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Deposition of thin films based on silica on polycarbonates by pulsed dielectric barrier discharge

Summary — The process of thin organo-silica film deposition on polycarbonate in pulsed dielectric barrier discharge was studied. Thin film was deposited from the gas mixture comprising helium, oxygen and tetraethoxysilane under atmospheric pressure without pre-heating of polycarbonate plate. Influences of process parameters, namely the current of single pulse of discharge, PC plate arrangement and position, and plasma-generating gas composition on the deposition rate were investigated. Deposition rate increased from 3.4 to 40.8 nm/min when the current of single pulse increased from 50 to 100 A. The presence of oxygen in plasma-generating gas was necessary to thin organosilicon film forming, but the excess of O₂ concentration caused decreasing of film deposition rate, for example: deposition rate was 14.9 or 6.0 nm/min when concentration of O₂ was changed from 5 to 20 % by vol. In the films, the following elementary composition (Si, C, O, H) and morphology of deposited films were characterized. These films were smooth and transparent.

Key words: pulsed discharge, tetraethoxysilane, thin films, polycarbonates.

Polycarbonates (PC) have very useful properties of the bulk, such as low density and thus reduced weight, high elasticity and transparency. They have been widely used in industry to replace the glass in many applications, such as headlights, windscreens, lenses and for compact disc manufacturing. However, their use is sometimes limited by unwanted properties of the surface such as low hardness, low scratch resistance and UV degradation. Various deposition technologies for producing thin, protective silicon compound films on PC for these limits remedying were investigated.

Until now, the best effects were achieved using plasma methods. These methods are based on microwave plasma techniques at low pressures — from 0.1 to 100 hPa. Low pressure is a practical limit of this way of thin film depositing in large scale [1–3]. For this reason, deposition of thin films of silicon compounds under atmospheric pressure can be very interesting. Dielectric barrier discharge (DBD) is a well known technique of

plasma generation under atmospheric pressure. This process was used for deposition of thin silica films on silicon wafers heated to 100–400 °C [4, 5]. However, this temperature range is too high when plastic substrates are used.

In this work, we present the results of thin film deposition on polycarbonates in the pulsed dielectric barrier discharge (PDBD) under atmospheric pressure. Vapor of tetraethoxysilane (TEOS) was used as a starting organosilicon reagent in a mixture with helium and oxygen. TEOS was transformed into precursors of the organo-silica films deposited on PC surface. Helium was used as a carrier gas. Oxygen, being an oxidizing reagent, accelerated the transformation of TEOS into the precursors because oxidation of the organic residues proceeds in the gas and solid phase.

EXPERIMENTAL

Materials

- TEOS (purity >98 % delivered by Schuchardt, Germany),
 - PC (“Lexan” in the form of plates produced by GE Plastics, USA),
 - Oxygen and Helium (both of purity N5,0 from Multax, Poland),
- All materials were used without further purification.

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Equipment

Gas supply system

The gas supply system is shown in Fig. 1. The reactor was fed by plasma-generating gas which consisted of helium, oxygen and the vapor of TEOS. Helium and

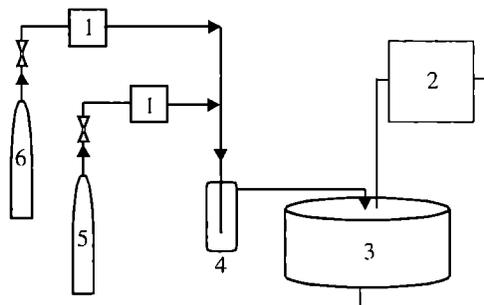


Fig. 1. Block scheme of gas supply system: 1 — mass flow controllers, 2 — electric power supply system, 3 — reactor, 4 — bubbler with TEOS, 5 — gas cylinder with O₂, 6 — gas cylinder with He

oxygen were taken from gas cylinders through mass flow controllers and they were mixed. Next step was to pass gases through a bubbler with liquid TEOS and then let them go into the reactor. The concentration of TEOS in the plasma-generating gas was calculated based on flow rates of helium and oxygen and the decrease in liquid TEOS mass in the bubbler.

Plasma reactor

Plasma deposition was performed in PDBD reactor, which is shown in Fig. 2. The reactor consists of two round stainless steel electrodes enclosed in Plexiglas casing. Dielectric barrier was made of PC plate characterized by the relative electric permittivity of 2.3 (measured by Precision LCR Meter HP 4284A). We investigated two kinds of arrangements of PC plates. First arrangement (PC-PC): the high-voltage and passive elec-

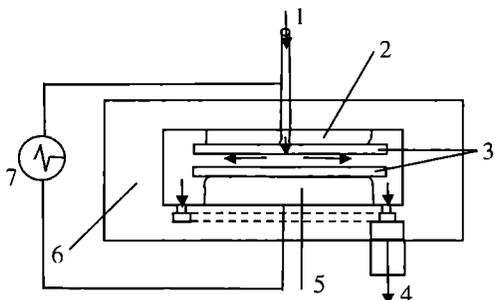


Fig. 2. Scheme of PDBD reactor: 1 — gas inlet, 2 — high inlet, 3 — high-voltage electrode, 3 — PC plates, 4 — gas outlet, 5 — passive electrode, 6 — Plexiglas casing, 7 — electric power supply system

trodes were covered with PC plates; thin films were deposited on both PC plates. Second arrangement (PC-M): only the passive electrode was covered with PC plate and the high-voltage electrode was base metal. Thin films were deposited on PC plate and on the surface of the high-voltage electrode. In all experiments PC plates of thickness 0.75 mm were used. The discharge gap distance was always 0.75 mm.

Electric power supply system

The reactor was powered by a pulsed electric system, which consisted of an autotransformer, high-voltage transformer, high-voltage resistor, Blumlein line and spark-gap (Fig. 3).

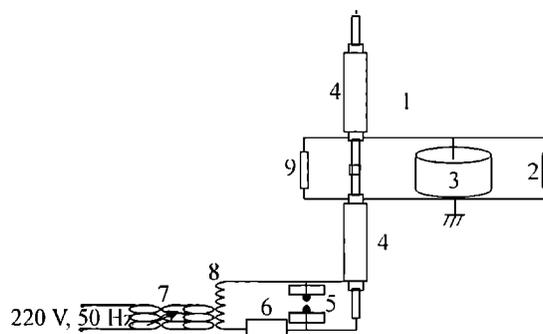


Fig. 3. Block scheme of electric power supply: 1 — current probe, 2 — high-voltage probe, 3 — reactor, 4 — Blumlein line, 5 — spark-gap, 6 — high-voltage resistor, 7 — autotransformer, 8 — high-voltage transformer, 9 — resistor

Electric parameters, such as voltage and current, were recorded using a Tektronix TDS 3054 oscilloscope. The real energy released in a single pulse (E in J) was calculated from the following formula:

$$E = \int_{\tau_1}^{\tau_2} U(t) \cdot I(t) dt \quad (1)$$

where: U — voltage (in V), I — current (in A), t — time (in s), τ_1, τ_2 — duration of the single pulse (in s).

Parameters of film deposition process

Total flow rate of the gas mixture was kept at 100 dm³/h in all experiments, which were performed under

Table 1. Experimental parameters of film deposition

Series	Arrangement	Concentration of He, vol. %	Concentration of O ₂ , vol. %	Concentration of TEOS ppm	Frequency of pulse repetition Hz
A	PC-M	85	15	320	350
B	PC-PC	85	15	320	350
C	PC-PC	95	5	270	400
D	PC-PC	80	20	350	400

atmospheric pressure without pre-heating of PC plates. Other parameters of experiments runs are described in Table 1. One series of our earlier results [6] is shown additionally in Table 1 as series D.

Film characterization

Mass deposition of the thin film was determined gravimetrically. PC plates were weighed before and after the deposition. Changes of the mass of PC plates were determined using Sartorius BP 221S balance. The average thickness of the thin film (D in nm) was calculated from the following formula:

$$D = m \cdot (s^* \cdot d)^{-1} \cdot 10^{-7} \quad (2)$$

where: m — change of the mass of PC plate (in g), s^* — area of PC plates covered by thin film (in cm^2), d — density of deposited thin film (in $\text{g} \cdot \text{cm}^{-3}$).

As it is known from literature, densities of thin films deposited in radio frequency (RF) (13.56 MHz) TEOS/ O_2 plasma were in the range from 1.6 to 2.1 $\text{g} \cdot \text{cm}^{-3}$ and were larger than 2 $\text{g} \cdot \text{cm}^{-3}$ for TEOS fractions larger than 33 % [7]. Densities of thin films deposited in microwave plasma were in the range from 1.3 to 2.0 $\text{g} \cdot \text{cm}^{-3}$ and were larger than 2 $\text{g} \cdot \text{cm}^{-3}$ for O_2 to TEOS ratio higher than 14 [8]. Based on these literature review the value of density (d) of thin film was assumed as 2 $\text{g} \cdot \text{cm}^{-3}$, because O_2 and TEOS molar ratio was higher than 100 in all our experiments.

The homogeneity of the thickness of thin film was appraised by observation of the color of thin film. The color depended on the thickness of thin film and changed every 5–50 nm of film thickness. The interference colors were observed only near the center of PC plate and on the periphery of the surface covered by thin film. No interference colors were observed on the main surface between center and periphery. Therefore the border variation of thickness was negligible and the surface of PC plate (s^*) was defined as the all area of PC plate covered by thin film.

The morphology of a film was investigated with using Nanoscop 1030 Digital Instruments atomic force microscope (AFM/TM) and scanning electron microscope LEO 1530. This let measure the surface roughness (R_a).

The chemical composition of the deposited film was investigated using Spectrum 2000 infrared spectrometer with Fourier transformation (FT-IR). IR spectrometer worked with a horizontal reflection accessory (attenuated total reflectance — ATR) and Gripper pressure device designed to FT-IR analysis of films. Pressure device was used to provide the uniform contact between the polycarbonate sample and ATR crystal needed for reproducible results. Light transmittance of wavelengths 400–800 nm was investigated using CARY 3E Varian UV-VIS spectrometer.

RESULTS

Chemical characteristics of the films

FT-IR spectra of thin films deposited in PDBD from TEOS and on the original PC are shown in Fig. 4. The

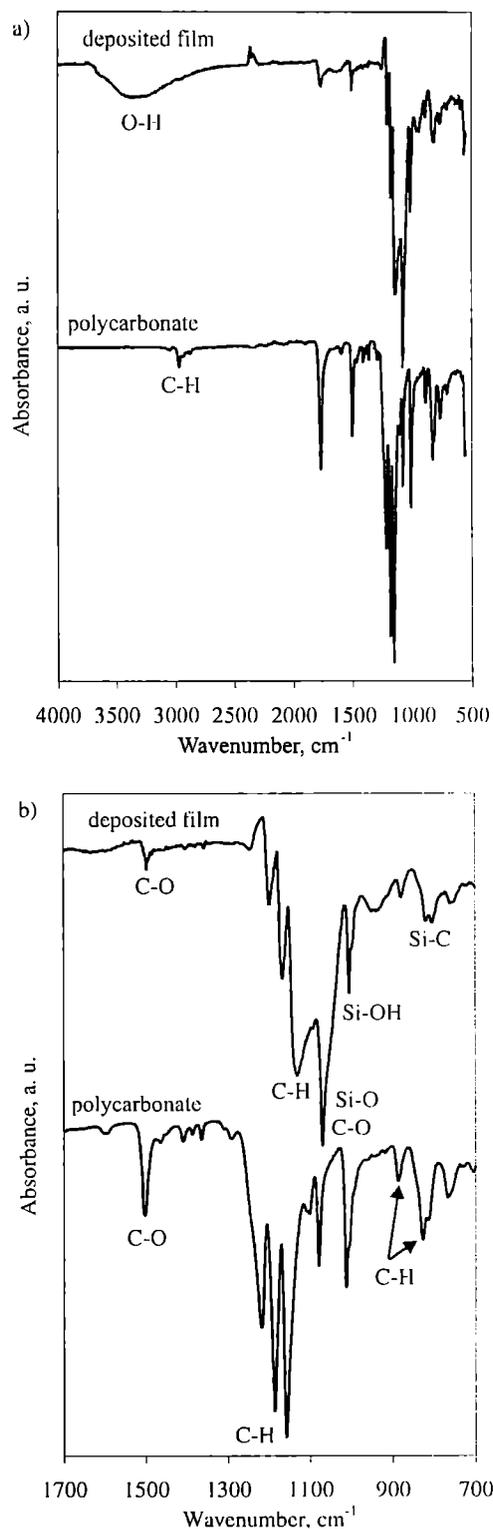


Fig. 4. Typical FT-IR spectra of the deposited thin film and original PC: a) in wavenumber range of 500–4000 cm^{-1} , b) in wavenumber range of 700–1700 cm^{-1}

broad band in the range of 3000—3700 cm^{-1} is assigned to SiOH groups, COOH groups and water. The peak at 1700 cm^{-1} is attributed to C=O stretching vibrations, the peak at 1600 cm^{-1} is due to H₂O and the peak at 970 cm^{-1} corresponds to Si-OH stretching vibrations. Moreover, thin films are characterized by strong absorption in the range of 1000—1250 cm^{-1} . There are a few peaks which are due to symmetric deformation of silylmethyl, ethoxy and aliphatic groups like C-O-C, Si-O-C and Si-O-Si at 1050 cm^{-1} , and network vibration of SiO₂ at 1110 cm^{-1} , asymmetric deformation of C-O-C, Si-O-C and Si-O-Si at 1170 cm^{-1} , rocking vibration of CH₃ in Si-O-CH₃ at 1200 cm^{-1} , and symmetric deformation of CH₃ in Si-(CH₃)_x at 1240 cm^{-1} . It seems as if Me groups are formed from Et ones at plasma conditions. The peak at 800 cm^{-1} is characteristic to symmetrical stretching of Si-C bond. The band in the range of 1350—1500 cm^{-1} is associated to the aliphatic group vibrations.

Surface morphology

AFM micrographs and SEM micrographs of the surface of the original PC plates and of the films are shown

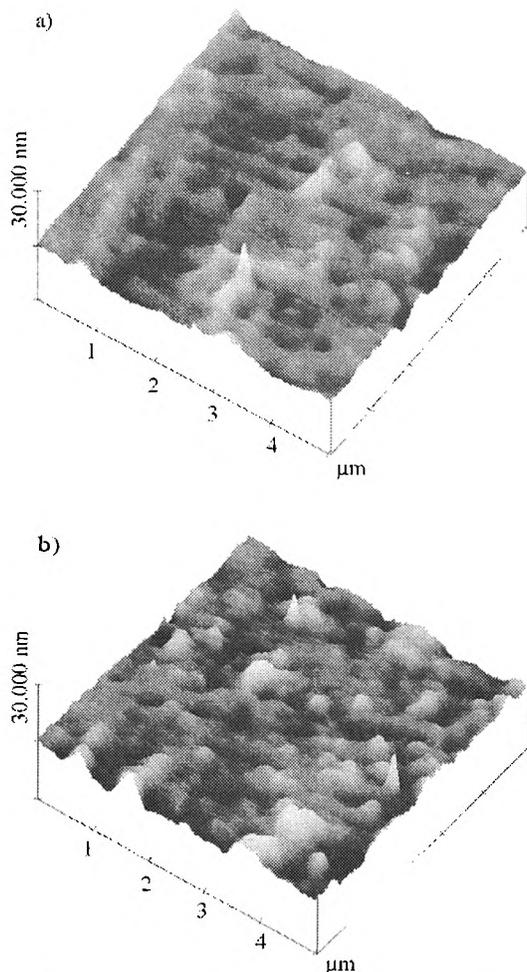


Fig. 5. AFM micrographs of the surface: a) of original PC, b) of the deposited thin film

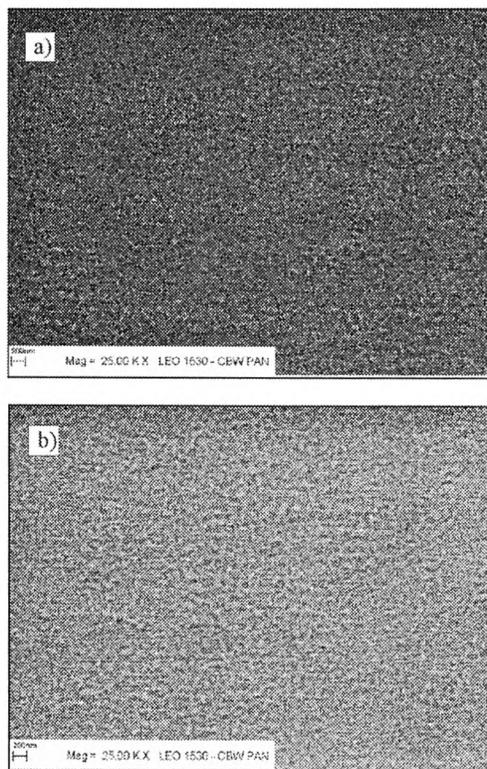


Fig. 6. SEM micrographs of the surface: a) of original PC, b) of the deposited thin film

in Fig. 5 and Fig. 6, respectively. Presented micrographs show that the films are homogenous.

Deposition rate

The changes of thin film thickness versus deposition time and the deposition rate at various experimental conditions are presented in Figs. 7—10 and Table 2.

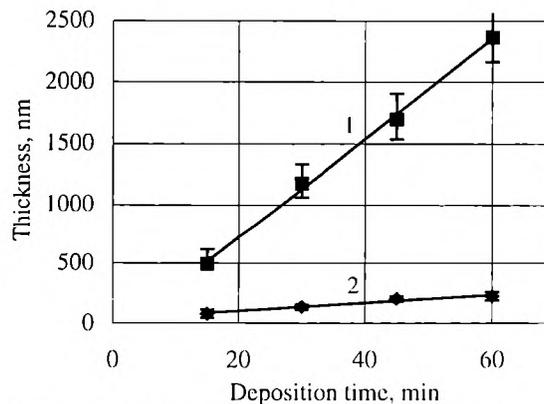


Fig. 7. The effect of PC plates arrangement on the film thickness versus deposition time under following process conditions: gas composition He — 85 vol. %, O₂ — 15 vol. %, TEOS — 320 ppm; frequency of pulse repetition — 350 Hz; 1 — arrangement PC-PC (energy of single pulse — 6.2 mJ; current — 50 A); 2 — arrangement PC-M (energy of single pulse — 9.1 mJ, current — 100 A)

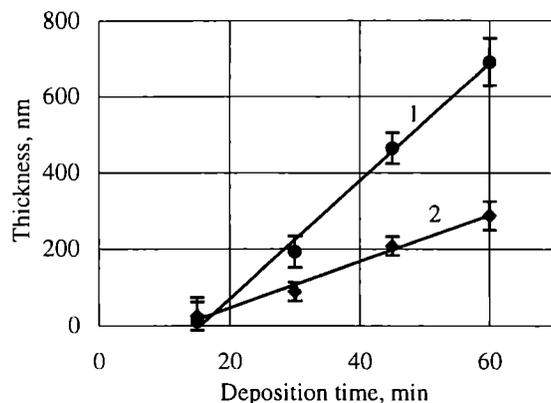


Fig. 8. The effect of O_2 concentration on the film thickness versus deposition time under following process conditions: gas mixture 1 — He — 95 vol. %, O_2 — 5 vol. %, TEOS — 270 ppm; 2 — He — 80 vol. %, O_2 — 20 vol. %, TEOS — 350 ppm; energy of single pulse — 6.2 mJ; frequency of pulse repetition — 400 Hz; PC plate placed at the passive electrode; arrangement — PC-PC

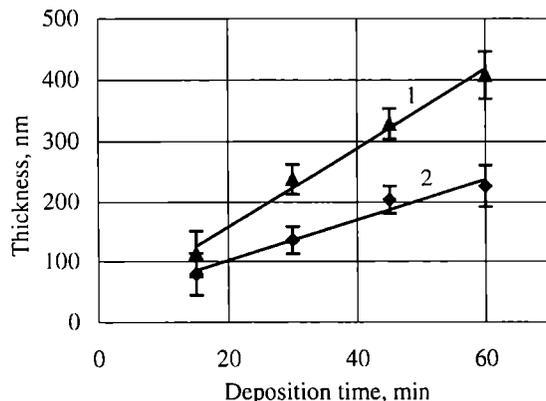


Fig. 9. The effect of position of PC on the electrode, in PC-PC arrangement with frequency of pulse repetition 350 Hz, on the film thickness versus deposition time under following process conditions: composition see Fig. 7; energy of single pulse - 6.2 mJ; 1 — PC placed on high-voltage electrode, 2 — PC placed on passive electrode

Table 2. Comparison of thin film deposition rates at various parameters

Series	Arrangement	PC plates placed on electrodes	Energy of single pulse mJ	Deposition rate nm/min
A	PC-M	passive	9.1	40.8 ± 1.4
B	PC-PC	passive	6.2	3.4 ± 0.4
B	PC-PC	high-voltage	6.2	6.5 ± 0.2
C	PC-PC	passive	6.2	15.4 ± 0.8
C	PC-PC	high-voltage	6.2	14.9 ± 1.0
D	PC-PC	passive	6.2	6.0 ± 0.5

The thickness of thin film depends on process parameters such as concentration of oxygen in the feed gas, pulse energy, and deposition time. The deposition rate

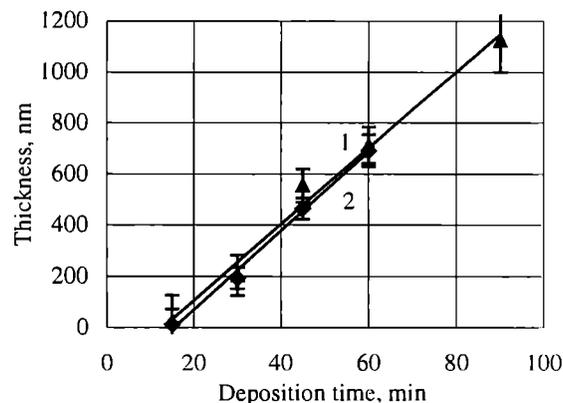


Fig. 10. The effect of position of PC on the electrode, in PC-PC arrangement with frequency of pulse repetition 400 Hz, on the film thickness versus deposition time under following process conditions: 1 — PC placed on high-voltage electrode, 2 — PC placed on passive electrode; arrangement — PC-PC; gas composition see Fig. 7; energy of single pulse — 6.2 mJ

was determined from the slope of the linear regression lines, which describe the changes of thin film thickness versus deposition time.

Electric parameters

The real energy released in the single pulse, the voltage and current depended on the arrangement of the plate and electric capacity of the reactor. This last parameter strongly influenced the current of single pulse. Electric capacity of the reactor with single PC plate was 23.2 pF and the value of pulse real energy was 9.1 mJ, calculated according to the equation (1). Electric capacity of the reactor with two PC plates was 17.8 pF and the real energy was 6.2 mJ.

DISCUSSION

FT-IR spectra (Fig. 4) of thin films were very complex and not only Si-O but many other chemical groups were identified. The presence of peaks from $Si-(CH_3)_x$ groups indicate that the product of deposition was not pure silica but was of mixed composition (organo-silicon).

All PC plates surfaces were uniformly coated and remained transparent after deposition of the films. Light transmittances of wavelength 400–800 nm are similar to original polycarbonates (97 %) and polycarbonates with thin films (97 %).

Thin films were smooth and homogeneous (Figs. 5 and 6). No breaches were observed on the surface after thin film deposition, but the calculated roughness of original surface of polycarbonate ($R_a = 6.6$ nm) was less than roughness of thin organo-silicon film ($R_a = 7.4$ nm).

The morphology of thin film obtained from TEOS was similar to the morphology of the film obtained from hexamethyldisiloxane (HMDSO) by homogenous plasma, which was generated by RF discharge at

13.56 MHz [9]. In the mentioned work, it was also found the surface roughness of thin film has been bigger than that of the original PC surface.

Our present and former investigations on morphology of surface of thin film proved that PDBD was probably homogeneous. Shapes of run of voltage and current of single pulse of this discharge are different from DBD, which is filamentary discharge, and confirm this conclusion [10].

Deposition rate and the thickness of deposited film strongly depend on the energy of a single current pulse of the discharges (Fig. 7, Table 2). The real energy released in the single pulse was 6.2 or 9.1 mJ for reactor arrangements PC-PC and PC-M, respectively. The quite small change of the real energy released in the single pulse of the discharge (from 6.2 to 9.1 mJ *i.e.* ~50 %) caused a great increase in the film thickness (Fig. 7) and the film deposition rate increased from 3.4 to 40.8 nm/min (Table 2). As it results from equation (1), E is a function of I .

For the discussed conditions the current of single pulse was changed from 50 to 100 A. The current is the measure of quantity of electrons. The quantity of electrons transported in the single pulse of discharge is the most important electric parameter in the process of the film building.

The films, which were obtained from the gas mixture of TEOS and He (without O₂) in our former work, were soft and not transparent, and their structure was like a gel [10]. They were quite different from the present films. All these results show that oxygen is an important agent in formation of thin films, with silica being the main component. This observation is in agreement with the earlier opinion about the mechanism of the thin film formation from TEOS [11]. This mechanism demonstrated that TEOS in the reaction with oxygen radicals was decomposed to (Et)₂Si=O (diethoxysilanone), HO•, Et• and EtO•. (Et)₂Si=O was considered the major film-forming precursor, which led to formation of organo-silicon film. More diethoxysilanone was produced through secondary reactions of HO•, Et• and EtO• radicals with TEOS. Diethoxysilanone was not produced without any oxidizing agent in plasma-generating gases and thin films were formed slower than from other, less active precursors [11]. Additionally TEOS was probably polymerized from gas phase on solid surface in non-oxidizing plasma and not transformed to other chemical compounds like SiO₂ [6].

The presence of oxygen in plasma-generating gas was necessary for thin organo-silica film formation, but the concentration of oxygen should be optimized because the excess of O₂ in plasma-generating gas mixture resulted in the decreasing deposition rate of the film. The film deposition rate decreased from 14.9 to 6.0 nm/min with increasing O₂ concentration from 5 to 20 % by vol. (Fig. 8, Table 2, series C and D, see Table 1). This is in agreement with other works [6, 12] and can be explained in two ways. Namely this can be a result of

— dilution of monomers (TEOS) in the excess of oxygen, or

— increased etching rate of a surface with the increasing concentration of O₂ in plasma-generating gas.

It is possible that both mentioned effects may occur together.

At frequency of pulse repetition of 350 Hz the films were deposited faster on the PC plate placed at the high-voltage electrode than at the passive electrode (Fig. 9, Table 2, series B). At frequency of pulse repetition of 400 Hz the deposition rate of thin film was almost the same on the both PC plates (Fig. 10, Table 2, series C). This effect is probably a result of non-symmetric work of the electric power supply system at the frequency of pulse repetition of 350 Hz and symmetric at the pulse repetition frequency of 400 Hz. Asymmetric work of two electrodes depends on the construction of electric power supply system.

In all experiments the thickness of deposited films increased with increasing deposition time. It was linear dependence except the first period (Figs. 7–10). This result was similar to those obtained by other authors [13–15]. However, it is difficult to examine the very start of film deposition and thus this induction period is not recognized well. Probably during first minutes the other processes proceeded in polymer material, such as crystallization, crosslinking, etching or activation [16]. The duration of induction period depended on magnitude of polymer material modifications. This problem was discussed in our other work [17].

CONCLUSIONS

— Pulsed dielectric barrier discharge can be used for deposition of thin, based on tetraethoxysilane, organo-silicon films on polycarbonate under atmospheric pressure without pre-heating of PC plates.

— Thin films deposited by PDBD from He, O₂ and TEOS gas mixtures were transparent and smooth, but the roughness of original surface of polycarbonate was less than roughness of thin organo-silicon film.

— The presence of oxygen in plasma-generating gas was necessary for the thin organo-silica film forming, but the excess of O₂ caused the decrease in deposition rate of thin film.

— Deposition rate and the thickness of deposited film depended on the current of single pulse. Deposition rate markedly increases with the increasing of current of single pulse.

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