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The structure and molecular orientation of polytetrafluoroethylene coatings deposited from active gas phase

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ABSTRACT

The molecular structure of polytetrafluoroethylene (PTFE) coatings deposited on aluminium substrates was investigated by the method of attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR). It has been shown experimentally that PTFE coatings deposited by the electron-beam dispersion method have molecular orientation and are ordered nonmonotonously during the process of coating growth. Maximum order and orientation of molecules along the normal to the substrate are observed in an interfacial layer located within up to 100 nm to the substrate. The observed morphological and orientation features of the formed layers were explained using the proposed adsorption-diffusion mechanism of polymer coating formation.

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1. Introduction

Research on physical and chemical processes taking place during formation of thin polymeric layers from a gas phase, their structure and properties are regarded to be one of the most active and effectively developing directions in physics of thin films at present time [1–3]. A number of works, devoted to the research of structure of thin polymeric coatings of polytetrafluoroethylene (PTFE), produced by various methods such as: plasma polymerization of monomer [1,2], laser ablation [4], sputtering (synchrotron or high-frequency magnetron) [5,6], etc. have been published. It has been established that depending on the method of production, conditions and modes of deposition, the structure and orientation of formed layers vary in a wide range: from completely off-oriented [7] up to those having the expressed orientation relating to the substrate [8–10].

During the process of layer deposition from the active gas phase, generated as a result of destruction of an initial polymer by the concentrated flux of particles or radiation, morphology and molecular structure of the layers are defined, first of all, by the mechanism of formation processes of a polymeric phase. In the

research [11,12] it is shown that under certain conditions of gas phase generation, the layers grow as a result of adsorption and following polymerization, including adsorption on surfaces and their secondary polymerization of dispersed volatile products. In this case the process of synthesis of molecules and their molecular organization proceeds simultaneously in conditions of active influence of a substrate surface at the initial stages of deposition. On the other hand, these conditions define the features of molecular and supramolecular structure of the boundary layers of a polymer [12], character of their transformation during the growth of a coating.

In the given research morphology, structure and orientation of PTFE molecules in a boundary layer deposited from the active gas phase, generated by electron-beam dispersion of an initial polymer in vacuum is studied to define the features of their changes during the growth of a coating.

2. Experimental

The coatings PTFE 2–400 nm thick were deposited from the active gas phase formed by electron-beam dispersion of the initial polymer in vacuum by the method, described in Ref. [13]. The silicon wafers and aluminium-plated polyethylene terephthalate films were used as the substrates.

The coating deposition of a required thickness gradient was reached by using a computer-controlled shutter. The growth rate

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(0.5–1 nm/s) was measured with a quartz crystal microbalance (QCM).

Morphology of the polymeric films surface was investigated by the AFM method using the multimode scanning microscope Solver-PRO (NT-MDT) in a tapping mode. The silicon cantilever of NSG 10 series with the elasticity constant of 11.5 N/m and the radius at top less than 10 nm was used. The surface morphology of the films was also analyzed with a Hitachi S-806 scanning electron microscope (SEM).

Studies of the polymeric coating structures were carried out by the method Fourier transform infrared spectroscopy with a spectrometer Vertex 70 (Bruker Optik GmbH) in a mode of the attenuated total reflection (ATR) employing a special unit by 'Carl Zeiss'. The parallelogram-shaped plate from KRS-5 with 14 reflections and the face angle $\nu = 45^\circ$ was used as a reflecting element. The angle of incidence (ν) of the infrared radiation at the interface between the ATR crystal and the polymer film was constant and equal to 45° . When mounting the polymer film to the ATR crystal, a torque wrench was used to maintain constant pressure between them. For polarization measurements, the infrared radiation was polarized with a KRS-5 wire-grid polarizer (model F 350 MIR, Bruker Optik GmbH). Spectra were taken in a spectral range of $400\text{--}4000\text{ cm}^{-1}$ with a resolution not worse than 4 cm^{-1} , signal accumulation was spent on 24 spectra. Visualization and mathematical processing of the ATR-FTIR spectra were carried out by a specialized software OPUS-NT (Bruker Optik GmbH).

The band at 1156 cm^{-1} , which is a combination of bands 1210 (valence vibrations $-\text{CF}_2$ and $-\text{CF}_2-\text{CF}_2-$) and 1156 cm^{-1} (valence and deformation vibrations CF_2) [14,15], as a band of the internal standard was used instead of the commonly recommended band of 2365 cm^{-1} [14]. This decision was taken taking in account fact, that the recommended band (2365 cm^{-1}) is practically not resolved for the investigated PTFE thin coatings with the thickness up to 500 nm . The measurements have shown that the linear dependence of optical density of 1156 cm^{-1} band on the thickness of PTFE coating takes place with high reliability (correlation factor $R^2 = 0.977$). It is necessary as well to point out that the advantage of choosing the band of 1156 cm^{-1} (instead of 1210 cm^{-1}) lies on its relative isolation— 1210 cm^{-1} band is blocked by the closely situated band of 1246 cm^{-1} , which is responsible for the valence vibrations of C–C groups and deformation vibrations of $-\text{CF}_2$ groups [16].

3. Optical evaluation of molecular orientation

It is known that the degree of molecular orientation of polymeric layers can be characterized by the dichroic ratio [17,18]:

$$DR = A_{//}/A_{\perp}, \quad (1)$$

where $A_{//}$ is the optical density of the polarized light extending in the direction parallel of molecules orientation and A_{\perp} is the optical density of polarized light in the direction, which is perpendicular to the orientation.

Let's take into consideration that in the general cases the density of absorption is [18–20]:

$$A = k\langle(\mathbf{E} \times \mathbf{M})^2\rangle, \quad (2)$$

where k is the factor of absorption, \mathbf{M} is a vector of the transition dipole moment of a molecule, and \mathbf{E} is a vector of an electric field. The angular brackets specify averaged value in all possible directions of fluctuating molecules.

Let us accept, that the analyzed coating and the surface of the ATR crystal are in a plane (X and Y), and coordinate Z is counted in a direction normal to the surface of the coating. Then at the chosen scheme of measurements the light extends in the direction of axis X . At the same time, the parallel polarized light will have

oscillations of vector \mathbf{E} in parallel to the plane of incidence (X and Z), and perpendicularly polarized light will have oscillations, which are perpendicular to the plane of incidence. In our case in point (2), it is possible to write:

$$A_{\perp} = k E_y^2 \langle M_y^2 \rangle = k_y E_y^2, \quad (3)$$

$$A_{//} = k E_x^2 \langle M_x^2 \rangle + k E_z^2 \langle M_z^2 \rangle = k_x E_x^2 + k_z E_z^2, \quad (4)$$

where $E_{x,y,z}$ is the vector of amplitude of an electric field in the direction of corresponding axis; k_x, k_y, k_z is the integrated factors of absorption in direction X, Y, Z accordingly.

In our case, producing thin polymeric layers from a gas phase it is possible to consider that the axis of symmetry of PTFE spiral molecule has orientation only in the direction of growth, i.e. axis Z , and then, according to the model of uniaxial orientation offered by Fraser and co-workers [21,20], the following equation can be applied for calculation k_x, k_y, k_z :

$$k_z = kM^2 \left(f(\gamma) \cos^2(\Theta) + \left(\frac{1}{3}\right)(1 - f(\gamma)) \right), \quad (5)$$

$$k_x = k_y = kM^2 \left(\left(\frac{1}{2}\right) f(\gamma) \sin^2(\Theta) + \left(\frac{1}{3}\right)(1 - f(\gamma)) \right), \quad (6)$$

where $f(\gamma)$ is an orientation parameter of the sample along axis Z , γ is an angle between axis Z and an axis of molecule symmetry, Θ is an angle between the axis of symmetry and the transition dipole moment of a molecule.

The equality $k_x = k_y$ holds truth when a molecule is oriented along axis Z .

Expression (1) taking into consideration (3)–(6) can be written in the following way:

$$DR = \frac{E_x^2}{E_y^2} + \frac{E_z^2 [1/2 f(\gamma) \sin^2(\Theta) + (1/3)(1 - f(\gamma))]}{E_y^2 [f(\gamma) \cos^2(\Theta) + (1/3)(1 - f(\gamma))]} \quad (7)$$

The solution of the given equation regarding $f(\gamma)$ can be given by the following expression [20,22]:

$$f(\gamma) = \frac{2}{3 \cos^2(\Theta) - 1} \frac{E_x^2 + E_z^2 - DR E_y^2}{E_x^2 - 2E_z^2 - DR E_y^2}, \quad (8)$$

In the given work we only consider the absorption band at 1210 cm^{-1} , which is typical for molecules with A_2 type symmetry. In this case $\Theta = 0^\circ$ [23,24]. Then expression (8) has the following solution [20,22]:

$$f_0(\gamma) = \frac{E_x^2 + E_z^2 - DR E_y^2}{E_x^2 - 2E_z^2 - DR E_y^2}. \quad (9)$$

The electric field amplitudes (E_x, E_y, E_z) depend on the film thickness as well as on the refractive indexes of the ATR crystal and film. The refractive index of KRS-5 is equal to 2.45 and is fairly independent of the wavelength in the infrared region. In our case the refractive indexes of thin PTFE films were determined from the reflectance spectra. We have found difference between the maximum of interferogram and to define the thickness of PTFE coatings we have calculated the refractive indexes of polymer films. The relative values of refractive indexes of the investigated polymer films differed less than 15% while the DR values changed in a dozen times in the region $2000\text{--}500\text{ cm}^{-1}$. Thus we have taken as a first approximation the value of refractive index of polymer films fixed and equal to $n_2 = 1.375$. The normalized values of amplitudes of electric vectors were defined from the known expression for the thick coatings [17]. Assuming that the angle of incidence in the internal reflection element is equal to $\nu = 45^\circ$, one can get $E_x = 1.234$; $E_y = 1.725$; $E_z = 2.105$.

For the polymer chains with a cylindrical symmetry, the order parameter of the chain axis, $\langle P_2(\cos(\gamma)) \rangle$, can be calculated from the order parameter of the transition moment, $f_0(\gamma)$, using the Legendre addition theorem [25,26]:

$$\langle P_2(\cos(\gamma)) \rangle = f_0(\gamma) = \frac{3\langle \cos^2(\gamma) \rangle - 1}{2} \quad (10)$$

If the function of orientation distribution of the polymer chains is infinitely narrow, it is possible to calculate the average tilt angle (γ) from the expression (10). The analysis of values of the presented function shows that for $f(\gamma) = 1$ the average tilt angle γ will be equal to 0° , i.e. the molecules will be aligned in parallel to the axis Z, and for $f(\gamma) = -0.5$ the angle γ will be equal to 90° (molecules will be oriented perpendicularly to the axis Z). It is necessary to mention that within the limits of the given model it is possible to consider only the bands of A_2 type symmetry concerning axis Z. Because high values of the measured dichroic attitude for the investigated polymeric coatings (>10) put given restrictions.

4. Results and their discussion

It was found that in the ATR-FTIR spectra (unpolarized light, range of bands $1400\text{--}1000\text{ cm}^{-1}$) of PTFE thin coatings with the effective thickness of 2–400 nm the change in the parity of optical density and displacement for $4\text{--}6\text{ cm}^{-1}$ of the bands with wave numbers 1156, 1210, and 1246 cm^{-1} take place. The exact position of maxima of these bands was defined by deconvolution of a registered spectrum. One should take in account that the vibrations at 1156 and 1246 cm^{-1} have E_1 type symmetry (the dipole moment of vibrations is perpendicular to the axis of a molecule), and 1210 cm^{-1} have A_2 type symmetry (the dipole moment of vibrations is parallel to the axis of a molecule) [23,24]. The analysis of spectra shows that the significant change of relative optical density (the bands with E_1 symmetry, Figs. 1 and 2 have the greatest relative optical density) takes place with the growth of effective thickness of PTFE coating (up to 100 nm) and at the initial stages of growth (thickness up to 50 nm).

Qualitatively the given features are presented in a spectral interval of $600\text{--}450\text{ cm}^{-1}$, in which, according to works [14,24], it is possible to identify bands active at 520 cm^{-1} (a wide band of pendulum vibrations of --CF_2 groups, having A_2 symmetry) and a band of 556 cm^{-1} (deformation vibrations of --CF_2 groups with symmetry E_1) (Figs. 3 and 4).

The variation of relative intensities of the presented bands indicate the change of concentration of molecules of different type symmetry taking place during the growth of PTFE coating. The experimentally established higher concentration of molecules with E_1 type symmetry at the initial stages of growth indicates the

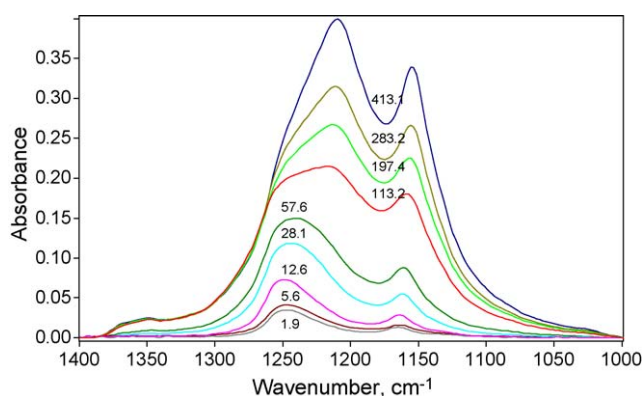


Fig. 1. Unpolarized IR ATR spectra of PTFE coatings with the thickness 1.9–413.1 nm in the spectrum field of maximum absorption of $1400\text{--}1000\text{ cm}^{-1}$.

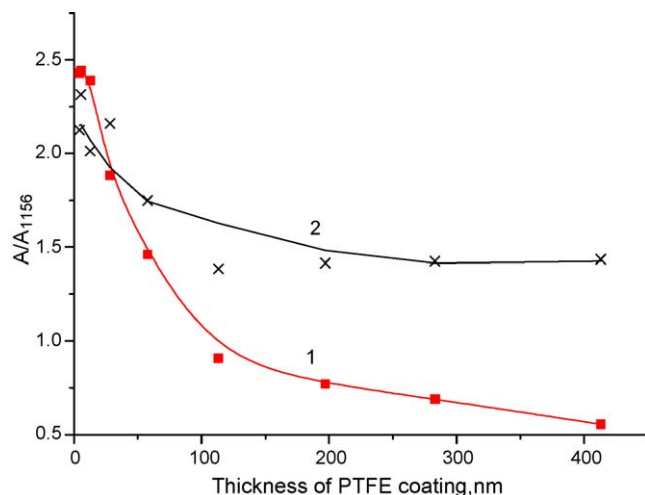


Fig. 2. Dependence of the relative optical density A_{1246}/A_{1156} (1) and A_{1210}/A_{1156} (2) on the effective thickness of a PTFE coating.

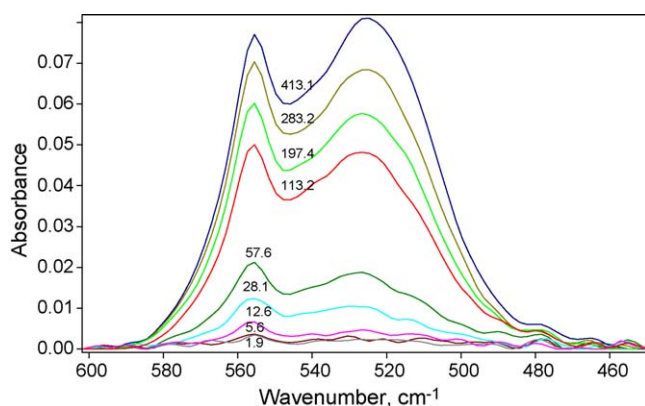


Fig. 3. Unpolarized IR ATR spectra of a PTFE coating with thickness 1.9–413.1 nm in the range of $600\text{--}450\text{ cm}^{-1}$.

primary molecule orientation in parallel to the surface of a substrate.

Using the ratio (1) the dimensional dependences of dichroic attitudes DR of bands, active at 1156, 1210, and 1246 cm^{-1} have been found (Fig. 5). The parameter of orientation and the average

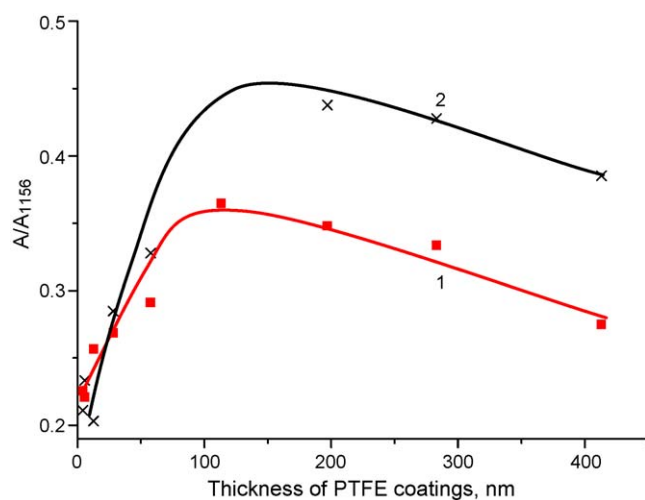


Fig. 4. Dependence of the relative optical density A_{556}/A_{1156} (1) and A_{520}/A_{1156} (2) on the effective thickness of a PTFE coating.

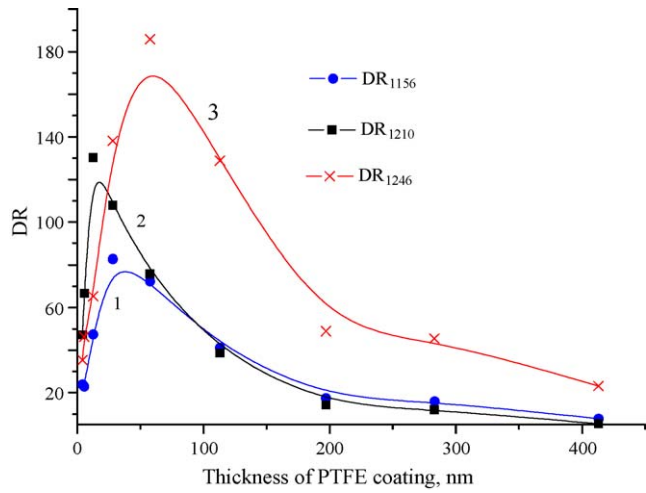


Fig. 5. Dependence of the dichroic attitude DR of bands 1156 cm^{-1} (1), 1210 cm^{-1} (2), and 1246 cm^{-1} (3) versus the thickness of a PTFE coating.

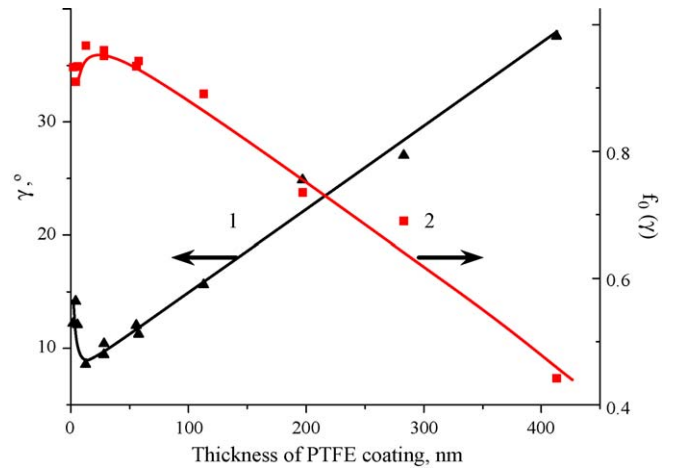


Fig. 6. Dependence of the orientation parameter f_0 (2) and average tilt angle γ (1) between molecule axis and axis Z versus the thickness of a coating.

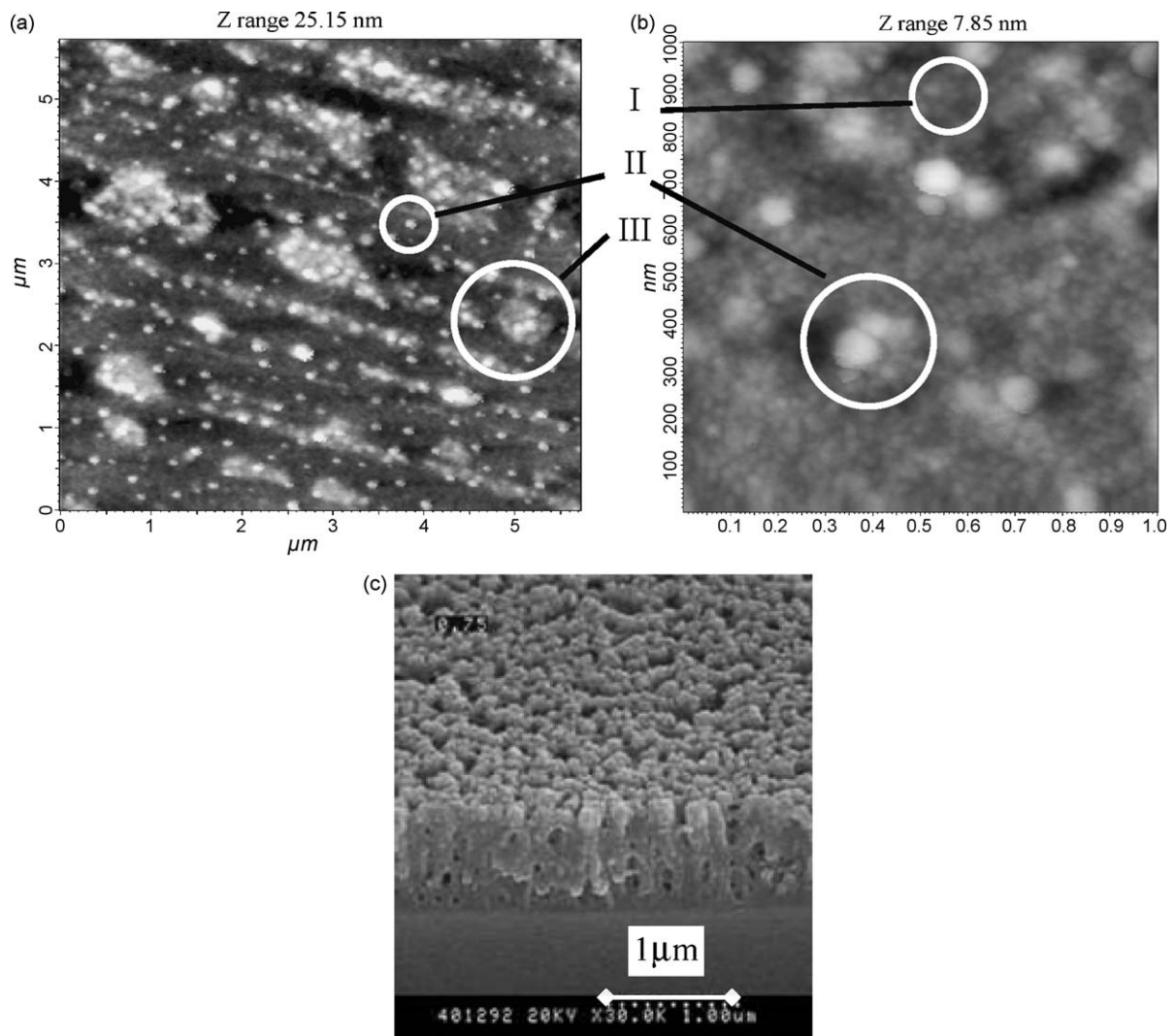


Fig. 7. Morphology of a PTFE coatings: (a) and (b) AFM topography, thickness 80 nm; (c) SEM image of the cross-section of the PTFE coating with thickness 750 nm. (a) Scan size $5.7\ \mu\text{m} \times 5.7\ \mu\text{m}$; (b) $1\ \mu\text{m} \times 1\ \mu\text{m}$.

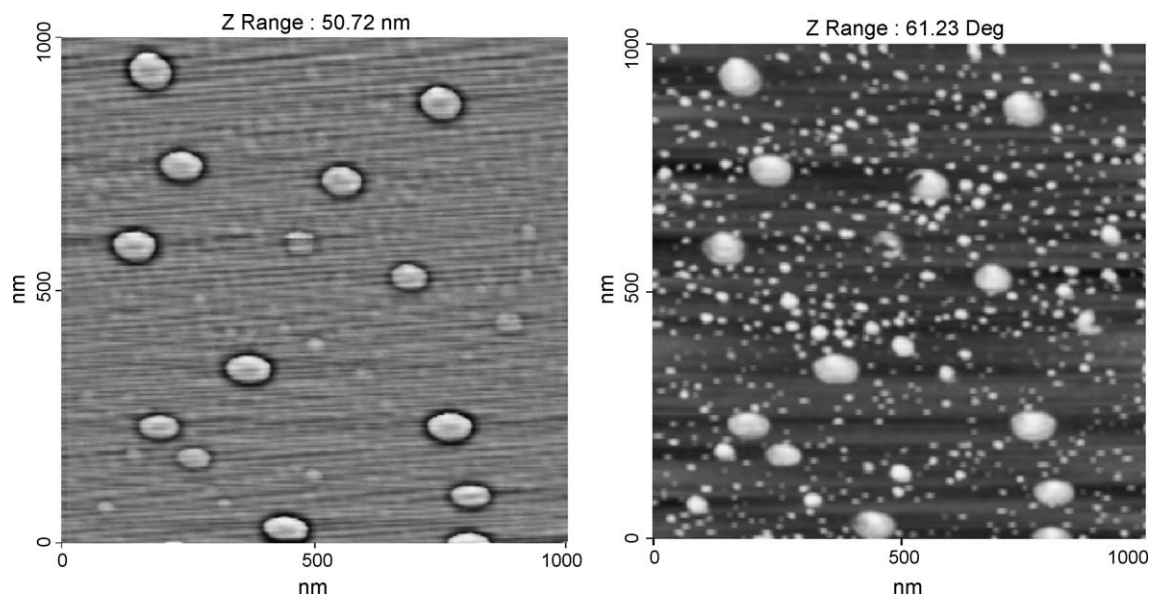


Fig. 8. AFM topography (a) and phase contrast (b) of a PTFE coating with thickness 80 nm after etching in glow-discharge plasma. Scan size $1 \mu\text{m} \times 1 \mu\text{m}$.

tilt angle between the molecule axis and axis Z, calculated by means of ratio (9) and (10) for the band of 1210 cm^{-1} , are presented in Fig. 6.

During the deposition process of a coating with orientation parameter $f_0(\gamma)$ and related average tilt angle between a molecule axis and axis Z, the nonmonotonic change has also been established. At the initial stages of growth the strong increase in orientation parameter is observed (Fig. 6). Its maximal value is reached at the effective thickness of 10–20 nm; further increase in thickness of a coating is related with a monotonous decrease of the orientation parameter. The average tilt angle between the axis Z and PTFE molecule axis changes in a range from 8° up to 38° in a nonmonotonic way as well. It is necessary to mention as well that orientation maximum of the analyzed bands appears at different thickness and it indicates the complex organization of the boundary layers.

The given data correspond to the results of a qualitative analysis in the FTIR-spectrometry studies that were done using the unpolarized light. The orientation of formed layers sharply increased in a layer with effective thickness up to 20 nm (at the initial stage of polymeric coating formation). In thick layers (thickness more than 250 nm), the value of dichroic attitudes of bands 1156 and 1210 cm^{-1} reached up to 10 and changed slightly.

The given molecular features of the thin polymeric layers define their morphology. So far applying AFM measurements, for the PTFE coatings with thickness of 80 nm deposited on a silicon monocrystal the multilevel organization of supramolecular structures was found (Fig. 7). It is possible to allocate structural formations of the nanometer range (type-I). The round-shaped particles with diameter of 20–100 nm (type-II), and larger formations with a diameter of 100–600 nm (type-III), that are probably result of combination of the first two structures, have also been registered. Coatings with thickness over 100 nm are basically formed from the round-shaped particles (type-II). The vertical structure of the films was observed in the cross-section of the films on the micrographs of scanning electron microscope (Fig. 7c). The structural elements with normal orientation to the surface are well visible in the coating profiles.

Etching of the sample with thickness of 80 nm in glow-discharge plasma ($U = 1200 \text{ V}$, $\nu = 400 \text{ Hz}$, $t = 15 \text{ min}$) was done to estimate the contribution of polymer-diffusion mechanism on the growth of structures of different orientation (Fig. 8). One can

see some formations, which are steady against the etching in glow-discharge plasma. They are close to the spherical ones in shape; their diameter is of 100–150 nm and height up to 30 nm over the coating. Finer spherical formations are formed in a near surface layer; however their height is less than 5 nm. At the initial stages the given structural formations are completely latent by a layer of low-molecular non-structured fragments of the macromolecules.

The observed morphological and orientation features of the formed layers can be explained using the proposed adsorption-diffusion mechanism [11,13]. According to this model there is a formation of nuclei of the polymeric phase deposited on the sites of a substrate with high absorption features at the initial stages of growth. The molecules are poorly ordered in a direction parallel to the surface until effective thickness of a layer up to 10–20 nm is reached. Further, layers with the high orderliness and orientation along to axis Z are produced due to lateral growth of particles by the capturing of the active particles of the adsorbed molecular fragments. The influence of substrate surface decreases in rather thick layers and, as a consequence of it, orientation of the macromolecules becomes less expressed and the formation of the particles with a diameter up to 140 nm is observed.

5. Conclusion

Morphology and molecular structure of the polymeric PTFE coatings deposited by the electron-beam dispersion method, character of its transformation during the process of growth have been studied. It has been found that orientation and order of the formed layers varies nonmonotonously during the process of coating growth. Maximum order is observed in an interfacial layer located within up to 100 nm to a substrate. It has been shown that at the initial stages of dispersion the average tilt angle γ between the molecule axis and normal to the substrate surface is 14° where the maximum parameter point of orientation is no more than 8° , i.e. the molecules are mainly oriented along the normal to the substrate. The following growth leads to off-orientation of the layer and increase of the average tilt angle γ up to 38° (with effective thickness 400 nm). The given molecular features of the deposited layers, their morphology testify to the main polymer-diffusion mechanism of PTFE coatings growth from an active gas phase.

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