

# Structure and Properties of Nanosized Coatings Deposited onto Polymers

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**Abstract**—Results of studies aimed at developing a new approach to measuring stress–strain properties of nanosized solids (strength, yield stress, and the value of plastic deformation at uniaxial tension) are generalized. This approach is based on the analysis of the parameters of microrelief arising upon the deformation of polymer films with thin coating. It is demonstrated for the first time that the stress–strain properties of aluminum coatings deposited onto lamsan substrates depend on the level of stresses in the substrate, the value of its deformation, and the thickness of the coating. The evolution of these parameters is related to the strain hardening of metal and the effect of nanostructuring of crystalline materials in the region of small thicknesses. When precious metal (Au, Pt) nanosized films are deposited onto polymers by ion–plasma sputtering, in the course of metal deposition, polymer surface layers interact with cold plasma. Stress–strain properties of polymer surface layers modified by plasma are quantitatively estimated for the first time. The model is proposed that makes it possible to take into account the contribution of the properties of precious metal and plasma-modified polymer surface layer to the strength of the coating.

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## INTRODUCTION

At present, science studying the fundamental properties of nanosized substance is progressing rapidly. As was recently shown [1–7], the transition of the substance from a micro- to nanostate leads to qualitative changes in its physical, mechanical, physicochemical, and other properties. Regardless of the extreme importance of the information on the properties, particularly in the mechanical properties of the substance in the nanostate, this problem is still far from being solved. There is some evidence in the published literature that indicates the development of complex and expensive devices, which makes it possible to estimate the mechanical properties of micron-sized substances under conditions of uniaxial tension [8–10]. At the same time, reliable data on the stress–strain properties of materials whose particles vary from one to dozens of nanometers are almost absent, which is associated above all with the absence of dependable research techniques. Indeed, it is hard to imagine how the properties of a solid with geometric sizes of tens or hundreds of angstroms can be tested using traditional methods. The majority of information about the mechanical properties of substance in nanostate was obtained using indentation methods [11–13]. These methods are characterized by a number of drawbacks; in particular, they do not permit one to really estimate the most significant characteristics of solids such as relative elongation and breaking strength. In connection with this, studies of the development of new approaches to studying the properties of solids (in par-

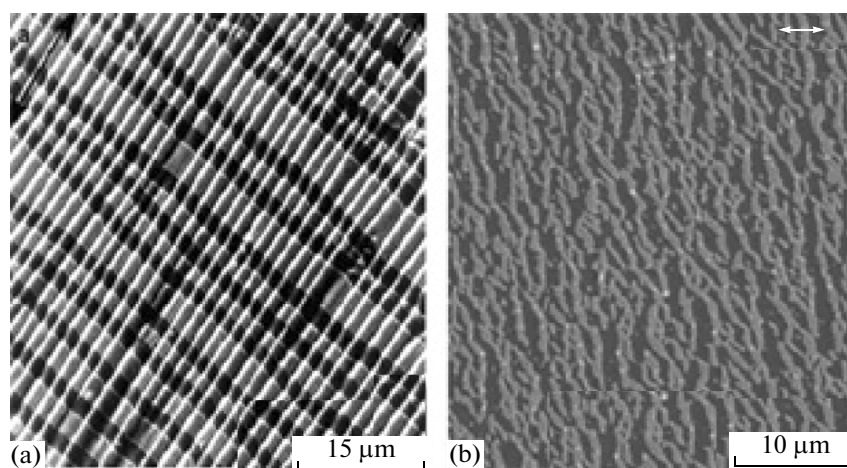
ticular, stress–strain properties) of solids ground to nanostate are especially urgent.

This review is primarily devoted to an analysis of authors' studies on the development of new experimental approaches to the estimation of the stress–strain properties of nanosized solids and the discussion of first results obtained by this method.

## 1. PHYSICAL BASIS OF APPROACH USED TO ESTIMATE STRESS–STRAIN PROPERTIES OF SOLIDS IN NANOLAYERS

To estimate the stress–strain properties of solids in nanosized layers, one must first consider the results of experimental studies that makes it possible to relate their mechanical properties with trustworthy structural data. In connection with this, rapidly developing studies of structure-related mechanical behavior of polymer films with deposited thin solid coatings should be mentioned [14–20]. Similar studies pave the way for experimental approaches that enable us to realize aforementioned aims to estimate the properties of nanosized solids.

Indeed, this approach permits us to obtain coatings of any thicknesses on polymer surface including nanosized coatings. This means that solids can be ground to almost any size using the simplest procedure. On the other hand, the deformation of polymer films with coating leads to a unique type of surface structuring (relief formation) that makes it possible to directly relate the properties of such coatings (in essence, sol-



**Fig. 1.** SEM images of PET films with thin (10 nm) gold coating stretched at (a) 90°C by 50% and (b) room temperature with the formation of neck.

ids ground to nanostate) with some reliably measured parameters of arising microrelief.

Let us consider the theoretical basis of the proposed approach in greater detail. The surface of polymer films with thin rigid coatings after their deformation was studied directly with electron microscopy [16–20]. The SEM images of two poly(ethylene terephthalate) (PET) samples with thin (10 nm) gold coating deformed at (a) 90°C and (b) at room temperature are shown in Fig. 1. It should be noted that the first image was taken from the sample deformed above PET glass transition temperature ( $T_g = 75^\circ\text{C}$ ); the second image was taken at a temperature below  $T_g$ . Clear bands are fragments of fractured coating; dark bands denote cracks in fractured coating.

According to the data presented in Fig. 1, as a result of the simple stretching of the polymer-substrate at a temperature above its  $T_g$ , the coating on its surface is fragmented into a multitude of regularly arranged islands of approximately equal sizes. At the same time, a regular relief is developed in the coating. The regularity of this relief and its strict orientation with respect to the axis of stretching is striking. The cavities and apices of the relief are always orientated strictly along (parallel) the axis of stretching. In the case of the deformation of polymer-substrate at temperature below  $T_g$  (Fig. 1b), only the regular fragmentation of the coating is observed, whereas no regular relief is formed.

Thus, simple stretching of polymer film with thin solid coating leads to the unique type of surface structuring. It is worth noting that both formed structures (regular relief and regular system of the fragments of coating structure) are highly organized and periodic and can be easily characterized using direct microscopic examination. Further studies demonstrated that the formation of these structures has general character and is independent of the nature of materials

comprising the substrate and the coating; therefore, this type of system is known as a “rigid coating on a soft substrate” (RCSS) [14, 19]. Necessary conditions that determine the possible appearance of regular structures described above that result from the deformation of RCSS are as follows: (1) negligibly small thickness of coating compared to the thickness of substrate and (2) substantial difference between the values of rigidity (elastic modulus) of coating and substrate. The material that makes up the coating should have a much higher elastic modulus than the material makes up the substrate. This situation is implemented in polymer film with metal coating because the metal deposited onto the film surface is always harder and more rigid than the material that makes up the substrate.

### 1.1. Mechanism of Formation of Regular Microrelief

The question is raised of how the simple polymer film with coating can organize such a regular structure during simple stretching. The fact that a polymer film subjected to uniaxial stretching simultaneously undergoes to two types of deformation is very significant for understanding the mechanism of observed phenomena. Elongation in one direction is accompanied by the contraction (Poisson compression) in the perpendicular direction. Hence, a rigid coating on the film surface is also simultaneously subjected to two types of deformation, i.e., compression and stretching. This peculiarity of polymers makes it possible to separately consider two phenomena observed in [21–23], i.e., the formation of regular microrelief and regular fragmentation of the coating.

The compression of the coating on polymer surface is responsible for the formation of regular microrelief, which is fundamentally important for understanding the mechanism of this physical phenomenon. The coating is an anisometric solid subjected to uniaxial

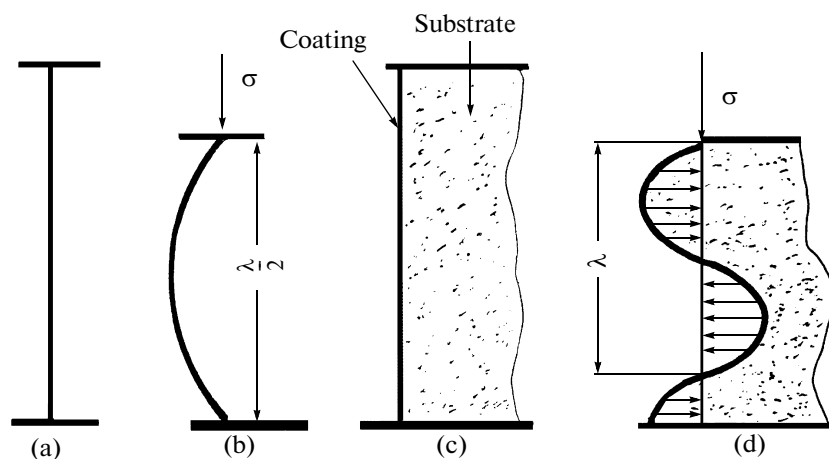


Fig. 2. Scheme of the loss of stability by anisometric solid (a, b) in a free state and (c, d) on soft substrate.

compression on the surface of stretching polymer film. The phenomena that accompany the uniaxial compression of anisometric solids were first considered by Euler, a famous physicist and mathematician, more than two centuries years ago. Euler demonstrated that, when a critical load is achieved in the course of the uniaxial compression of anisometric solid (filament, film, or membrane), it loses its stability and acquires the shape of a half wave (known now as an Eulerian classical loss of stability). However, the situation with a loss of stability by the indicated coating changes crucially when an anisometric solid, which is undoubtedly a thin rigid coating, is strongly bound to a soft substrate (Fig. 2). When the critical compression load is achieved, the body cannot acquire the shape of a half-wave because, upon the deviation from rectilinear shape, it is subjected (from the side of substrate) to the action of restoring force proportional to the value of deviation. As a result of this interaction between the external applied force and arising internal resistance facing the substrate, the coating is inevitably collapsed to acquire sinusoidal shape with wave period equals  $\lambda$ .

The value of the relief period is determined by the following circumstances. The work of deformation upon the compression of anisometric solid (in our case, coating) evidently increases with the number of performed bends (with a decrease in the relief period). It is not accidental that, in the absence of substrate, an anisometric solid acquires the shape of a half wave, i.e., the relief with the largest period is realized. However, a soft, though quite extended substrate attached to the coating introduces corrections into this process. Evidently, the larger the relief period, the higher the amplitude of this relief, all other conditions being equal. An increase in the amplitude of relief implies pulling out the part of the polymer attached to the substrate to a relatively large distance from its originally uniform surface. To perform this deformation of the substrate, one must to apply substantial force, i.e., do some work. In other words, an increase in the period of

the relief that develops, which is favorable for the coating, is quite unfavorable for a soft polymer substrate. The period of relief observed in reality can be calculated from the minimum condition of the total force (stress) balance in the coating and substrate [21].

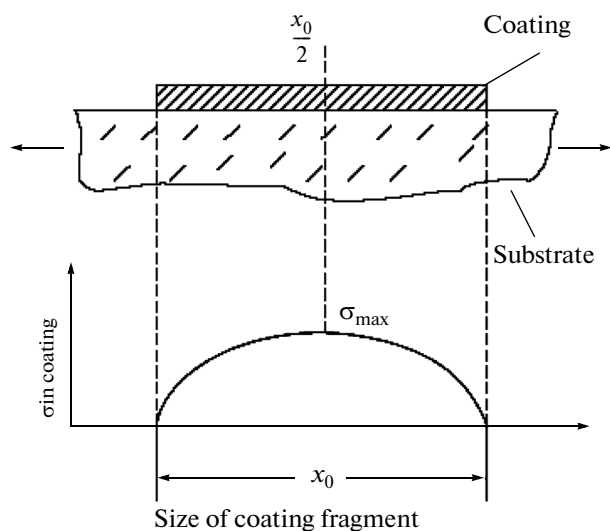
This minimization of the energy of system yields a value of the relief period in the case of the deformation of the plastic substrate

$$\lambda = 2h\sigma_y/\sigma_m(1 - \varphi), \quad (1)$$

where  $h$  is the thickness of coating,  $\sigma_y$  is the yield stress of coating,  $\sigma_m$  is the tensile yield stress of coating, and  $\varphi$  is the degree of coating compression on the surface of polymer-substrate. It is worth mentioning that the formation of a regular microrelief occurs when the substrate is deformed at temperature above its  $T_g$ . Substantial lateral contraction of stretching polymer, which is responsible for the compression of coating on soft substrate, takes place under these conditions.

### 1.2. Mechanism of Regular Fragmentation of Coating

The regular fragmentation of the coating takes place regardless of the physical state (glassy or rubbery) of the deformed polymer (Fig. 1). The fragmentation of the coating is also related to the peculiarities of the transfer of mechanical stresses across the interface from a soft substrate to solid coating. Here, it should be mentioned that the character of the fragmentation of coating depends in particular on the peculiarities of substrate deformation. It turned out that, at the first stages of the deformation of the polymer substrate, the coating is fractured into a set of fragments with quite different sizes [24]. However, after the formation of this initial broad size distribution of coating fragments, unique process of the fracture of each formed fragment starts. The point is that, after the random fracture of the coating, the stretching of the substrate proceeds further; thus, each formed fragment remains under the load. The stress in each



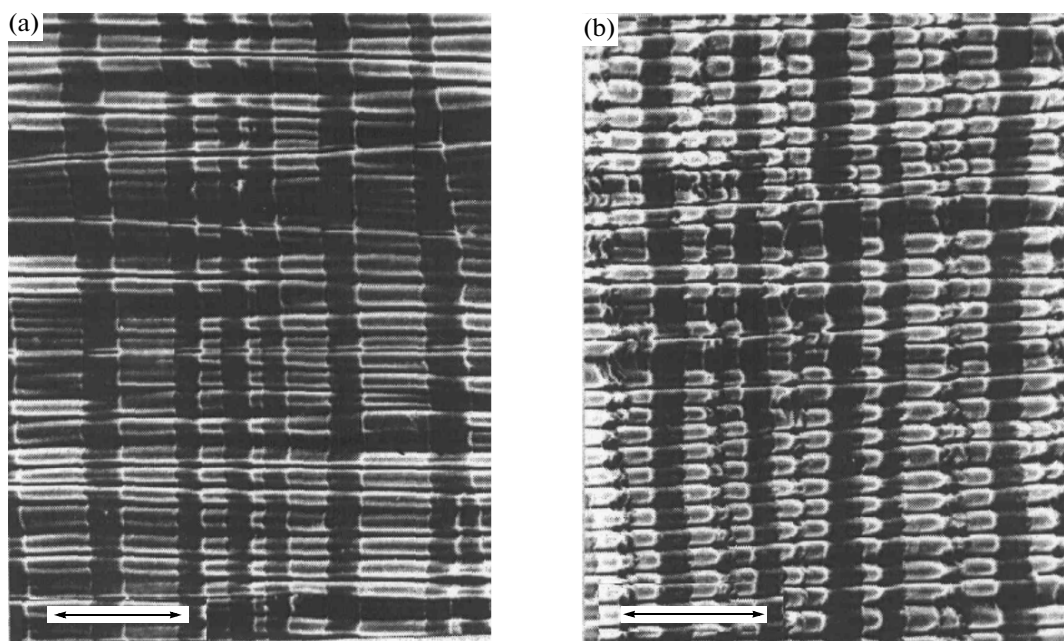
**Fig. 3.** Scheme of stress distribution in fragment of metal coating on surface of deformed polymer substrate.

fragment is distributed in a very nonuniform manner (Fig. 3). It is evident that this stress at the ends of fragment is equal to zero. When moving away from the ends of the fragment, the stress in each fragment of the coating rises and, finally, reaches its maximal value exactly in the center of the fragment. These circumstances lead to a surprisingly elegant process of the fracture of the coating by the disintegration of each fragment into two equal parts. This process is clearly illustrated by Fig. 4. The SEM image of polymer sam-

ple with thin metal coating deformed at relatively low stress is shown in Fig. 4a. It can easily be seen that the coating is fractured into a set of fragments. Afterwards, the stress in the same sample abruptly increased by lowering the temperature of stretching. It is distinctly seen that each fragment is disintegrated into two equal parts (Fig. 4b). This type of the fracture of coating by the disintegration of each fragment into two equal parts proceeds until polymer-substrate will transfer a stress sufficient for its disintegration to each fragment. When this limiting value of stress is reached, further stretching will not cause the disintegration of fragments and they will simply move far away from one another on a stretched substrate while retaining their dimensions. For these reasons, the sizes of fragments are leveled and the set of coating fragments with rather narrow size distribution is formed on substrate surface.

It is worth mentioning that, in the case of a coating fractured by the disintegration of each fragment into two equal parts, there is an independent method of identifying the aforementioned mechanism of fragmentation. Fragment size distributions in the coating were analyzed in [24] as functions of value, rate, and other parameters of the deformation of polymer-substrate. It was shown that, for this type of fragmentation, the dispersion of obtained distributions is low and is equal to 0.2–0.3. Note that, for the random fracture of the coating, this value is approximately equal to 1.0.

Regardless of whether the soft polymer substrate is deformed in a uniform or nonuniform manner (above or



**Fig. 4.** SEM images of (a) PET films with 4-nm-thick platinum coating stretched by 100% at 100°C at a rate of 0.1 mm/min and (b) the same sample after additional tension at higher stress.

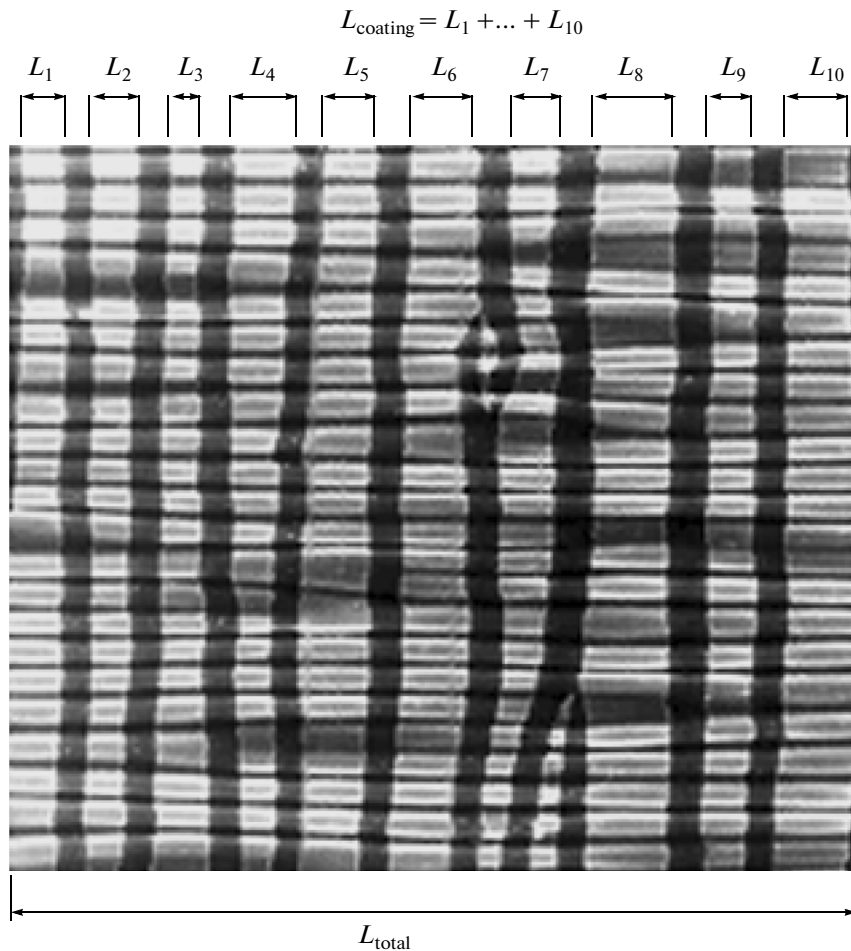


Fig. 5. Scheme of calculating value of plastic deformation of coating upon stretching of polymer-substrate.

below  $T_g$ ), the mean size  $L$  of fragment disintegrated in the direction of the axis of stretching is equal to [17, 25]

$$L = 2h\sigma^*/\sigma_0, \quad (2)$$

where  $h$  is the thickness of coating,  $\sigma^*$  is its ultimate strength, and  $\sigma_0$  is the stress in substrate.

Equations (1) and (2) were confirmed experimentally [21]. Good coincidence between the theory and experiment testifies to reasonable suggestions made with respect to how the regular relief and regular fragmentation of the coating appear on the surface of deformed polymer film.

### 1.3. Procedure for Estimating Plastic Deformation of Coating

The potentialities of the approach developed in [14–25] are not exhausted by the estimation of the aforementioned parameters of the samples of nanosized solids. The deposition of coatings onto polymer films with their subsequent deformation makes it possible to directly determine another important

mechanical characteristic of nanosized solids, i.e., their plastic deformation.

The following procedure, which enables one to use the data of direct microscopic observation, was developed to determine the value of plastic deformation of metal layers deposited onto the surfaces of polymer films [26, 27]. We consider a photomicrograph that demonstrates a typical picture of the fragmentation of metal coating upon the stretching of polymer-substrate with rigid coating (Fig. 5). Evidently, the sum of the lengths of metal (or any other) fragments of fractured coating in the direction of the axis of stretching is equal to  $L_{\text{coating}} = 1 + \varepsilon_{\text{coating}}$ , where  $\varepsilon_{\text{coating}}$  is the value of irreversible (plastic) deformation of coating. For the same sample (or its certain part), for which the value of  $L_{\text{coating}}$  was measured, it is evident that its total length is equal to  $L_{\text{total}} = 1 + \varepsilon$  ( $\varepsilon$  is the deformation of polymer-substrate, which is preset by tensile device). Then,

$$\frac{L_{\text{coating}}}{L_{\text{total}}} = \frac{1 + \varepsilon_{\text{coating}}}{1 + \varepsilon} = \frac{\lambda_{\text{coating}}}{\lambda_{\text{polymer}}},$$

where  $\lambda_{\text{coating}}$  and  $\lambda_{\text{polymer}}$  are draw ratios of coating and substrate, respectively.

Consequently, the desired value of plastic deformation of the coating is equal to

$$\lambda_{\text{coating}} = \frac{L_{\text{coating}}}{L_{\text{total}}} \lambda_{\text{polymer}}.$$

If the value of irreversible (plastic) deformation is expressed in percentage points, then

$$\varepsilon_{\text{coating}} = [(L_{\text{coating}}/L_{\text{total}})\lambda_{\text{polymer}} - 1] \times 100\%. \quad (3)$$

According to Eq. (3), the value of plastic deformation of the coating can easily be determined by directly measuring the sum of lengths of coating fragments in the direction of stretching  $L_{\text{coating}}$  and the total length of sample  $L_{\text{total}}$ , for which  $L_{\text{coating}}$  was measured from micrographs (Fig. 5) with allowance for the known value of the deformation of polymer-substrate  $\lambda_{\text{polymer}}$  set by tensile device.

Test experiments demonstrated [26, 27] that, upon the stretching of PET substrate by 60% at 90°C, the value of plastic deformation of carbon coating,  $\varepsilon_{\text{coating}}$ , is equal to zero. This result indicates that, first, carbon film is incapable of noticeable inelastic deformations and, second, formula (3) actually can be used to estimate the real values of plastic deformation of thin coating upon inelastic stretching of polymer-substrate. Thus, the deformation of polymer with a thin solid coating is accompanied by the formation of regular surface structures. The authors of [14–27] managed to relate the most significant properties of material comprising nanosized coatings, such as strength, yield stress, and the value of plastic deformation, with the parameters of microrelief, which can be readily determined in direct microscopic examinations. It is obvious that disclosed correlation is essentially the basis for simple and direct method of the estimation of stress–strain properties of solids (coatings) in the layers of any thicknesses, including in the nanosize range.

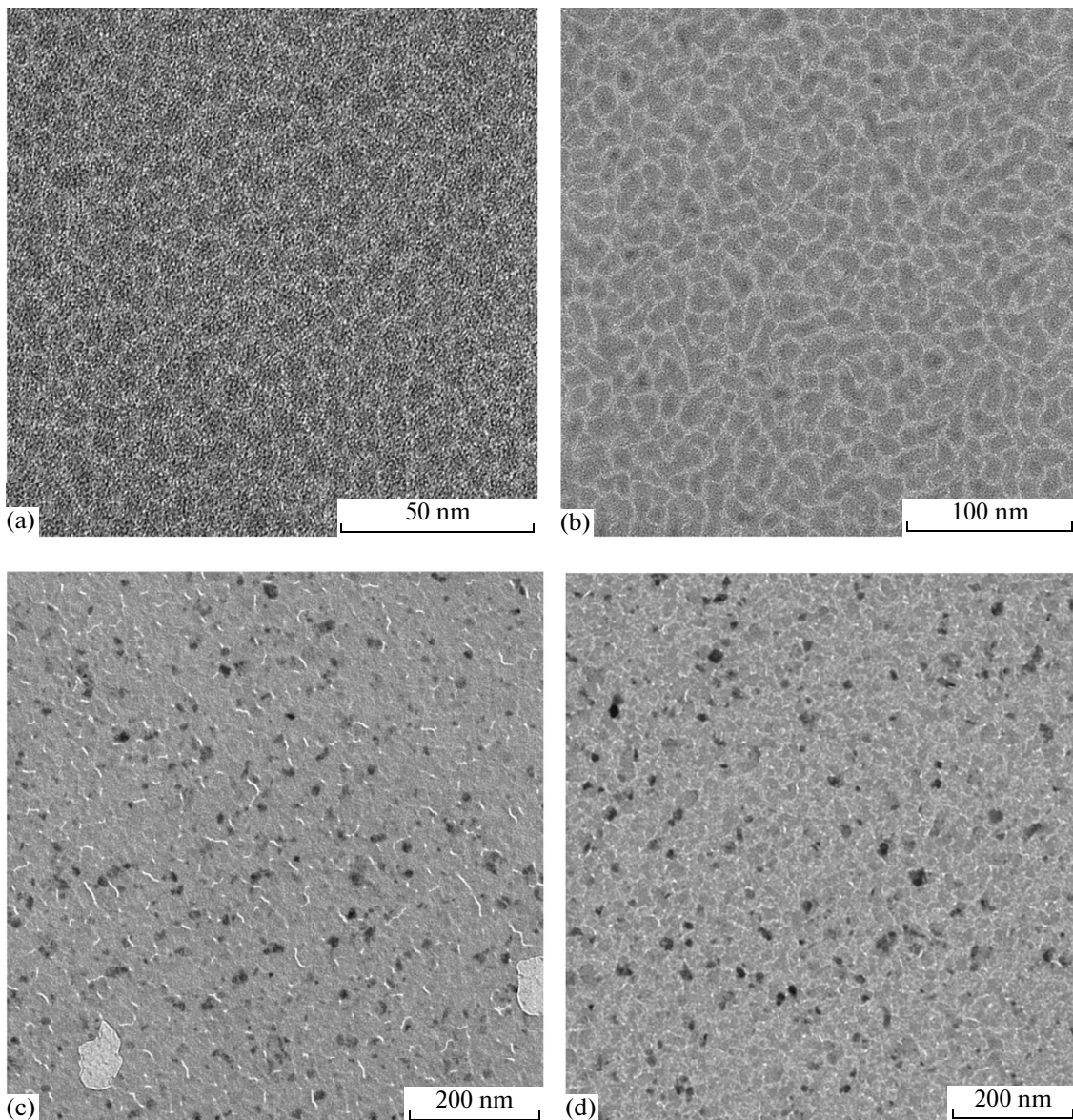
## 2. ESTIMATION OF STRESS–STRAIN PROPERTIES OF NANOSIZED ALUMINUM COATINGS DEPOSITED ONTO POLYMERS BY THERMAL SPUTTERING IN VACUUM

Before proceeding to the specific estimates of stress–strain properties of nanosized aluminum layers deposited onto polymer substrates, we consider some data concerning the structure of such thin metal layers. Figure 6 shows TEM images of Formvar films with aluminum layers of different thicknesses deposited by thermal sputtering in a vacuum. In the case of aluminum, a continuous metal layer is formed on a polymer surface, even at the shortest time of sputtering that corresponds to a coating thickness of  $h \approx 1.8$  nm (Fig. 6a). Regardless of the continuity of the layer, this layer has nonuniform thickness, which leads to mosaic structure, which is clearly seen on photomicrographs. An increase in thickness to 4 nm does not significantly

change the observed picture (Fig. 6b). A further increase in the thickness of an aluminum coating to 16 nm is accompanied by the formation of a large amount of single crystallites (dark spots on photomicrographs) with sizes of 10–30 nm (Figs. 6c and 6d). The formation of a continuous aluminum coating on a polymer surface creates prerequisites for the appearance of regular periodic structures on the surface upon the stretching of the polymer substrate and for the estimation its stress–strain properties using the developed procedure. Figure 7 demonstrates typical photomicrographs of a PET substrate with deposited aluminum coating after the stretching of polymer substrate 50% at 90°C taken at different magnification. These photomicrographs make it possible to both estimate the sizes of disintegrated fragments (Fig. 7a) and the regularity of the microrelief that develops (Fig. 7b). It can be seen that, upon the stretching of this two-layer sample, all of the aforementioned peculiarities of surface structuring, which are typical for RCSS systems, such as the fragmentation of the coating and the appearance of regular periodic microrelief, actually take place (cf. Figs. 1 and 7).

The approach developed in [14–24] allows significant characteristics of nanosized solids (coatings), e.g., yield stress  $\sigma_y$ , to be estimated. SEM images (Fig. 7) and formula (1) make it possible to perform this estimation for the PET–Al system. The results of the calculation of  $\sigma_y$  as a function of the thickness of aluminum coating  $h$  using relation (1) are shown in Fig. 8. It follows from these data that, beginning with a thickness of 10–12 nm, the  $\sigma_y$  values of the coating begin to increase rapidly with a decrease in  $h$  and achieve a value of  $\sim 150$  MPa. At  $h > 10$ –12 nm, the yield stress tends to the value corresponding to bulk aluminum (35 MPa) [28]. The results obtained allow one to suggest that the decrease in the thickness of aluminum coating to the nanosized region gives rise to a structural transition that greatly affects the properties of coating.

This conclusion is fully confirmed by the results of the determining strength  $\sigma^*$  of nanosized aluminum coatings using the approach described in [14–24]. Figure 9 demonstrates graphical dependences of  $\sigma^*$  of the aluminum coating on its thickness calculated from electron microscopy data using relation (2) at two values of deformation temperatures (20 and 90°C). One should note to two facts. First, the  $\sigma^*$  values of aluminum coatings obtained in experiments with the deformation of the PET substrate–coating system at different temperatures are substantially different. The strength of the coating obtained upon the deformation at room temperature is much higher than that measured upon the deformation at 90°C, i.e., above  $T_g$  of PET substrate. Second, when the thickness of aluminum coating becomes smaller than 4 nm, its  $\sigma^*$  value increases, regardless of the deformation temperature. Note that  $\sigma^*$  of an aluminum coating increases in proportion to its  $\sigma_y$  values (cf. Figs. 8 and 9).



**Fig. 6.** TEM images of aluminum coatings with thicknesses of (a) 1.8, (b) 4, (c) 14, and (d) 16 nm deposited by thermal sputtering in vacuum onto Formvar films.

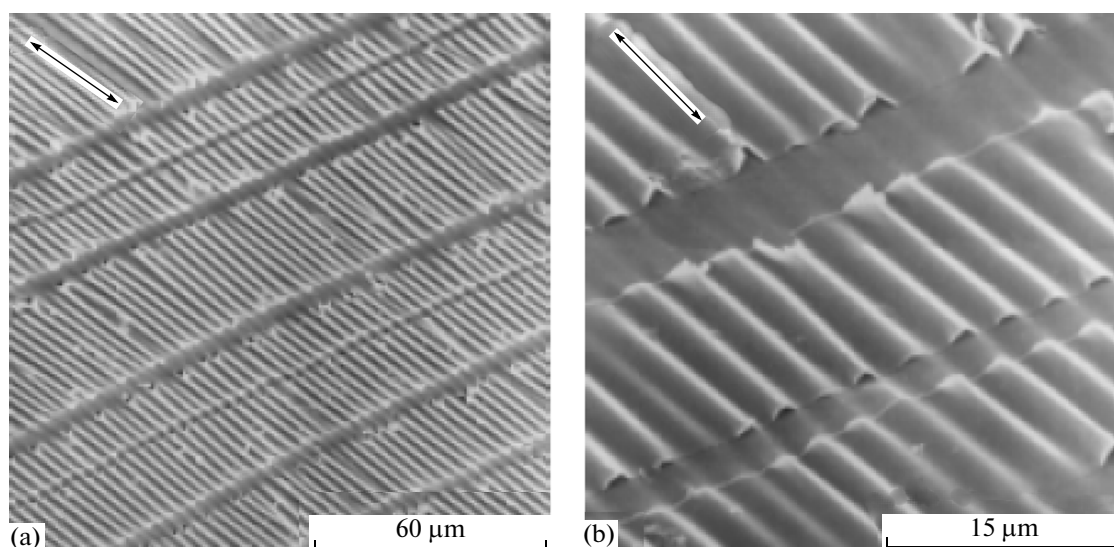
Using the approach described in [26, 27], we also obtained the dependence of the value of plastic deformation of aluminum coating,  $\varepsilon_{\text{coating}}$  on its thickness  $h$  using relation (3) (Fig. 10). Regardless of the deformation temperature (20 or 90°C), we observed a decrease in  $\varepsilon_{\text{coating}}$  with increasing  $h$ . At the same time, it should be noted that the absolute values of the plastic deformation of aluminum coating turned out to be substantially higher upon the deformation of PET with coating at 20°C than at 90°C. In the first case, the  $\varepsilon_{\text{coating}}$  value can achieve 140%, which is much larger than the known values of plastic deformation for bulk aluminum (40–50%) [28].

Thus, at small values of the thickness of aluminum coatings, a rather unusual combination of their stress–

strain properties is observed, i.e., the rise in the yield stress and strength is accompanied by the substantial increase in their plasticity. Note that, in the case of crystalline solids, an increase in their strength is accompanied by a decrease in their plasticity [29]. This regularity is observed for both coarse crystalline and nanostructured materials.

The following questions arise. What are the reasons for the differences in the strength of aluminum coatings determined in experiments with the deformation of the PET substrate at different temperatures (20 and 90°C)? Why, in the region of small thicknesses of coatings, do their strength and yield stress drastically increase regardless of the temperature of the deformation of the polymer substrate? How is the rise in the





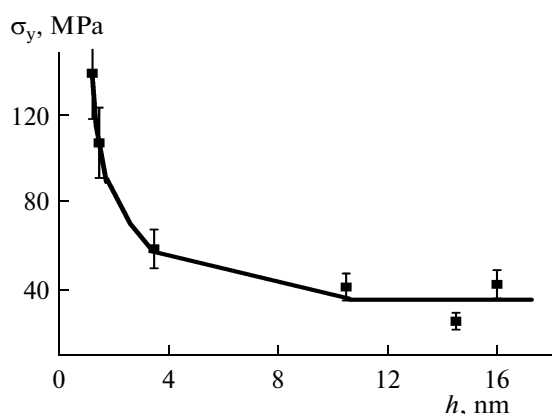
**Fig. 7.** SEM images of (a) PET films with 10-nm-thick aluminum coating after stretching by 50% at 90°C taken at different magnifications. Arrow indicates axis of stretching of polymer substrate.

plastic deformation of aluminum coatings deposited onto the PET film related to the decrease in their thickness?

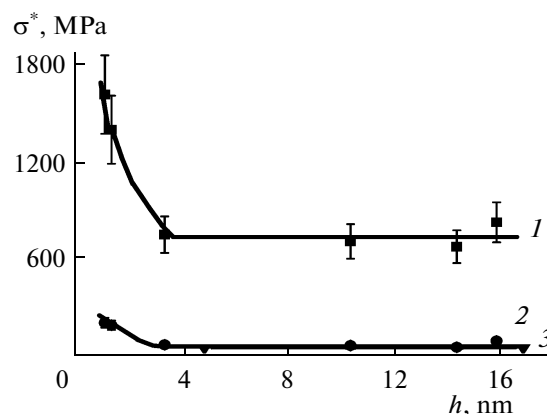
To explain the first of these peculiarities, it is necessary to consider the differences in the conditions of PET deformation with aluminum coating at two indicated temperatures (20 and 90°C) in greater detail. Since  $T_g$  of PET is equal to approximately 75°C, the polymer is deformed at 20°C in a glassy state (with the formation of neck); whereas, at 90°C, it is deformed at rubbery state, i.e., uniformly. However, this is not the only difference. The deformation of glassy PET proceeds at much higher (by order of magnitude) stress than for PET in a rubbery state. It is also significant that, at 20°C, the polymer-substrate is deformed by

275% (into the neck), whereas, at 90°C, it is only deformed by 50%.

Let us consider how this circumstance affects the deformation behavior of the aluminum coating. To answer this question, we prepared PET samples with 9-nm-thick aluminum coatings, which were deformed to different draw ratios of 0–800% at 90°C. It was impossible to study the effect of the draw ratio on the deformation behavior of the aluminum coating at 20°C because the deformation of PET under these conditions proceeds with the formation of neck which is characterized by a fixed natural draw ratio (275%). It is important that relations (2) and (3) allows for the independent estimation of the strength and plastic deformation upon the stretching of the polymer-substrate. When the strength of bulk solids is determined

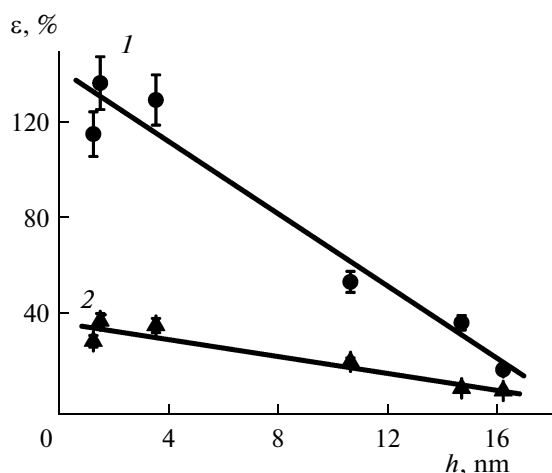


**Fig. 8.** Dependence of yield stress of aluminum coating on its thickness upon deformation of polymer substrate by 50% at 90°C.

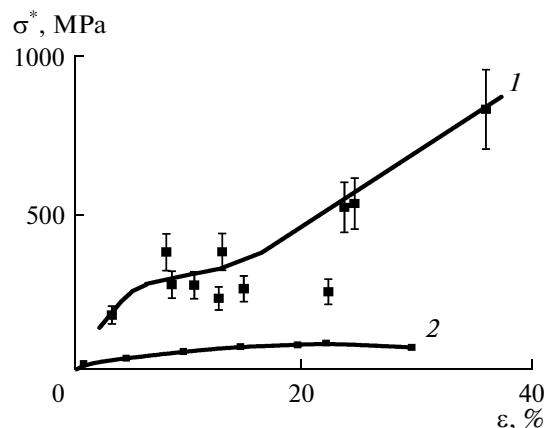


**Fig. 9.** Dependences of strength of aluminum coating on thickness upon deformation at (1) 20 and (2) 90°C.





**Fig. 10.** Dependences of plastic deformation of aluminum coating on its thickness upon stretching by 50% at (1) 20 and (2) 90°C.



**Fig. 11.** (1) Dependence of the strength of 9-nm-thick aluminum coating on its plastic deformation at 90°C and (2) stress-strain curve of bulk aluminum at room temperature [28].

by standard procedure after the breaking stress (the propagation of main crack) is achieved, the stress in the material drops to zero and the experiment is stopped. At the same time, when studying the fracture of coating on a substrate, its fragmentation proceeds also after the propagation of cracks through coating cross section and the appearance of the entity of single fragments by means of further disintegration of each formed fragment. This circumstance makes it possible to plot the true stress-strain curve for the coating upon its deformation on the surface of polymer-substrate. This dependence is shown in Fig. 11. Stress-strain curve of bulk aluminum obtained at room temperature [28] is shown in the same figure for comparison. According to Fig. 11, the strength of aluminum coating is many times higher than that of bulk aluminum. Moreover, as the stretching of aluminum coating increases to 40%, its strength rises from 190 to ~800 MPa, while the stress in bulk aluminum remains nearly unchanged within the same deformation range.

These data indicate that, upon the deformation of aluminum coating on the PET substrate, the effect of its strain hardening becomes distinctly exhibited. This effect may be responsible for the differences in the strength of aluminum coatings observed during the deformation of PET substrate at 20 and 90°C (Fig. 9). Indeed, at 90°C, the substrate is only deformed by 50%, whereas, at 20°C, it is deformed by 275%. Additionally, the deformation of polymer-substrate at 20°C occurs at much larger (by order of magnitude) stress than at 90°C, which in turn tends to increase the plastic deformation of aluminum coating and, hence, to enhance the effect of its strain hardening, other conditions being equal.

To explain an increase in the strength and yield stress of aluminum coatings at small thicknesses, we turn to the consideration of electron microscopy structural data (Fig. 6). The structure of aluminum

coating depends to greater extent on its thickness. When a fairly thick (10 nm or more) coating is deposited, its crystalline structure can clearly be revealed (Figs. 6c and 6d). The sizes of single crystallites in this structure are equal to 10–30 nm. Their structure changes considerably upon the sputtering of thinner layers. It can clearly be seen that, in this case, continuous aluminum film with mosaic structure is formed (Fig. 6a).

Electron diffraction data of Formvar films with thicknesses of 4 (Fig. 12a) and 16 (Fig. 12b) nm demonstrated that these coatings are characterized by different internal structures. Perfect crystalline structure of aluminum is only registered for coatings with thicknesses of larger than 5 nm. At lower coating thicknesses, only an amorphous halo is observed, which is evidence of the amorphous state of the metal or, at least, to very low degree of its crystallinity. Obviously, the effect observed is related to the fact that, at thicknesses of the sputtered layer of less than 5–10 nm, the aluminum cannot form an extended crystal lattice characterized by long-range order.

Thus, a decrease in thickness of aluminum coatings to less than 10 nm resulted in the amorphization of metal. Quite recently, procedures for making amorphous metals and their alloys have been developed [30]. One of these procedures consists of high-speed ion-plasma sputtering of metals and alloys [31, 32]. This process can be performed so that metal coatings with nanosized thicknesses can be obtained. Naturally, in the case when the thickness of sputtered metal layer did not exceed (as in our experiments) dozens of nanometers, their structure was amorphous, since crystalline phase with long-range order cannot be formed under these conditions.

It is significant that intermediate cases between completely amorphous and crystalline states of metals are so-called amorphous-nanocrystalline composites

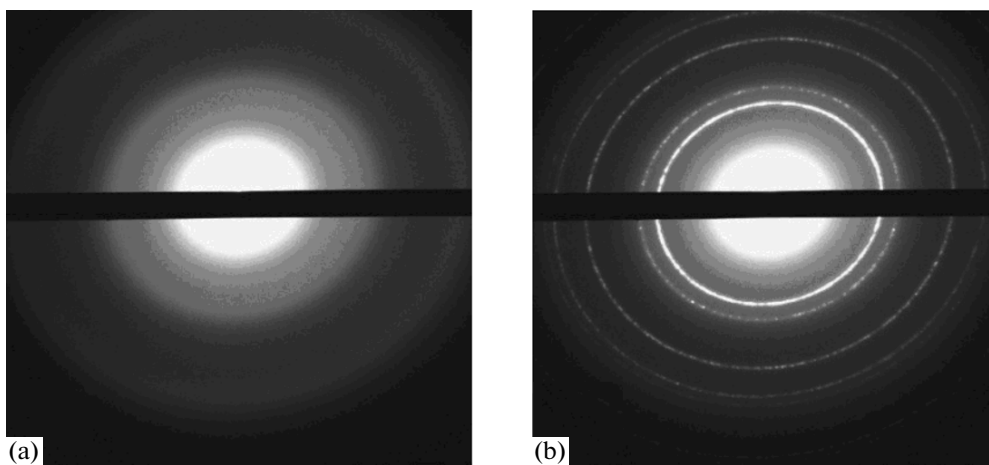


Fig. 12. Electron diffraction patterns of aluminum coatings with thicknesses of (a) 4 and (b) 16 nm.

which present amorphous metal matrix with nanocrystallites in the form of single inclusions. Similar structures attracted attention for the first time in the mid-1980s [33, 34] when studying the microstructure of alloys prepared by fast quenching from melt [33], as well as by the annealing and partial crystallization of amorphous alloys [35]. Based on microstructure studies, Glezer et al [33] proposed the model of the structure of state obtained (Fig. 13) and stated the emergence of new class of amorphous–crystalline materials with extremely high strength. The study of the mechanical properties of the prepared composition demonstrated that this composition is characterized by unusually high microhardness ( $\approx 21$  GPa), which exceeds the microhardness of an amorphous alloy of the same composition ( $\approx 9$  GPa) more than twofold. The breaking strength of band samples at uniaxial stretching at room temperature was very high (6–

6.5 GPa). At the same time, it was shown that materials of this type retain a high degree of plasticity. A theoretical study of the model shown in Fig. 13 made it possible to explain how unusually high mechanical characteristics (microhardness, yield stress, and breaking strength) are combined with the high plasticity of this material [31]. It is assumed that main factors in abrupt increase in these characteristics are high mechanical characteristics of nanocrystallites due to their small sizes and the presence of disclinations, as well as their extremely high concentration in amorphous matrix.

Note that the structure of amorphous–nanocrystalline composites (Fig. 13) is very similar to that of thin aluminum coatings revealed by us with transmission electron microscopy (Fig. 6). This analogy and cited literature permit us to make substantiated assumption on the mechanism of aforementioned phenomena (an increase in the strength and yield stress regardless of the deformation temperature of the polymer-substrate at small thicknesses of coatings and the rise in their plasticity with a decrease in the thickness of the metal layer).

Thus, the peculiarities of the stress–strain properties of aluminum coatings revealed in this work can be explained by the size effects. An increase in the strength and yield stress, as well as in plasticity are related to a decrease in the thickness of deposited coating and, hence, to the effect of nanostructuring. Using a new direct microscopic procedure, for the first time, we estimated the stress–strain properties of aluminum in its ultrathin (nanosized) layers deposited onto the polymer-substrate. It was demonstrated that these characteristics depend on the level of stress in the substrate, the values of its deformation, and the thicknesses of the coating. The evolution of these characteristics is related to the strain hardening of metal upon stretching and the effect of the nanostructuring

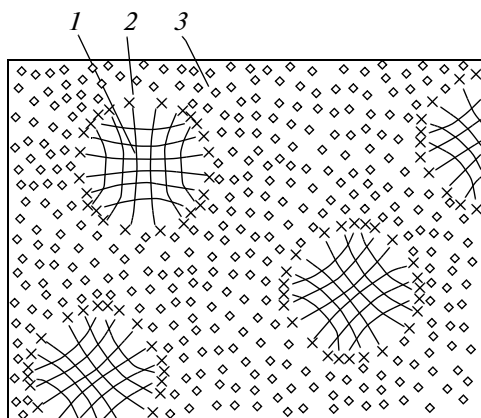


Fig. 13. Suggested structural model of amorphous–crystalline transition state upon the cooling of metal melt at a high rate: (1) crystallite with variable lattice parameter, (2) the region of smooth transition from crystalline to amorphous states, and (3) thin amorphous interlayers.

of crystalline materials in the region of small thicknesses of their layers.

### 3. ESTIMATION OF STRESS–STRAIN PROPERTIES OF COATINGS OF PRECIOUS METALS DEPOSITED ONTO POLYMERS BY ION-PLASMA SPUTTERING

Before proceeding to the discussion of the properties of coatings of precious metals deposited onto polymers by ion-plasma sputtering, we consider direct microscopic data concerning their structure. Figure 14 shows the TEM images of gold layers with effective thicknesses of (a) 0.2 and (f) 29 nm deposited onto Formvar substrates. It can be seen that continuous coating is formed on polymer surface only beginning with the effective thickness of about 10 nm. This conclusion is confirmed by the results of measuring the surface conductivity of polymer films sputtered with thin gold layers (Fig. 15) [36]. Data presented in Fig. 15 evidence that, up to an effective thicknesses of the metal layer of  $\approx 7$  nm, the metal is deposited onto the polymer by the island mechanism and an integral continuous coating is not formed on polymer surface. Therefore, it is impossible to estimate stress–strain properties of coatings using the procedure elaborated in [14–27]. Figure 16 illustrates this statement. It can be seen that, in the presence of individual clusters (particles) of metal on the surface of polymer-substrate, the stretching of this system is not accompanied by the surface structuring described above and the metal particles simply move apart.

It turned out to be unexpected (Fig. 17) that, upon the deformation of PET films coated by a gold layer with a thickness that is deliberately smaller than the film at the surface of which continuous metal film is formed (the time of sputtering varies from 3 s to 2 min, which corresponds to a nominal coating thickness of 0.2–5 nm), images of surface structuring appeared that are surprisingly similar to those observed upon the deformation of polymer substrate with continuous metal coating. It can be seen that, in all cases, the set of asymmetric fragments of metal coating oriented perpendicular to the axis of polymer stretching is formed on the polymer surface.

The use of an atomic force microscope allows the process of the fragmentation of coating upon the stretching of polymer substrate to be elucidated and studied in detail. Typical results of this study are presented in Fig. 18. It can be seen that, despite the absence of a continuous metal coating on the surface of the deformed polymer, extensive fragmentation takes place on its surface layer. These fragments are distinctly revealed on polymer surface and their parameters can easily be measured. Atomic force microscopy makes it possible to quantitatively estimate not only the extension (dimension in the direction of the axis of stretching), but also to estimate the depth of cavities between fragments of the fractured

surface layer and characterize the evolution of the above-mentioned parameters in the course of the deposition of metal coating onto polymer surface by ion-plasma sputtering [20].

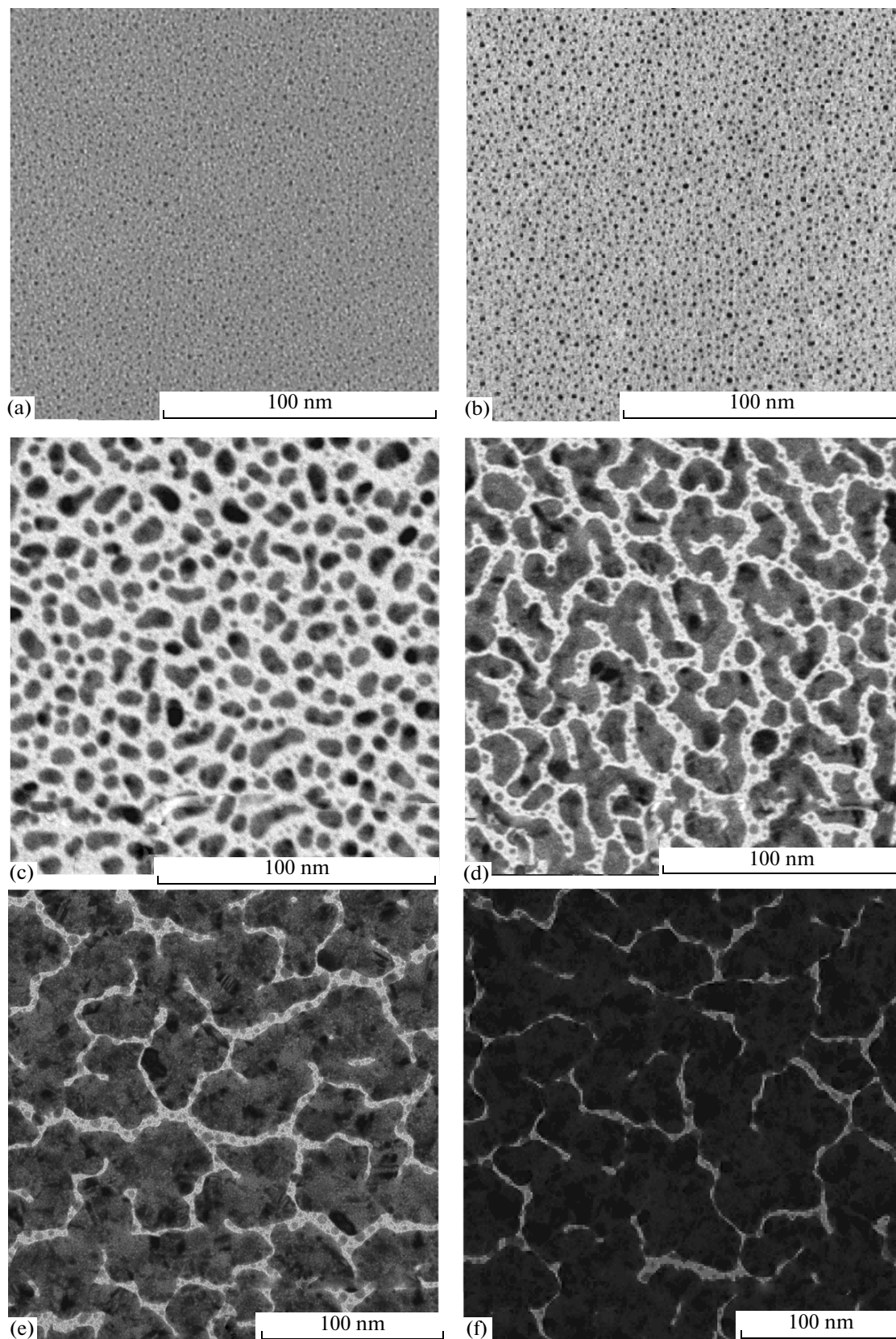
The question of the mechanism of the revealed phenomenon is raised. To determine this mechanism, it is necessary to remind that, upon ion-plasma sputtering, polymer interacts with plasma, as well as the deposition of metal onto the polymer surface.

It is well known that, upon the action of cold plasma on polymers, the chemical modification of their surfaces takes place. This phenomenon was studied in detail and is widely applied in practice [38, 39]. The action of plasma on the polymer surface is mainly used to modify the contact properties (wettability, adhesion to thin metal films, bonding ability, the control of adhesion of printing dyes, etc.). There is no doubt that the treatment of polymers with plasma leads to the emergence of nanosized modified surface layers, which are characterized by variable chemical composition, as well as by the specific physicochemical, electric, and other properties.

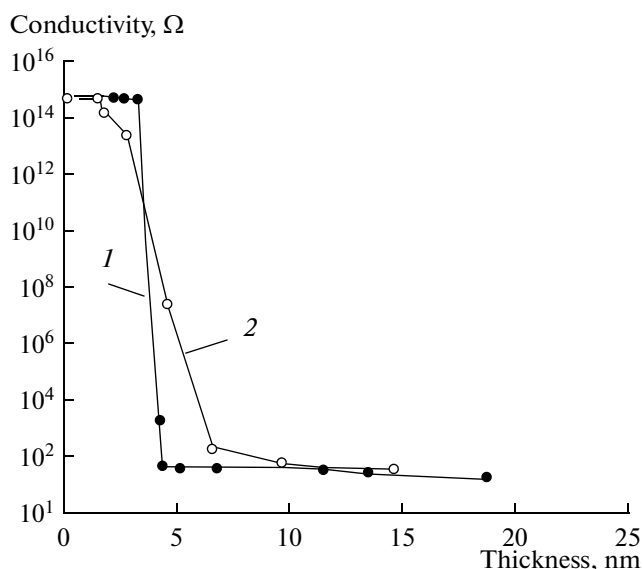
It is evident that stress–strain properties of these surface nanolayers resulted from plasma treatment should differ from the properties of unmodified initial polymer. However, by the beginning of these studies, results of which are summarized in this review, data of this kind were not available in published literature. The main reason for this situation is seemingly the absence of relevant experimental techniques. The approach to the estimation of stress–strain properties of coatings developed and substantiated by us present real experimental opportunities for estimating these properties relative to the surface nanolayers of polymers. Naturally, this approach can only be realized in the case when the layer with breaking elongation lower than that of the polymer-substrate is formed on the polymer surface due to plasma treatment. Otherwise, there will be no fragmentation of this layer, which provides a basis for estimating the stress–strain properties using relation (1).

To check this assumption, it is sufficient to deform the polymer sample treated with plasma and study its surface with the AFM technique. The results of this study, which are shown in Fig. 19, demonstrate an AFM image of PET film treated with plasma for 1 min and stretched by 50% at 90°C (Fig. 19a), its 3D reconstruction (Fig. 19b), and the corresponding profilogram (Fig. 19c).

According to the AFM data shown in Fig. 19, upon the deformation of polymer films pretreated with plasma, structuring takes place on the surface, which is completely analogous to that observed upon the deformation of polymer films with a thin metal coating. The obvious similarity between the observed microrelief and that formed upon the deformation of the same polymer films with a thin metal coating is worth mentioning (Figs. 18 and 19). The regular microrelief and the fragmentation of the surface layer



**Fig. 14.** TEM images of Formvar films with gold layers with thicknesses of (a) 0.2, (b) 0.4, (c) 3, (d) 5, (e) 16, and (f) 29 nm deposited by ion-plasma sputtering.

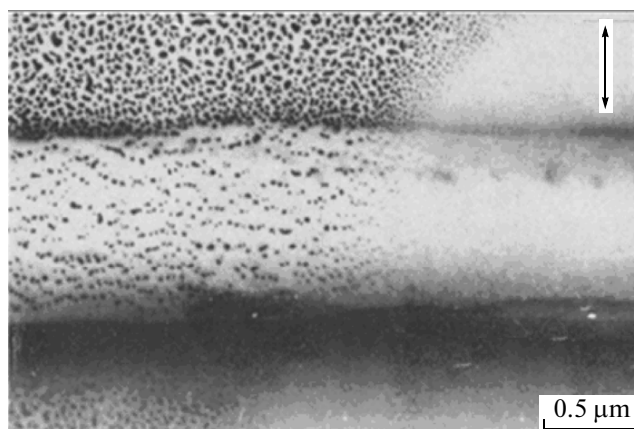


**Fig. 15.** Dependences of conductivity of thin gold layers on their thickness. Metal was deposited onto PET by (1) ion-plasma and (2) thermal sputtering.

are clearly seen in both cases. This similarity is evidence that, in both cases, the rearrangements responsible for surface structuring are based on similar mechanisms.

Thus, the treatment of polymers with cold plasma leads to the formation of rather rigid surface layers that imparts them the properties of RCSS. This circumstance makes it possible to estimate stress-strain properties of nanosized layers using the approach proposed in this work. Of course, to use Eq. (2), one must know the thickness of polymer surface layer modified with plasma. To obtain this information, we studied sections of plasma-treated PET films using the TEM technique. It turned out that a certain layer, which is stained darker than the initial polymer, is formed on film surface after its treatment with plasma. The thickness of this dark layer hardly depends on the time of treatment with plasma and is equal to about 80 nm. It can be assumed that the dark layer on photomicrographs is none other than plasma-modified polymer.

Assuming that the thickness of the modified layer is  $h = 80$  nm, we estimated its strength using relation (2). For the deformation of polymer-substrate at 20°C, stress in the substrate  $\sigma_0 = 40$  MPa, and a mean size of the fragment of a fractured coating  $L = 0.2$   $\mu\text{m}$ , we arrive at a coating strength of  $\approx 33.3$  MPa. Similarly, we estimated the strength of layer formed upon the deformation of a polymer film treated with plasma at 90°C ( $\sigma_0 = 2$  MPa and the mean size of fragment of fractured coating  $L = 0.44$   $\mu\text{m}$ ). In this case, calculations by Eq. (2) yields the strength of the plasma-modified layer of approximately 3.7 MPa. As can be seen from data presented, the strength of the modified polymer layer varies greatly depending on the deformation

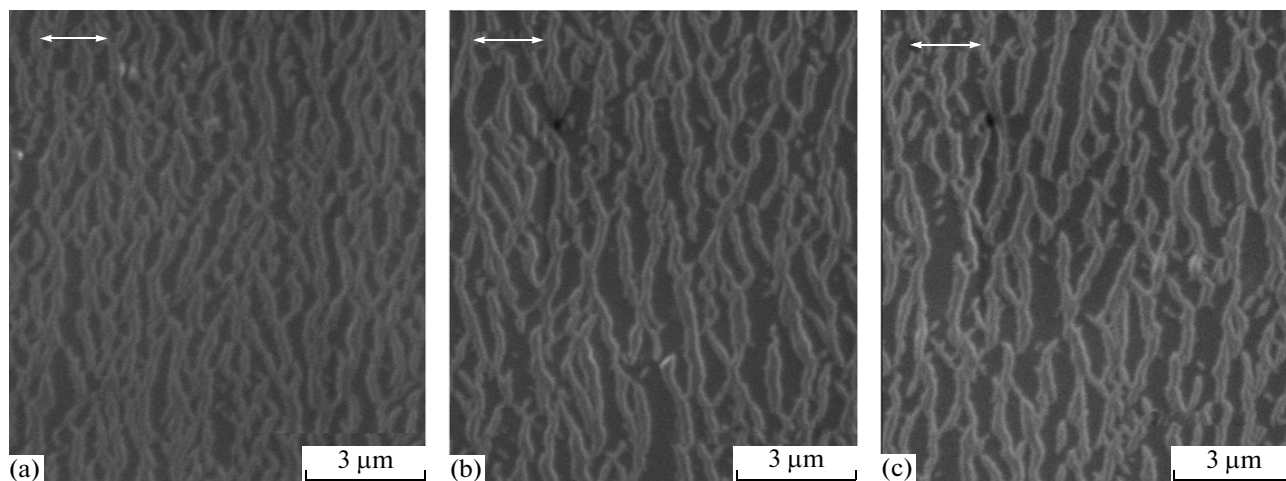


**Fig. 16.** TEM image of polystyrene surface of with gold particles upon stretching. Direction of stretching is indicated by arrow.

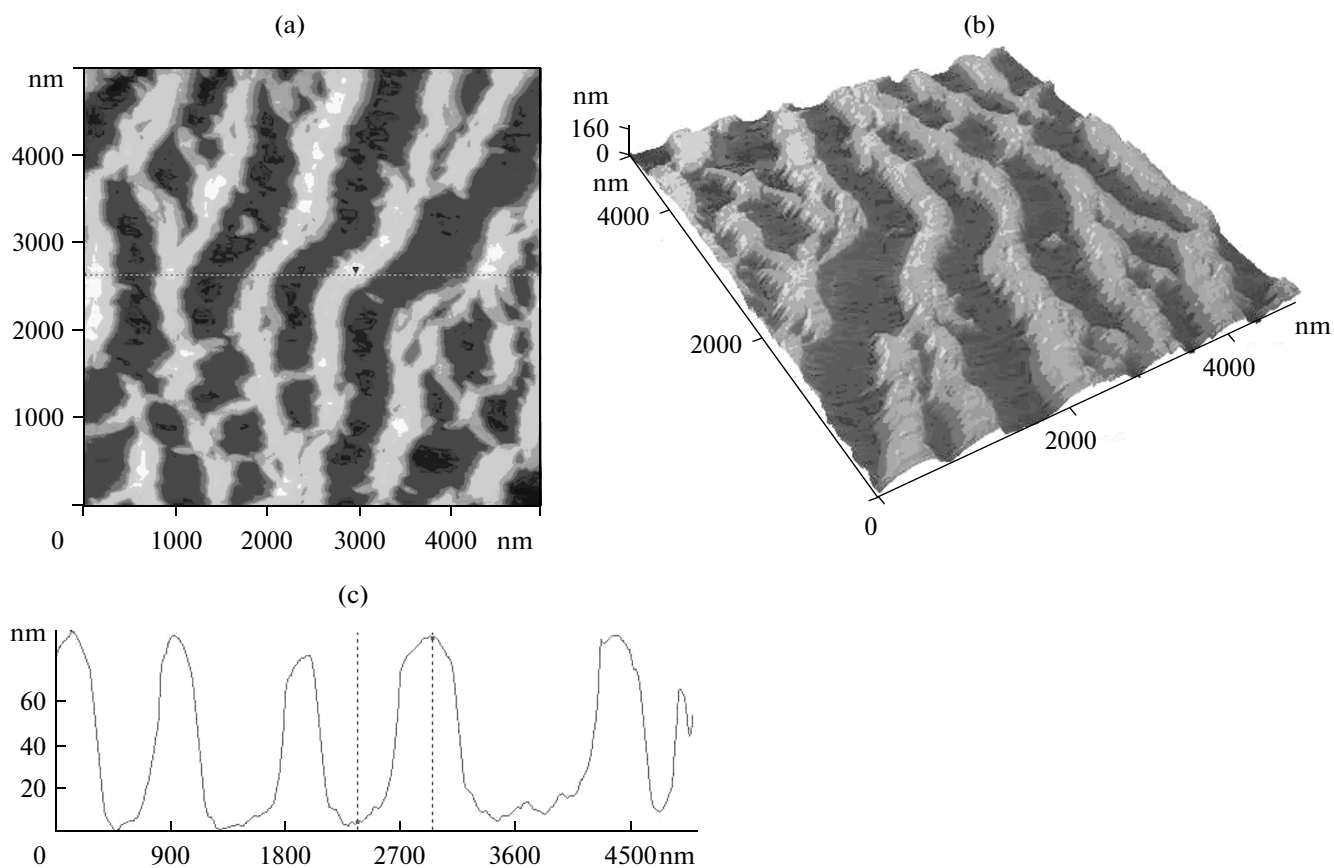
temperature. This is the first and so far the only estimate of the strength of polymer surface layer modified by plasma. There are serious reasons to believe that numerous chemical reactions, including crosslinking, proceed in the surface layer of polymer during its treatment by plasma [38, 39]. Apparently, it is the crosslinking of this type that leads to the drop in breaking elongation of polymer in plasma-modified surface layer below the value of initial polymer. As a result, the fragmentation of the surface layer occurs and the estimation of its stress-strain properties becomes possible. Nevertheless, this layer retains its polymer nature and, thus, the sensitivity to the transition from glassy to rubbery states.

In addition to strength, we estimated the value of plastic deformation of the surface layer modified by plasma during the deformation of polymer. Figure 20 demonstrates the dependence of the plastic deformation of rigid surface layer on the time of PET treatment by plasma after the subsequent deformation of the sample at 90 (curve 1) and 20°C (curve 2).

It can be seen that the modified layer formed on PET surface is fairly plastic. The value of its plastic deformation varies from  $\approx 20$  to  $\approx 95\%$  during deformation at 90 and 20°C, respectively. Apparently, the disclosed effect can be associated with the fact that the polymer substrate at 20°C (below PET glass-transition temperature) is deformed under stress that is an order of magnitude higher than at 90°C (above PET glass-transition temperature). An additional factor that affects the value of the plastic deformation of surface layer is the deformation of polymer substrate. Indeed, deformation at 90°C was equal to 50%, whereas deformation at 20°C took place with the formation of a neck in PET, the natural draw ratio of which was 275%. It is worth mentioning that, unlike metal coatings (Fig. 11), surface layers formed upon the treatment of a polymer by plasma do not demonstrate an



**Fig. 17.** SEM images of PET films with gold coating after uniaxial stretching at 20°C. Time of metal sputtering: (a) 30, (b) 15, and (c) 10 s.

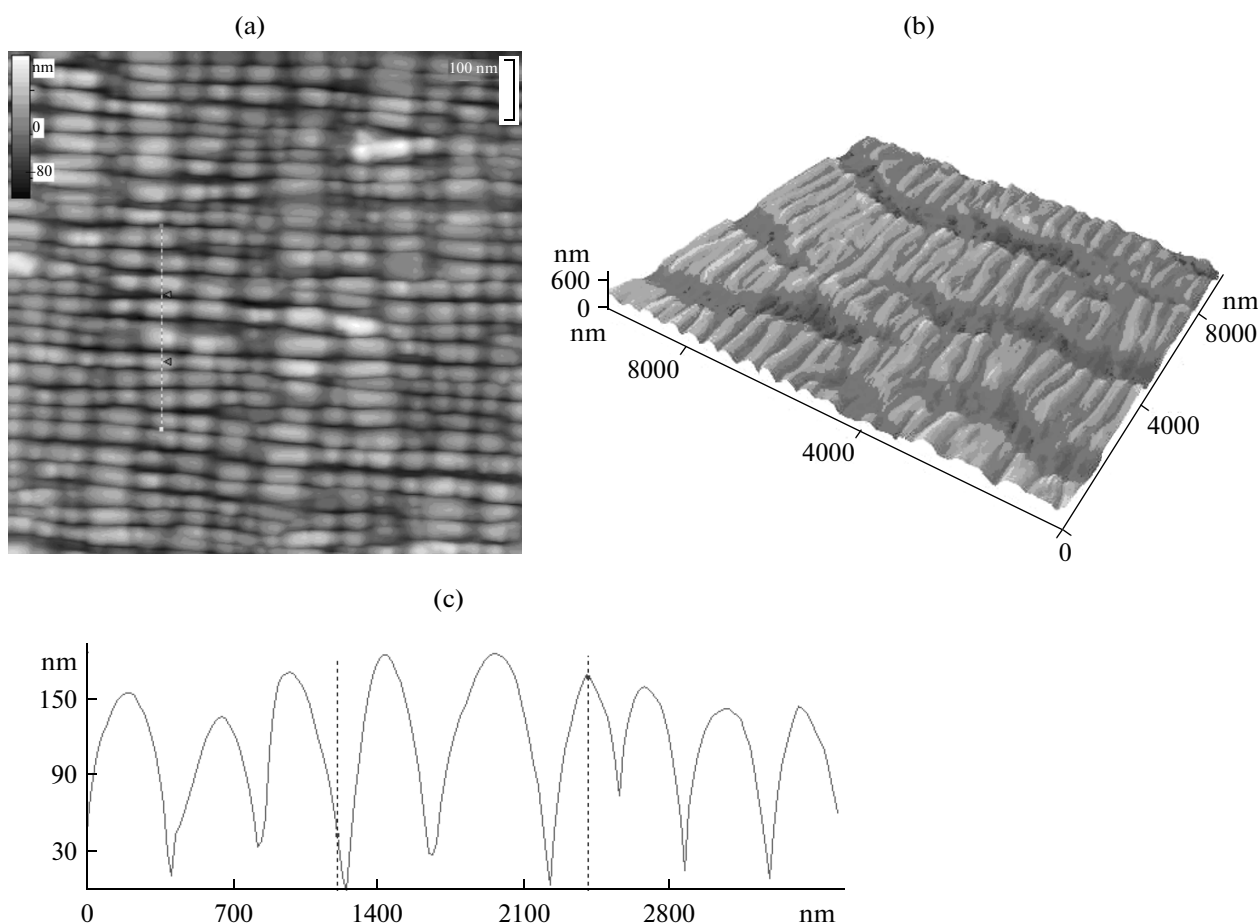


**Fig. 18.** Panel a: AFM image of PET film with gold coating (time of sputtering is 5 s) stretched at room temperature with the neck formation; panel b: 3D reconstruction; and panel c: corresponding profilogram.

increase in plasticity at small thicknesses (i.e., at short-time treatment).

Thus, it was shown that the employed method of the direct estimation of coating fragmentation upon

the deformation of polymer-substrate appeared to be suitable also for the description and estimation of the stress-strain properties of modified surface layers formed upon the treatment of polymers by plasma.



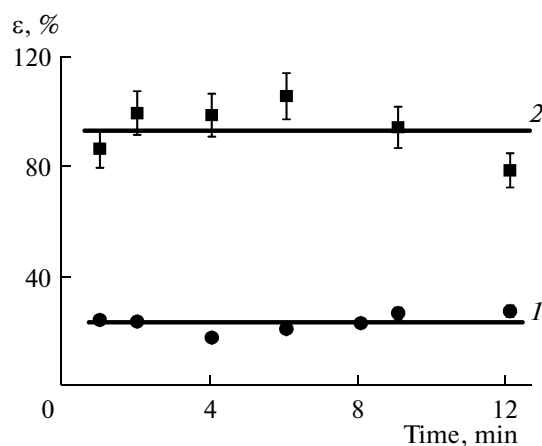
**Fig. 19.** Panel a: AFM image of PET film treated by plasma for 1 min and stretched by 50% at 20°C; panel b: 3D reconstruction, and panel c: corresponding profilogram.

Data obtained make it possible to conclude that this layer is formed at short (shorter than one minute) periods of time of treatment of polymer by plasma; further irradiation does not substantially influence the thickness of layer and its mechanical properties. Using the approach developed in [14–24], we quantitatively estimated the mechanical properties (breaking strength and the value of plastic deformation) of PET surface layers modified by plasma and demonstrated that these characteristics are sensitive to the physical state of the polymer-substrate.

The procedure for estimating stress–strain properties proposed in [14–24] has limited applications. Specifically, formula (2) used in this work to estimate the strength of coatings only gives an adequate value of strength for a polymer–metal coating two-layer system known as a “rigid coating on soft substrate” [14–24]. In this case, the basic parameter that makes it possible to estimate the strength is the mean size  $L$  of fragments of fractured coating formed during the stretching of polymer-substrate. At the same time, as was shown before, a metal–plasma-modified layer–polymer-substrate three-layer system, rather than a two-

layer system, is formed upon the ion-plasma sputtering of precious metals onto polymers. Moreover, as follows from these data and numerous studies of other authors [40–42], continuous coating on polymer-substrates is formed not immediately upon ion-plasma or thermal sputtering of precious metals onto polymers. As a rule, first portions of sputtered metal are condensed on polymer surface according to island mechanism. In other words, at the first stages of metal sputtering, the system of discrete nanoclusters is formed on polymer surface. The mean size of these nanoclusters and their size distribution, as well as their mutual arrangement on substrate depend on the rate of sputtering, temperature of substrate, reactivity of metal ions, etc. In connection with this, the notion of the thickness of coating at short times of metal sputtering on polymer surface, which is the crucial factor for the procedure of coating strength [14–24], becomes indefinite. This circumstance offers obvious problems for estimating stress–strain properties of coatings in the range of their small thicknesses, since thickness  $h$  enters into formulas (1) and (2).





**Fig. 20.** Dependences of plastic deformation  $\varepsilon$  of rigid surface layer of PET film after its treatment in plasma obtained after film deformation at (1) 20 and (2) 90°C.

Hence, the problem arises of obtaining quantitative relations for analyzing the stress–strain properties of metal–plasma-modified polymer surface layer–polymer–substrate three-layer systems, which, in particular, are formed upon the ion-plasma sputtering of precious metals onto polymers. Let us try to formulate a quantitative approach to analyzing this type of three-layer system, the structure of which is schematically presented in Fig. 21.

As was mentioned above, one of the main features of the three-layer system under consideration is the assumption that the thickness of plasma-modified sublayer formed during the first moments of ion-plasma sputtering of metal remains constant. In the course of further sputtering, only the thickness of the layer of pure metal localized on the sublayer is changed. To analyze this situation, we consider thin coating composed of two layers (Fig. 21). Let the strength of layer 1 (in our terms, sublayer) with thickness  $h_1$  be equal to  $\sigma_1$  and that of layer 2 (the layer of pure metal localized on the sublayer) with thickness  $h_2$

be equal to  $\sigma_2$ . Then, upon fracturing, this two-layer coating will carry the following load:

$$F = \sigma_1 h_1 w + \sigma_2 h_2 w,$$

where  $w$  is the width of coating (sample). In this case, the effective strength of a two-layer coating is calculated by dividing the total applied force  $F$  by the coating cross section  $w(h_1 + h_2)$

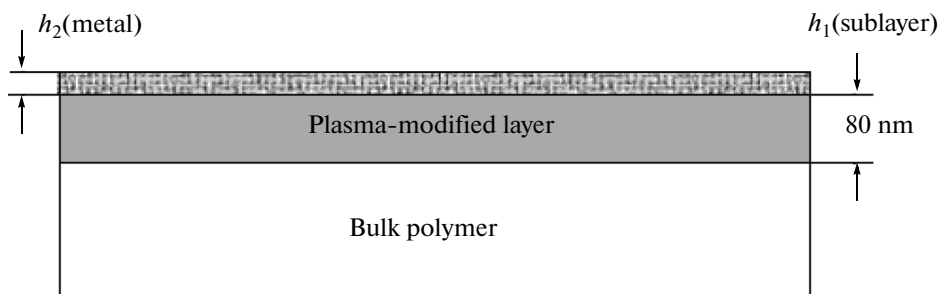
$$\sigma_c = \frac{\sigma_1 h_1 + \sigma_2 h_2}{h_1 + h_2},$$

where  $\sigma_c$  is the total thickness of the coating that can be calculated by Eq. (2). This dependence can be rewritten in the following form:

$$\sigma_c(h_1 + h_2) = \sigma_1 h_1 + \sigma_2 h_2. \quad (4)$$

Once the dependence of the product of the strength of two-layer coating by its total thickness,  $\sigma_c(h_1 + h_2)$ , on the thickness of metal coating  $h_2$  is plotted, we can calculate the strength of bulk metal from the slope of straight line; the product of the strength of sublayer by its thickness  $h_2$ , can be calculated from the intercept on ordinate axis. Naturally, we should confine ourselves to  $h_2$  values larger than 10 nm, because, at lower thicknesses, continuous metal coating is not formed on polymer surface. If the assumption of two-layer structure of coating is true, this dependence should be straightened in coordinates of Eq. (4).

The result of such processing of experimental data is shown in Fig. 22. First, one should note the satisfactory straightening of experimental data in the coordinates of Eq. (4). This fact evidences that the assumption of two-layer structure of coating rests on solid basis. The straightening of experimental data in the coordinates of Eq. (4) evidences also that, in the case of ion-plasma sputtering, the strengths of both the gold layer and the sublayer of a plasma-modified polymer are constant quantities. According to the obtained data, in this case, the effect of an increase in the strength of a gold coating at small thicknesses (the effect of nanostructuring) is absent. Most likely, this effect is not exhibited because the continuous metal coating is not formed at small nominal thicknesses;



**Fig. 21.** Schematic representation of polymer film with the layer of precious metal deposited onto its surface by ion-plasma sputtering.

hence, the proposed method cannot be applied to determine the strength. The estimation of the strength of pure metals by the slope of dependences shown in Fig. 22 gives values of 243 MPa for platinum and 168 MPa for gold. These values are quantitatively consistent with the known values of the strengths of bulk metals (240–350 MPa for platinum and 176–250 MPa for gold) [43].

The corresponding  $\sigma_1 h_1$  values were determined by the extrapolation of straight lines 1 and 2 (Fig. 22) to the ordinate axis. Taking the thickness of plasma-modified polymer layer (sublayer) as equal to 80 nm, we arrive at the value of its strength  $\sigma_1 \approx 77$  MPa for the case of ion–plasma sputtering of a gold coating and  $\approx 66$  MPa for a platinum coating. As can be seen from the presented data, in both cases, the strengths of sublayers are close to one another.

In the previous section, we estimated the strength of a plasma-modified polymer surface layer in experiments when only PET was treated by plasma without metal sputtering. In this case, we dealt with RCSS two-layer system; hence, the use of Eq. (2) for estimating the strength of coating seems to be quite correct. The strength of sublayer was  $\sim 33.3$  MPa. Thus, in both cases, the strength of plasma-modified polymer (PET) surface layer with thickness of 80 nm was equal to a few dozens of MPa. These estimates agree with directly determined values of the strength of plasma-modified polymer surface layer, thus confirming the reasonability of assumptions made for deriving formula (4) and, above all, the assumption of three-layer structure of system formed upon the ion-plasma sputtering of precious metals onto the PET surface.

Observed differences in the values of strength can be due to two reasons. First, the sublayer containing a certain amount of metal is formed on the polymer under the combined action of plasma and atoms (clusters) of precious metals. It is clear that this structure is not formed upon treating polymer with pure plasma. It is possible that it is the incorporation of atoms (clusters) of metals into this plasma-modified polymer layer at the first stages of metal sputtering that leads to its strengthening. Second, it appears that this layer does not have a strict boundary, which is why its schematic representation in Fig. 21 is idealized to some extent. New proposed procedure for estimating the strength of coating deposited onto polymeric substrates makes it possible to analyze the stress–strain properties of three-layer systems, which, in particular, are formed upon the deposition of nanosized layers of precious metals onto polymer films by ion–plasma sputtering.

Thus, in this review, the new method of studying the stress–strain properties of nanosized coatings deposited onto polymer substrates is described. This method is based on an analysis of the parameters of the microrelief that arises upon the deformation of polymer films with thin coatings. Examples of using this approach to determine the stress–strain properties of

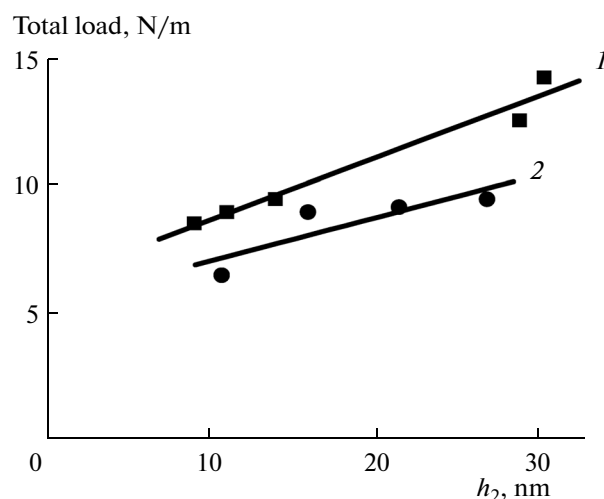


Fig. 22. Dependences of product of strength of two-layer coating by its total thickness,  $\sigma_c(h_1 + h_2)$ , on thickness  $h_2$  of (1) platinum and (2) gold layers deposited onto PET substrate by ion-plasma sputtering.

aluminum and precious metal coatings are given and first quantitative estimates of elastic modulus, breaking stress (strength), and plastic deformation of metals in nanosized layers are obtained. The uniqueness of proposed method, i.e., its possible applicability for estimating the stress–strain properties of nanosized coatings, irrespective of their nature, was demonstrated.

#### ACKNOWLEDGMENTS

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