Defect formation in fluoropolymer films at their condensation from a gas phase

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Abstract. The questions of radiation defects, factors of influence of electronic high-frequency discharge plasma components on the molecular structure and properties of the fluoropolymer vacuum films synthesized on a substrate from a gas phase are considered. It is established that at sedimentation of fluoropolymer coverings from a gas phase in high-frequency discharge plasma in films there are radiation defects in molecular and supramolecular structure because of the influence of active plasma components which significantly influence their main properties.

1. Introduction
Thin polymeric films thanks to the chemical resistance to hostile environment and high dielectric properties of wide are used in microelectronic, micromechanical devices [1] and touch sensors [2–4]. For receiving thin-film coverings on the basis of fluoropolymer sedimentation methods from a gas phase and polymerization of molecules of C₂F₄ monomer on a firm surface under the influence of the F₂ [5] catalyst are used. Here the stimulating radiations such as X-ray and gamma beams can be applied to polymerization of monomer. There is a row of the elionic technological and ecologically safe technologies where the principle of dispersion of an initial fluoropolymer in a vacuum under the influence of the accelerated electrons and ions at the subsequent secondary polymerization on a substrate of products of dispersion is used [6–8]. Dispersion of a block fluoropolymer on gas environment can also be carried out in plasma of high-frequency (HF) gas discharge [9, 10]. Sedimentation of a fluoropolymer covering at the secondary polymerization on a substrate can proceed in the same conditions as well as at polymerization from C₂F₄ monomer. Use of the elionic technologies for such purposes is well combined with vacuum technology of microelectronic devices and creates a possibility of steady production control of drawing films of a fluoropolymer. The received vacuum fluoropolymer films on the molecular structure and a supramolecular structure are close to industrial films of the fluoroplast, however by the structure they differ from industrial films because of the existence of defects in the received films. In the process of sedimentation from the gas environment in the high-frequency discharge on a surface of a solid body as processes synthesis of polymer of the growing layer and its destruction under the influence of active components (electrons, UF-radiation, ions) plasmas at the same time proceed [7, 11]. For the purpose of receiving polymeric coverings with the set properties identification of physical and chemical mechanisms of growth of fluoropolymer films is necessary to define ways of production control of their receiving [12].

In the article factors of influence of electronic high-frequency discharge plasma components on molecular structure and properties of the fluoropolymer vacuum films synthesized on a substrate from a gas phase are investigated.
2. Samples and technique of an experiment

The studied samples of fluoropolymer coverings were formed in a vacuum by sedimentation on a substrate in the high-frequency discharge at a frequency of 13.56 MHz of an active molecular stream of products of dispersion of a target from an industrial polytetrafluoroethylene (PTFE) by the technique stated in [10]. In the process of condensation the growing fluoropolymer covering was exposed to electronic processing by the active component of the high-frequency discharge plasma. As a substrate served the silicon polished plates and monocrystals of KCl. Growth rate of coverings was 0.05…1.0 μm/min. Temperature of a surface of a substrate changed within 300…500 K. Molecular structure of films of fluoropolymer on a substrate from KCl estimated on IK-spectrums and data of electronic paramagnetic resonance (EPR). Molecular, electric and adhesive properties of fluoropolymer with coverings 0.5…7.0 μm were investigated.

Structural properties of films of fluoropolymer were investigated by method of the differential and thermal analysis (DTA). The structure of films was investigated by methods of IK-spectroscopy and X-ray photoelectronic spectroscopy (PES) on substrates of silicon and monocrystals of KCl. The degree of crystallinity was determined by method of X-ray spectroscopy, and concentration of radiation defects and communications by keeping of radicals in structure was determined by method of the EPR.

3. Results of researches and their discussion

In Figure 1 the results of a research of films structure are presented by method of the differential and thermal analysis (DTA). Curves 1, 2 and 3 correspond to samples of the vacuum films received at impact on the growing layer of a film electronic radio-frequency-generated plasma stream components with a current density ~ 0.07, 0.6 and 1.3 A/m².

According to the ranges of DTA (Figure 1a) characteristic maxima of temperatures change at loss of mass (Figure 1b) of the substance of a fluoropolymer synthesized on a substrate which was exposed in the course of condensation of a layer to continuous electronic processing by high-frequency discharge particles are observed. So the film of a fluoropolymer besieged on a substrate without the influence of electronic components of the high-frequency discharge plasma has $T_{m1}$ maximum (curve 1, Figure 1a) corresponding to decomposition of polymer at 315 °C. At the influence of
electronic components of high intensity plasma (curve 3, Figure 1a at the density of current of 1.3 A/m²) are shown two additional maxima of \( T_m \) and \( T_m^2 \) in the field of temperatures of 225 °C and 339 °C respectively. Influences of the high-frequency discharge plasma of average intensity (at current \( \sim 0.6 \) A/m²) only one high-temperature maximum of \( T_m^2 \) in the field of 339 °C is shown. Curve losses of weight show that for samples of vacuum films the 1, 2 and 3 (Figure 1b) beginning of process of losses correspond to temperatures: 156 °C, 177 °C and 224 °C.

Researches by DTA method have shown that weak impact of the high-frequency discharge on the besieged layer of a fluoropolymer film leads to formation of cross stitchings of molecular links, which lead to hardening of structure of a fluoropolymer. However, the high intensity of influence leads to an additional radiation inoculation to a polymeric layer of fragments of a molecular chain with radical groups of a gas phase and also to formation of defects at partial decomposition of earlier settled molecules on a surface of the polymerized film [11].

4. Structure of films

In Figure 2 ranges of PES of the fluoropolymer films besieged from a gas phase without influence electronic components (a) of the high-frequency discharge plasma and at her intensive influence (b) are presented. Here peaks 1, 2, 3, 4, 5 and 7 which make ranges (a) (would) also correspond to communications of the molecular (– CF₃, – CF₃–CF₂–), (–(CF₂–CF₂)–), (–C–F), (–C=O), (–C–CF–), (–C–O–C–) and (–C–C–, –C–) groups respectively. From PES of films (Fig. 2) it is visible that electronic processing of the growing layer of a fluoropolymer by the active component of the high-frequency discharge plasma leads to essential change of maintenance of molecular complexes in structure towards their increase (Figure 2b). It also leads to emergence of high deficiency in molecular and supramolecular structures of the received fluoropolymer.

4.1. Structure of films

In Figure 2 PES-spectrums of the fluoropolymer films besieged from a gas phase without influence electronic components (a) of the high-frequency discharge plasma and at her intensive influence (b) are presented.

In Figure 3 IK-spectrums of the fluoropolymer films received in the high-frequency field are presented: 1 – without plasma influence; 2 – at weak influence electronic radio-frequency-generated plasma components; 3 – when processing by a strong stream of charged particles of plasma.
Figure 3. IK-spectrums of the fluoropolymer films received in the high-frequency field.

In Figure 4 the dependence of intensity of strips of absorption of 735 and 1050 cm\(^{-1}\) in IK-spectrum, the depreciation of structure of a film of a fluoropolymer corresponding to peaks, from degree of crystallinity of \(\chi\) is presented.

In Figure 5 the dependence of intensity of an absorption strip of 1710 cm\(^{-1}\) in IK-spectrum from concentration of \(C_p\) of radical backs in the besieged film of a fluoropolymer is presented.

The analysis of the obtained experimental data of IK spectrums and a PES ranges (Figure 2–5) shows that with increase in intensity of influence by the active components of a plasma flow of the high-frequency discharge depreciation of its structure increases by the growing fluoropolymer film. On changes of IK-spectrums it is possible to judge imperfections of the received films which are defined by conditions of their formation. Crystallinity \(\chi\) of the films received by polymerization in the high-frequency field without plasma stream (curve 1 Figure 3a) can reach \(\sim 25\ldots28\%\). In IK-
spectrums cross stitching’s in polymer correspond absorption peaks in the range of 1680…1780 cm⁻¹. The full IK-spectrum of a fluoropolymer has a number of additional strips of absorption in the area 525, 978, 1660…1710 and 1772 cm⁻¹ and also considerable expansion of the main peak of absorption of a fluoropolymer chain –C–C–C– in the area 1100…1300 cm⁻¹.

With increase in intensity of electronic processing of the growing polymer layer (curve 3, Figure 2a) increase in content of the C=C defects in a film layer is observed at simultaneous decrease in molecular weight of the main chain –C–C–C– of polymeric links. Also increase in maintenance of cross stitching’s in molecular structure of a fluoropolymer is observed. Electronic processing of the growing layer of a fluoropolymer leads to partial destruction of its natural structure with formation of radiation defects. Spin-radicals are formed due to radiation modification of the growing film layer in the course of her synthesis [11], similarly as in a graphite covering [13]. In the absence of plasma processing the received polymeric film in structure has concentration of C=C radicals no more (1…2)·10¹⁸ spin/g. Increase in maintenance of radical backs in a layer of a fluoropolymer leads to increase in its electric conductivity and deterioration in dielectric properties.

By thickness the fluoropolymer covering on a substrate in the process of its growth finds layered structure and in strong degree depends on the electric and thermal modes of her formation. The layered structure can conditionally be divided into three main types: – the adsorptive with thickness (0.2…1.5 μm); – the main, up to 5…8 μm; – superficial, depending on growth modes.

The polymeric layer grows in the mode of the adsorptive growth of a covering without influence of a plasma stream on the mechanism of kinetics of the first order. At the same time the film with the thickness of 1…1.5 μm repeats a substrate relief at volume uniformity has high uniformity. Then with increase in thickness of a film crystal areas in the form of "balls" with the primary growth of the developed surface are formed.

The main layer of such covering has pores of 0.05…0.3 μm directed on a normal to a substrate. The surface of polymer has the regional angle of wetting by water ~ 105° at a thickness of 2…5 μm. With the described epitaxial growth the covering has extreme thickness ~ 5.8…6.3 μm.

5. Conclusion

Thus, when receiving vacuum fluoropolymer thin-film coverings from a gas phase in radio-frequency-generated plasma in a polymeric layer there are radiation defects in molecular and supramolecular structure due to influence of active components of particles of the high-frequency discharge plasma which considerably influence their main properties. By the directed impact of a plasma stream on the growing polymer layer in technological process, it is possible to operate properties of the received polymeric covering.

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References

[1] Skorykh V J et al 2001 5th Korea-Russia International Symposium on Science and Technology - Proceedings: KORUS 2001 1 42–45 doi: 10.1109/KORUS.2001.975049
[2] Sessler G M 1987 Electrets (Verlag Berlin Heidelberg: Springer) doi: 10.1007/3-540-17335-8
[3] Pevtsov E Ph et al 2017 IOP Conf. Ser.: Mater. Sci. Eng. 168 012095 doi: 10.1088/1757-899X/168/1/012095
[4] Luchnikov P A et al 2017 IOP Conf. Ser.: Mater. Sci. Eng. 189 012027 doi: 10.1088/1757-899X/189/1/012027
[5] Enslin S E et al 1986 South African J. of Chemistry 39 23–26
[6] Krasovski A M et al 1989 Preparation of thin films by spraying polymers in vacuum (Minsk: Science and Technology) (in Belarus)
[7] Rogachev A V 2016 Micro- and Nanocomposite Polymer Coatings Deposited from Active Gas Phase (Moscow) (in Russia)
[8] Sokol R et al 2011 Proceedings of the 6th International Scientific Symposium on Electrical Power Engineering (ELEKTROENERGETIKA) 380–383
[9] Plotnikova I V et al 2017 Journal of Physics: Conference Series 881 012006 doi: 10.1088/1742-6596/881/1/012006
[10] Luchnikov P A et al 2017 IOP Conf. Ser.: Mater. Sci. Eng. 189 012014 doi:10.1088/1757-899X/189/1/012014
[11] Luchnikov P A et al 2017 IOP Conf. Ser.: Mater. Sci. Eng. 168 012092 doi:10.1088/1757-899X/168/1/012092
[12] Petrova A.Y et al 2015 Technical Physics 60 592–594 doi: 10.1134/S1063784215040222
[13] Piliptsou D G et al 2017 IOP Conf. Ser.: Mater. Sci. Eng. 168 012103 doi:10.1088/1757-899X/168/1/012103