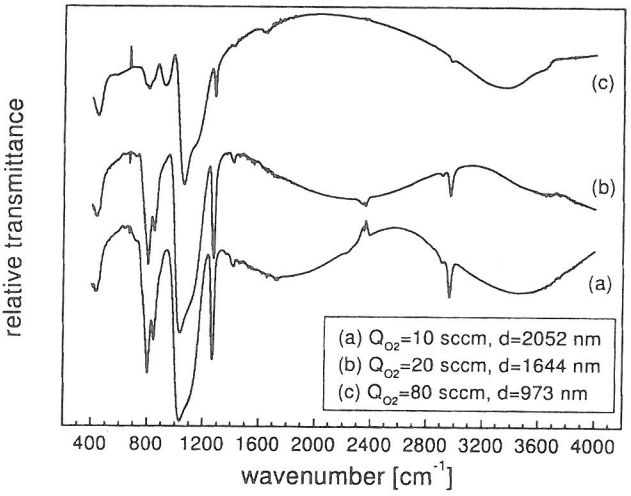

Figure 6: Infrared spectra for films deposited at rf power of 100 W, HMDSO flow rate of 4.0 sccm an different oxygen flow rates. Interelectrode distance was 55 mm. Film thicknesses are given in figure.

Si-O-C stretching around 1100 cm^{-1}. The peaks at 2340 cm^{-1} (CO_2 band [5]) and around 1630 cm^{-1} are caused by the absorption in air resting in spectrometer.

Acknowledgment

The authors wish to thank Dr. K. Navrátil for FTIR measurements. The present work was supported by the Grant Agency of the Czech Republic, contract 106/96/K245 and by the Ministry of Education, contract VS96084.

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