

BRIEF
COMMUNICATIONS

Morphology of Polytetrafluoroethylene Coatings Formed from the Active Gas Phase and Its Thermal Modification

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Abstract—Changes in the morphology and surface energy of polytetrafluoroethylene coatings in the course of their growth and after annealing were determined.

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Physicochemical processes occurring in the course of adsorption and nucleation of particles and in the initial steps of thin polymeric film growth from the active gas phase affect the structure of the resulting coatings and their properties [1, 2]. Previously we showed that the first deposition steps of polymer coatings from volatile products of electron-beam dispersion of the initial polymer, unlike adsorption and nucleation of, e.g., metallic phase, are obviously non-equilibrium [3, 4]. The parameters of the surface distribution of the polymer particles and the kinetics of the change in their density in the course of the deposition depend on the support and the degree of its activation [4]. We also found [5] that the volatile products of electron-beam dispersion are highly reactive and can react with the support during their adsorption. This feature, the long-range influence of the support surface, and selective desorption from the surface determine the physicochemical properties of the coatings and the structural nonuniformity of the boundary layers [6].

In the course of formation of thin polymer coatings from volatile dispersion products, the growth of the macromolecular chains and the films as a whole, as well as their structure and properties are determined by the mobility of the kinetic elements and by the intermolecular interactions [2]. Therefore, all external actions (heat treatment, irradiation, surface and bulk modification, etc.) affecting the synthesis and conformations of the macromolecules can be used to effectively control the deposition with the aim to change the structure and properties of the coatings.

In this study we examined the kinetic features of

the first steps of deposition of polytetrafluoroethylene (PTFE) coatings and the influence of heat treatment on their morphology and surface properties.

EXPERIMENTAL

The coatings were prepared by electron-beam dispersion of PTFE by the procedure described in [3]. The coatings with the required properties were deposited using a special device with a controlled damper. The growth rate and the effective thickness of the coatings were measured with a quartz thickness gage (QTG). Polished silicon single-crystal wafers pretreated with R-646 organic solvent were used as the supports.

We studied the morphological changes and the adsorption properties of PTFE coatings in the course of their growth and vacuum annealing. The coatings were annealed in a vacuum at 455 K for 20 min with the aid of a resistive heater and then were cooled at a rate of 8–12 K min⁻¹. The morphology of the as-grown or annealed coatings was studied by atomic force microscopy (AFM) using a NANOTOP-2003 measuring setup. The scanning was performed in the tapping mode. To analyze the cluster formation, additional mathematical treatment was performed. The surface cluster distribution was constructed by the horizontal cross-section procedure with marking of the clusters. The cross sections with the minimal cluster content were analyzed [7]. The minimal considered surface area of the cluster (0.03 μm²) did not exceed the microscope resolution. The maximal considered surface area of the cluster was 0.42 μm².

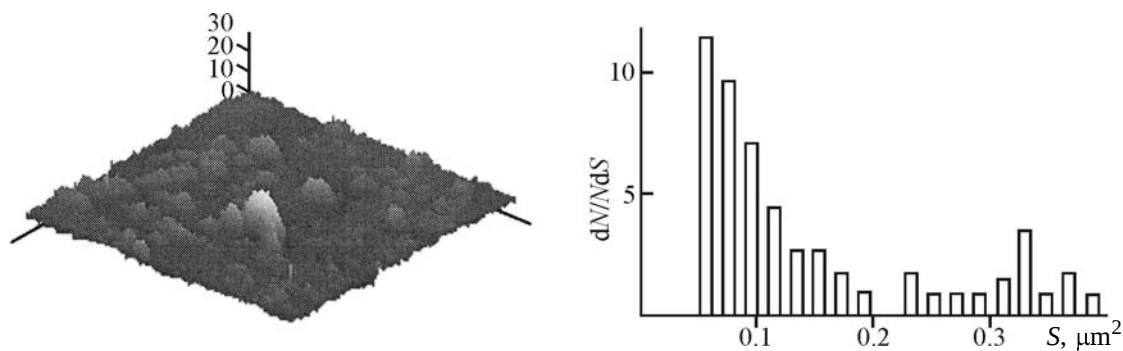


Fig. 1. AFM image of PTFE coating with the effective thickness of 9.1 nm and the particle distribution dN/NdS with respect to the surface area of their base S . Scanning area $13.5 \times 13.5 \mu\text{m}$.

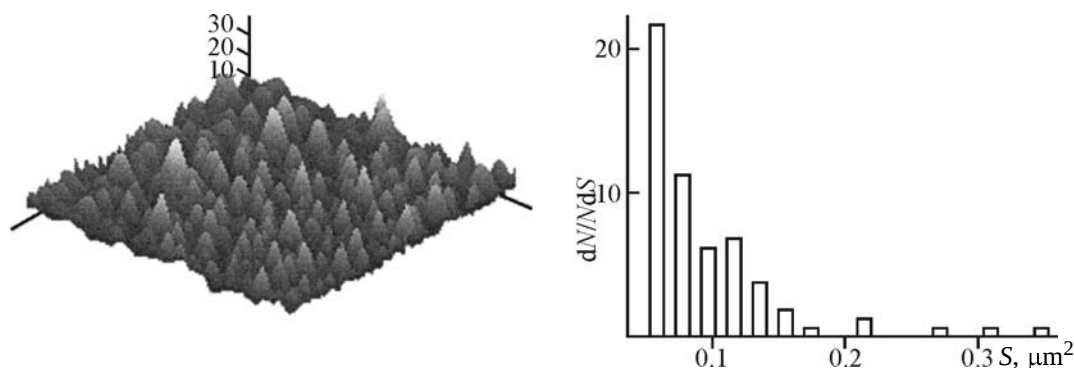


Fig. 2. AFM image of annealed PTFE coating with the effective thickness of 4.5 nm and the corresponding particle distribution dN/NdS with respect to the surface area of their base S . Scanning area $7.4 \times 7.4 \mu\text{m}$.

To study the surface properties of the coatings, the limiting wetting angles of their surface with distilled water and glycerol were measured. The polar and dispersion components of the surface energy were determined by the Fowkes procedure [8].

The shape of PTFE microparticles and their distribution over the surface of a silicon crystal in the initial deposition steps are determined by high adsorption nonuniformity of the support. The polymer microparticles grow on the active sites of the support, whose density is relatively low. This is consistent with our previous results [4]. The particle distribution with respect to the surface area of their base is complex (Fig. 1) and can be considered a superposition of the exponential distribution (in the range of low particle areas) and distribution with a maximum which is shifted to the larger particle size with increasing film thickness.

The density and height of polymer microparticles increase and the average surface area of their base decreases after annealing of the dispersed polymeric coating. The cluster density increases by a factor of 3.5, the weighted-average area decreases by a factor of 1.8, and the average cluster height increases from 7.6 to 12.2 nm after heat treatment of a PTFE coating

with the effective thickness of 4.5 nm. When thicker coatings (e.g., with the effective thickness of 9.1 nm) are heated, the average height of their microparticles increases from 11.4 to 27.1 nm. To understand this experimental result, it should be taken into account that the adsorption layer of dispersed particles involved in polymerization is formed on the support surface in the first deposition steps [3, 4]. On heating of the coating above the glass-transition point, the macromolecules become more mobile and hence their agglomeration intensifies. The temperature effect on the density of polymeric particles sorbed from solutions is similar [9]. The parameters of particle distribution in annealed coatings of different thickness were determined. We expected that, as in the case of the unannealed samples, larger polymer microparticles are formed with increasing coating thickness. However, our experimental results showed that in the annealed samples the weighted-average particle surface area ($0.12 \mu\text{m}^2$) did not noticeably change and the particle density decreased from 2.28×10^{12} to $1.12 \times 10^{12} \text{ m}^{-2}$. The distribution of the microparticles with respect to the surface area of their base is close to exponential (Fig. 2). This is probably due to the fact that the adsorption phase of the 4–10-nm coatings is

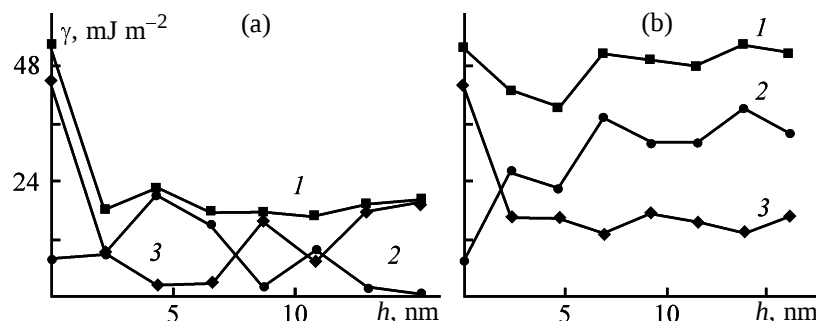


Fig. 3. (1) Total surface energy γ of PTFE coating and its (2) dispersion and (3) polar constituents as functions of the thickness h . (a) Before and (b) after annealing.

sufficiently continuous (the monolayer thickness is from 1 to 2 nm [10]) and the adlayer containing mobile particles is structured on heating. The increase in the average height of microparticles in the annealed samples can be due, on the one hand, to thermal desorption of low-molecular-weight fragments (decrease in the effective thickness of continuous adlayer) and, on the other hand, to thermal activation of structuring processes in the bulk.

It was found that the dependence of the surface properties of annealed and unannealed samples on the effective thickness of a polymer layer is complex. The surface energy of the coating increases by a factor of almost 2 after the heat treatment (Fig. 3).

As we expected, in both cases, the polar constituent of the surface energy substantially decreases in the course of monolayer deposition. This is caused by the features of adsorption interaction and appearance of more active sites of the macromolecules at the interface. The change in the dispersion and polar constituents of the surface energy is caused by this structuring.

The variation of the dispersion constituent of the surface energy correlates with that of the polar constituent. It should be noted that the run of the kinetic curves of the surface energy is similar to that of the fractal dimension determined in our previous study [4]. In both cases, the examined parameters are determined by the number of deposited monolayers, a change in the deposition conditions, and the transformation of the two-dimensional growth of the associates into the three-dimensional growth.

CONCLUSIONS

(1) The particle density and particle height of the polymer coatings increase and the average surface area of the particle base decreases after annealing of the coating.

(2) The surface energy of the annealed coating increases S by a factor of almost 2. The change in the dispersion constituent correlates with that of the polar constituent.

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