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Process of Formation of Vacuum Polymer Films in the HF Discharge Reactor

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Abstract. Forming processes of thin-film fluoropolymer coating in the HF discharge reactor on the surface at various technological modes of deposition are considered. The molecular and structural characteristics of the films are studied. Areas of optimum technological modes of producing of nano-sized and thin fluoropolymer films with better electro physical properties are determined.

1. Introduction

Secondary polymerization principle of products of spraying of industrial polymeric substances is used at creation of producing technology of fine and nano – sized polymer coatings [1, 2]. Decomposition of block polymer into the gas molecular atmosphere can occur under temperature influence, electron beam, laser radiation or ions of plasma of HF discharge [3-5]. In this case deposition of the polymer coating on the substrate can be carried out at conditions similar to polymerization of the polymer from the monomer.

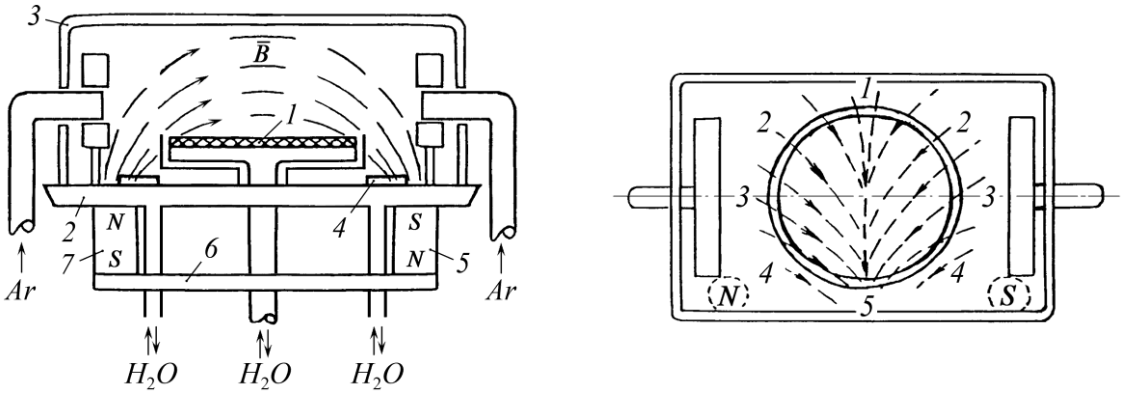
Fluoropolymer film coatings possess unique multifunctional properties due to their high electrical and physico – chemical protective characteristics, which allows to use their in electronics devices in extreme conditions and harsh atmosphere [6, 7]. Technological process of obtaining of fluoropolymer coatings with properties, close to the industrial polytetrafluoroethylene (PTFE), requires study. Secondary structure synthesis of PTFE on the surface of the substrate requires natural selection of molecules on the surface of the fluoropolymer layer during its polymerization and control of technological modes of deposition because of significant heterogeneity of molecular composition of resulting gas atmosphere.

2. Specimens and Experimental Method

Fluoropolymer films are inflicted on substrate in vacuum chamber in cathode HF discharge reactor with a frequency of 13.56 [MHz] from the vapors of sprayed block PTFE. The film thickness was 1...10 [μm]; it was measured by layer weight on the samples by quartz resonator and by ellipsometrical method. The substrate temperature was changed in the range of 20...150^{o}C during the deposition of films. Materials of the plates (of 14 type) of silicon, steel, copper and glass – ceramic were served as substrates.

Cathode HF discharge reactor and cathode HF discharge reactor in a heterogeneous constant magnetic field are used to form the fluoropolymer film coatings. The latter type of reactor allows forming the fluoropolymer films with desired characteristics. Figure 1 shows design scheme of HF

discharge reactor of magnetron type, where 1 is a cooled round cathode target 1; 2 is a refrigerated table for specimens 4, on which is formed film; 3 is a body-electrode of the reactor; 5–7 is a magnetic system. Inhomogeneous magnetic field *B* is created by the permanent magnets 5 and 7, which is directed perpendicular to the alternating electric field between the electrodes of the capacitive cell of cathode target 1 and the second body-electrode of reactor 3 using rigidly fixed on the body of the magnetic system 5–7, located on the periphery of the HF reactor.



a) b)

Figure 1. Design scheme of HF discharge reactor of magnetron type (a), where 1 is a cooled round cathode target; 2 is a cooled body-electrode; 3 is a removable electrode reactor; 4 is a sample substrate; 5, 7 are permanent magnets; 6 is ferromagnetic plate; and scheme of location of the samples (b), where 1–5 are location of the samples.

HF discharge is ignited between two cooled electrodes 1 and 3 during the inflow of working gas argon according to technological cycle after pumping of residual gases from the reaction chamber volume. HF electrodes 1 and 3 in the gap are exposed to the bombardment by electrons and ions of plasma, which leads to cleaning inner surface of reactor and substrates 4. Then on the electrode 1 the PTFE target begins to dissipate during bombardment by ions of HF plasma discharge that generates working fluorine gas atmosphere containing molecular fragments of fluoropolymer. Molecular polymer particles in plasma HF discharge is additionally subjected to plasma chemical reactions in a gas atmosphere; chemical connections with the active surface centers are formed and they deposited on the substrate 4.

Applied inhomogeneous magnetic field *B* has normal and tangential components, which create uneven etching on the target surface due to its bombardment by oscillating electrons and ions of plasma in a magnetic field (Figure 1a). The impact of charged plasma particles on the growing fluoropolymer film essentially depends on the substrate's location, which is determined by the tangential component of magnetic field *B* on the perimeter of round target 1. So the value *B* has a minimum value in the region of samples 1 and 2 (Figure 1b), which are away from poles of the magnets 5 and 7 (Figure 1a) and it has a maximum value in the region of samples 4 and 5 (Figure 1b) between poles 5 and 7 (Figure 1a). It is possible to control the density of electron plasma on the growing film of fluoropolymer on the substrate by changing the magnetic field *B*, which allows to significantly expanding the technological range of operating pressures and possibilities of regulating the concentration of the active gas atmosphere.

3. Results and Discussion

3.1. HF Discharge Reactor

Experimental dependences of kinetics of the deposition process of fluoropolymer coatings from active gas phase in the cathode HF discharge reactor without the magnetic system were determined.

Figure 2 shows dependences of fluoropolymer coating growth rate *V* from pressure of vapors *P* in the vacuum chamber (a) and substrate temperature T_s (b) with the plasma current density of 0.35

[A/m^2]. The curves 1–5 (Figure 2a) correspond to the substrate temperatures T_s of 20, 30, 50, 70 and 90 [^{o}C]; the curves 1–4 (Figure 2b) correspond to vapors pressure P of 0.3; 0.4; 0.5 and 0.6 [Pa] in the vacuum chamber.

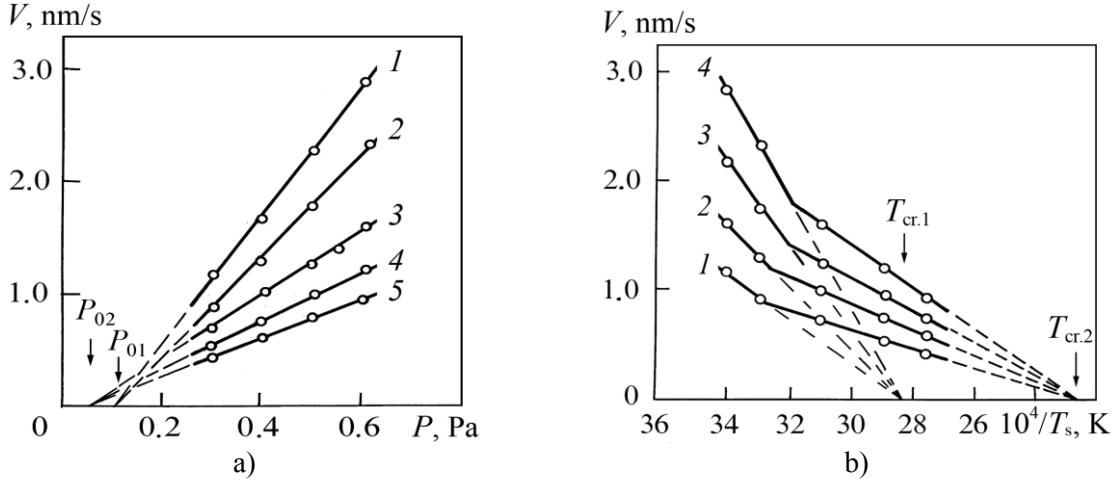


Figure 2. Dependences of fluoropolymer coating growth rate V from pressure of vapors P in the vacuum chamber (a) and substrate temperature T_s (b) with the plasma current density of 0.35 A/m^2.

Rate of V of coating growth significantly decreases at increasing vacuum and substrate temperature (Figure 2). The vapors pressure P in the chamber at decomposition by plasma of a block polymer PTFE has a threshold critical value of ~ 0.07...0.1 [Pa]; below this value the process of deposition of a layer of fluoropolymer on the substrate does not occur.

Dependence of fluoropolymer film V on temperature finds out the two regions corresponding to two types of the kinetics of coatings deposition. It allows determining the optimal temperature of resistant polymerization of molecular components of gas atmosphere, which is in the region of the critical temperature $T_{sr.1}$ and $T_{sr.2}$ between of 78^{o}C and lower of 165^{o}C. At a defined temperature polymer V exceeds the diffusion rate of deposited molecules into solid phase of polymer, where the propagation of reaction occurs. Reduction of V with increasing temperature is similar to the process of depolymerization and reduction of the fluoropolymer molecular weight. It plays an important role on impact growing layer of electrons and ion plasma flow [8, 9] and the high-frequency electromagnetic fields [10]. Here the impact on the growing layer of electron flow and plasma ions [8, 9] and the high-frequency electromagnetic fields [10] plays an important role. So polymer with the maximum value of molecular weight (870 000...1 080 000) is formed in the film in the temperature range of 78...150°C [11]. The most optimal molecular structure of the fluoropolymer film with a molecular weight is formed at the substrate temperature in the range of 95...127^{o}C; it coincides with the results of the experiment at the PTFE synthesis from monomer [8]. The morphology of the films significantly depends on the synthesis temperature. So on cold substrate a fluoropolymer structure is amorphous and homogeneous with crystallinity not more of 1.5%. Crystallinity of the films increases up to values of 15...18% at increasing temperature; the surface morphology is expressed by some relief.

3.2. HF Discharge Reactor with magnetic field

According to the considered design of HF discharge reactor with heterogeneous magnetic field the impact of the plasma flow on the growing polymer film will be different. So this impact will be minimal in region 1 of the reactor (Figure 1b); it will be maximum in the region of strong magnetic field 4 and 5. Fluoropolymer film in region 1, where there is practically no influence of the plasma on the growing film, has a molecular structure similar to the original PTFE with crystallinity values of 25...35%.

Fluoropolymer structure contains a wide range of components (short, medium and long) of the molecular chains of tetrafluoroethylene and also there is a large part of radiation-grafted chains with

the group of oxides and radicals in the region of the substrates 4 and 5 (Figure 1b), where the intense ionization of the growing polymer film occurs. The crystallinity of such films does not exceed of 3...5%. The morphology of last specimens has a more homogenous surface due to the high degree of cross-linking of molecules during exposure of the plasma discharge.

Figure 3 shows dependences of mass growth (of thickness L) (Figure 3a) and relative value of growth speed $V(t)/V_0$ (Figure 3b) on time t of fluoropolymer films from the gas phase on silicon substrate at temperature T_S = 23 °C. Curves were obtained at the density of discharge current on the surface of the growing film, where 1 – 0.05; 2 – 0.3; 3 – 0.63; 4 – 0.95 and 5 – 1.4 [A/m^2]. The V_0 values for the curves 1, 2, 3, 4 and 5 are 0.9, 1.36, 1.98, 2.41 and 2.8 [mg/m^{2}s] respectively.

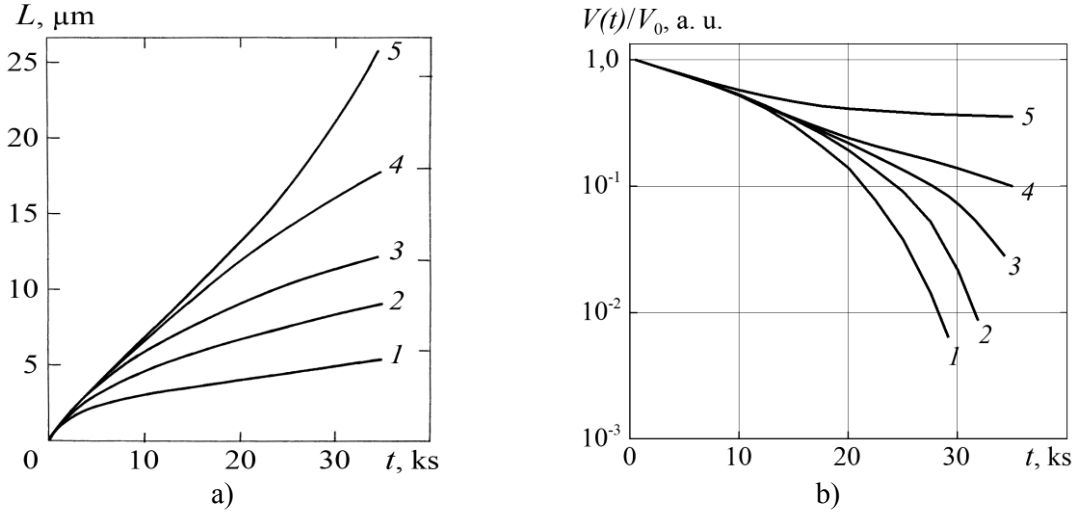


Figure 3. Dependences of mass growth (of thickness L) (a) and relative value of growth speed $V(t)/V_0$ (b) on time t of fluoropolymer films from the gas phase on silicon substrate at temperature T_S = 23 °C.

Figure 3 shows that the kinetics of fluoropolymer films growth in HF discharge reactor (Figure 1a) is strongly dependent from the location of the specimens 1–5 in the reactor (Figure 1b). Deposition process of fluoropolymer for specimens 1 and 2 (Figure 1b) has the first order; it becomes zero order at the increasing flow of electronic processing of growing film (from region 2 to specimens 4 and 5), i.e. radiation-induced polymerization of molecular fragments from the gas atmosphere on the substrate is dominated. The deposition rate of the coating $V(t)/V_0$ from the gas atmosphere is maximum at the initial stages; it is determined by the constancy of the electron-stimulated polymerization processes at increasing layer thickness L to some stationary value. Research of various modes of HF discharge reactor are showed that the growth rate of the film $V(t)$ depends on the value of the tangential component of rms value of constant magnetic field B between the capacitive electrodes 1 and 3 (Figure 1a), i.e. it depends on the intensity of the electronic processing of the growing polymer layer. Here radiation polymerization processes of adsorbed molecules on the surface of the substrate are played by the decisive role.

Analysis of kinetic dependences of specimens in region 1 and 2 on the reactor (Figure 1b), where negligible influence of active component of the gas phase on the formed polymer layer is, has indicated that the polymerization reaction has a first order (Figure 3, curves 1-3). Order of the growth kinetics changes from first to zero order (Figure 3, curves 4 and 5) at the coating thickness of 3...5 μm in the region of specimens 4 and 5 (Figure 1b), where the polymerization reaction proceeds rapidly. For the intermediate region 3 this transition occurs only at the final stage of the coating formation. This phenomenon in the film deposition process can be explained by the fact that the active centers of substrate are the deciding factor of the polymer film growth in the initial period of the layer condensation

Films are formed according to the mechanism of the adsorption-type polymerization at the absence of an electron-ion bombardment, when the neutral particles and macromolecules of products of plasma chemical reactions are deposited on the surface. For the case of intense plasma exposure on growing layer of fluoropolymer (Figure 3, curve 5) radiation-stimulating processes of transverse molecular linkings with the formation of cluster structures are dominated [8, 9]. Processes of temperature increasing of growing polymer layer due to the impact of high-frequency field [10-14] and the plasma particles of HF discharge [15, 16] also have an important role. Moreover, the short molecular -C-C- structures of main chain dominate in the polymer; it substantially impairs their electrical properties, but increases the adhesion and cohesion characteristics of the coating.

5. Conclusion

Technological HF discharge reactor with oscillating electrons in magnetic field, which allows significantly extending the technological range of operating pressures and possibilities of regulating the concentration of the active gas atmosphere, is proposed. Influence of various technological factors, which occur during the formation of polymer coatings from active gas atmosphere in HF discharge, is considered. The most effective directions of intensifying the process of deposition of coatings in HF discharge are investigated; the fields of optimal mode of the technological process of formation of the fluoropolymer coating are defined. The results of the conducted experimental studies are showed that polymerization process, the molecular and macroscopic structure of fluoropolymer films are mostly determined by the temperature mode of deposition of the molecular flow and intensity of exposure of the active gas atmosphere.

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