

Metal Nanoparticles on Polymer Surfaces: 4. Preparation and Structure of Colloidal Gold Films

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Abstract—The process of the enlargement of gold hydrosol nanoparticles adsorbed on the surfaces of glassy polymers (polystyrene and poly(2-vinylpyridine)) in mixed aqueous solution of chloroauric acid and hydroxylamine is studied. It is established that the character of this process depends on the intensity of metal–polymer interaction and the density of nanoparticle packing in an initial monolayer. At a high coverage of a poly(2-vinylpyridine) surface by “seeding” gold particles, their rather uniform growth is observed, whereas, at low coverage, the enlargement of adsorbed particles, as well as the nucleation and growth of new particles take place. At the same time, new Au nanoparticles are not formed on the polystyrene surface in the enlargement process, even at low coverages by preliminarily deposited “seeding” hydrosol particles. Adsorbed gold particles can also be enlarged after their preliminary incorporation into the polystyrene surface layer. Such an incorporation (partial embedding) is ensured by the annealing of a system at a temperature between “surface” (T'_g) and “bulk” glass transition temperatures. In this case, the T'_g value can be considerably decreased (up to room temperature) by the addition of small amounts of a homologue with a much lower molecular mass in the polystyrene matrix. Lateral conductivity of colloidal Au films formed on a poly(2-vinylpyridine) surface by the enlargement of adsorbed seeding particles is measured. According to these measurements, contacts providing the formation of conductive channels are formed in the process of nanoparticle enlargement.

INTRODUCTION

At the present time, ever-increasing researcher's attention is focused on the search for the optimal routes of the formation of densely packed monolayer ensembles of the nanoparticles of metals, semiconductors, and other compounds (so-called colloidal or nanoparticulate films) on various substrates. Such nanostructured systems possess unique optical and electronic properties, which depend on the particle size and shape, as well as on the interparticle distance (e.g., see [1–3]). These systems are quite promising for the application in microelectronics, for the creation of planar solid-state chemical and biological sensors, etc.

One can identify a few main procedures for the formation of colloidal (nanoparticulate) metal films such as metal vacuum evaporation [4–7], deposition (including electrophoretic deposition) of particles from the bulk of hydro- or organosols [8–16], and transferring of densely packed ensembles of metal nanoparticles from liquid surface by the Langmuir–Blodgett technique [17–19].

Thermal vacuum evaporation of a metal is widely used for the implantation of metal nanoparticles into the surface layers of the melts of amorphous thermoplastics [4, 5] and thermosetting plastics [6]. In this case, the nucleation and growth of nanoparticles can take place both in the subsurface layer of the polymer

melt and on the surface with the subsequent embedding of nanoparticles in the melt. Upon the deposition of metal vapors onto “cold” (i.e., heated to no higher than 30°C) solid polymer substrate, colloidal metal film is formed on the surface [7], and its structure greatly depends on experimental conditions (the rate of metal evaporation, the intensity of metal–polymer interaction, and other factors).

The analysis of published data demonstrated that the formation of continuous films of metal nanoparticles on a polymer substrate by thermal vacuum evaporation of a metal is not a simple task, because the size of metal clusters and their concentration on the polymer surface are rather difficult to control.

The second of aforementioned procedures, namely, the adsorption of metal nanoparticles from their colloidal solutions makes it possible to avoid such difficulties.

By now a considerable amount of experimental data on the deposition (adsorption) of metal particles from their hydrosols on the surfaces of various solids modified with aminosilanes [8–12], thiols [13], polyelectrolytes [12, 14, 15], and poly(2-vinylpyridine) [16] is accumulated. In addition, works devoted to the adsorption of metal nanoparticles on the surfaces of inert glassy polymers have been published in a last decade [20–22].

The results of these studies indicate that the adsorption from colloidal solutions can lead to the formation of quite densely packed monolayer ensembles of nanoparticles with preset dimensions (from 5 to 20 nm) and surface chemistry. However, it should be mentioned that the electrostatic repulsion of sol particles prevents the formation of *really* continuous nanoparticulate metal film. In addition, colloidal metal films of a slightly larger thickness are of significant applied interest [1–3, 13]. For example, the maximal effect of surface-enhanced Raman scattering is observed for silver particles with the sizes of 50–60 nm [13]. However, the formation of such colloidal films by the procedures described above is a fairly complicated task.

A series of works have been published recently [23–31] whose results open, in our opinion, new opportunities for the formation of “continuous” films on various substrates from metal nanoparticles with a diameter of 30–100 nm.

The essence of the approach proposed by Natan *et al.* [23–25] is in the enlargement of gold nanoparticles in the bulk of colloidal solution in the presence of hydroxylamine (NH₂OH) and chloroauric acid (HAuCl₄). This procedure is based on the ability of gold hydrosol particles prepared by standard citrate procedure to catalyze the reduction of Au³⁺ ions to Au⁰. In this case, only the nanoparticles already present in the solution are enlarged in the course of reaction without the nucleation of a new phase [23].

Experiments demonstrated [23, 24] that this procedure makes it possible to grow relatively monodisperse colloidal particles with a given diameter; moreover, ascorbic acid or sodium borohydride can be used as reducing agents [25, 26]. At the same time, the possibility of the formation of colloidal gold films on the modified glass by the enlargement of nanoparticles in mono- or multilayer ensembles was demonstrated in [23, 27–29]. Varying conditions of the process, authors of [27–29] succeeded in preparing the conducting film with metallic properties.

Note that the enlargement of metal nanoparticles deposited onto solid substrate in the presence of chloroauric acid and hydroxylamine is quite promising for designing nanoconductors with complex shape [30], as well as for preparing systems that enhance the Raman scattering with high efficiency [29, 31].

The formation of continuous colloidal metal films on *nonpolymeric* substrates was studied in [23, 27–31]. It should be mentioned that, in some cases, it is more reasonable to form such ensembles on the surfaces of glassy polymers, because it is then possible to “mechanically” fix nanoparticles (prior to the enlargement) in a substrate surface layer. This possibility is determined by the difference in the glass transition temperatures of polymer bulk and its surface layer.

By now a great deal of experimental data obtained by using X-ray photoelectron spectroscopy [7], ellipsometry [32, 33], atomic force microscopy (AFM) [34–38],

and other methods [39, 40] have been accumulated demonstrating that the glass transition temperature of polymer surface layer (T_g') is substantially lower than its “bulk” value T_g . The observed effect is explained by the presence of excess free volume in a polymer near its boundary with the air due to such effects as the segregation of end groups, constrained geometry, and the partial degradation of entanglement network.

In particular, in our previous work [37], we studied the specific features of the vitrification of the surface layers of amorphous polymers using polystyrene (PS) with a molecular mass $M \approx 270\,000$ as an example. For this purpose, after the adsorption of gold hydrosol nanoparticles on the PS film, the film was stepwise annealed at temperatures lower than T_g , then it was abruptly cooled (at each stage) to ambient temperature, thus freezing the structure formed during the thermal treatment, and was examined with atomic force microscope. The temperature at which nanoparticles begin to embed in the polymer surface layer was taken as equal to T_g' . The analysis of obtained AFM images demonstrated that, already at 40–50°C, the PS surface layer 3–4 nm thick is in the devitrified state; moreover, as the temperature increases to 80°C, the thickness of such a layer noticeable increases [37].

Note in conclusion that one can additionally (and controllably) lower T_g' by the incorporation of small amounts of oligomeric homologue into the matrix of high-molecular-weight polymer [35, 41, 42].

At present there is a fairly large number of published theoretical [43, 44] and experimental works [35, 41, 42, 45] devoted to the study of the segregation processes in the blends of amorphous polymers (both homologues and polymers of various chemical natures) at the boundary with air. Results of these works demonstrated that one of the main reasons for the accumulation of low-molecular-weight (oligomeric) component in the surface layer of a binary polymer mixture is a decrease in entropy “losses.” Indeed, macromolecular coils near the free surface are compressed in the direction normal to the interface and are characterized by much lower conformational entropy compared to the macromolecules in polymer bulk. In such a situation, the enrichment of the surface layer with shorter molecules is profitable, because it is accompanied by smaller entropy losses, even if “low-molecular-weight” component has higher surface tension.

The data obtained in [37] evidence that it is possible to create “continuous” nanoparticulate gold (in principle, other metals as well) films fixed in the polymer surface layer, according to the following scheme.

- (1) Adsorption of nanoparticles from colloidal solution on the surface of glassy polymer.
- (2) Annealing of a system at a temperature below polymer “bulk” T_g but above T_g' to ensure the partial embedding of nanoparticles in the polymer surface layer.

(3) The enlargement of particles after the formation of such a structure in a solution containing the Au^{3+} ions and hydroxylamine.

The aim of this work is to experimentally realize this scheme for the formation of nanoparticulate gold films on the surfaces of polystyrene and poly(2-vinylpyridine) (PVP) and to study the structure of these films.

EXPERIMENTAL

Materials and Methods

Poly(2-vinylpyridine)¹ and polystyrenes of various molecular masses (Polymer Source, Canada) were used. Main characteristics of the employed polymers are listed in the table.

Gold hydrosol was prepared by the Zsigmondy method [46]. According to electron microscopy, the mean size of colloidal particles was equal to 18 ± 2 nm (unless otherwise indicated) and their number concentration was about 10^{12} ml^{-1} .

The sizes of gold hydrosol particles were determined with a JEM 2000EX high-resolution transmission electron microscope (TEM) (Jeol, Japan). Accelerating voltage was 200 kV.

The AFM experiments were performed with a Nanoscope IIIa atomic force microscope (Digital Instruments, Santa Barbara, USA) with a D-scanner (the observation field is $14 \times 14 \mu\text{m}^2$) in contact and tapping modes. A FemtoScan-001 software was employed to process the AFM images, their graphical representation, and plotting the cross sections of surface relief [47]. When determining the sizes of gold nanoparticles (their height over the polymer surface), we performed the averaging over 30–50 particles using specially developed program.

To study the lateral dc conductivity of the samples, we employed the device whose scheme is shown in Fig. 1. This device consists of two electrode pairs connected together and switched on a B7-38 universal digital voltmeter. The first electrode pair represents thin (with thickness not exceeding $0.4 \mu\text{m}$) gold films deposited onto the sample surface by metal vacuum evaporation; the electrode gap was 1.2 mm. The second pair represents “dismountable” electrodes made of Nichrome wire.

Thermal deposition of gold (99.99%) electrodes was performed in a VUP-5 universal vacuum station at a pressure of 10^{-5} mm Hg.

Resistance R was measured in the air; no less than 3 measurements were made for each sample varying the positions of dismountable electrodes.

The resistance of bare (with no nanoparticles) polymer film was first measured, thus obtaining the “zero” value. Then, we measured the resistance of nanoparticle ensemble formed on the PVP surface before and

The employed polymers and their characteristics

Polymer	M_w	M_w/M_n	$T_g, ^\circ\text{C}$	Designation
Poly(2-vinylpyridine)	150000	–	≈ 120	PVP
Polystyrene	234000	1.04	≈ 110	PS-234
	4980	1.06	≈ 70	PS-5

after the immersion of the sample in the solution of HAuCl_4 and hydroxylamine mixture.

Preparation of the Samples

The polymer films were formed on the surfaces of polished silicon wafers ($1 \times 1 \text{ cm}^2$) by the spin-coating and dip-coating techniques. For this purpose, we used PVP solution in chloroform and PS solutions in toluene (all solutions with concentration of 2 wt %). To prepare films from the mixtures of low- and high-molecular-weight PCs containing 2 and 5 vol % of the first component, the solutions of these polymers were mixed in corresponding volume ratios.

The PS and PVP films were exposed to the air for 1–2 days to evaporate the solvent and then were annealed in the air for 6 h at 120 ± 1 and $140 \pm 1^\circ\text{C}$, respectively. The deposition of nanoparticles onto the polymer substrates was carried out by placing them into gold hydrosol for a time period varied from 3 to 330 min. For the partial embedding of adsorbed gold nanoparticles in the surface layer of pure PS, the samples were annealed for 1 h at 60°C .

The enlargement of gold nanoparticles was performed in both the hydrosol bulk and monolayer ensembles on polymer surfaces.

To enlarge nanoparticles in the sol bulk, 0.64 ml of aqueous 0.2% HAuCl_4 solution were mixed with 46 ml of aqueous 0.4 mM NH_2OH solution followed by the immediate addition of 12 μl of diluted gold hydrosol (particle concentration is 10^9 ml^{-1}). The process was performed under continuous stirring of a mixture for 2 or 10 min; then, the new portion (0.32 ml) of chloroauric acid solution was added to the reaction mixture and the enlargement was proceeded yet for 3 min.

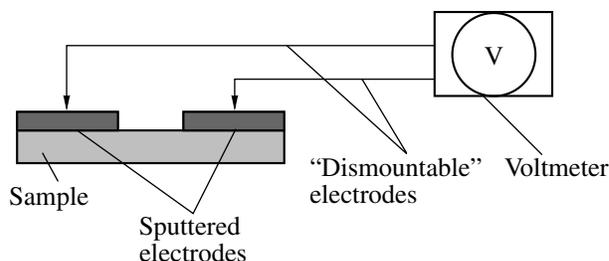


Fig. 1. Block diagram of a device for measuring conductivity of colloidal gold film on the surface of glassy polymer.

¹ The sample of poly(2-vinylpyridine) was kindly supplied by Prof. V.A. Kasaikin.

In order to enlarge gold nanoparticles preliminarily deposited onto the surface of polymer substrate, the sample was dipped in the mixture (1 : 1 by volume) of aqueous HAuCl_4 (0.01%) and NH_2OH (0.4 mM) solutions. The process was performed during the preset time (from 5 to 25 min) under continuous stirring; then samples were removed from the reaction vessel and rinsed with distilled water.

Samples for measuring electric conductivity were prepared as follows. Gold nanoparticles were deposited onto conventionally formed PVP films during the preset time (1 and 5.5 h). Then metal particles adsorbed on the polymer surface were enlarged according to the procedure described above. After this, gold electrodes were deposited onto the dried samples by metal vacuum evaporation. In the course of electrode formation, the middle part of PVP film with nanoparticles was protected (along its full length) from the deposition of gold vapors by paper screen with a width of about 1.2 mm. Electrodes were deposited in a similar manner onto bare (with no nanoparticles) PVP film and the film with deposited nanoparticles, which were not subjected to enlargement.

RESULTS AND DISCUSSION

At the initial stage of studies, we reproduced the procedure of the enlargement of gold nanoparticles in the bulk of colloidal solution proposed by Natan *et al.* [23]. To do so, we performed two series of experiments. In the first series, the Au^{3+} ions were reduced with hydroxylamine in aqueous solution in the absence of sol particles. Then, the droplet of reaction mixture was placed onto the copper grid coated with carbon and, after water evaporation, the substrate surface was examined with TEM. Electron microscopy analysis demonstrated that no metal nanoparticles are present in such a solution even after a relatively long time (i.e., the presence of seeding gold nanoparticles in the reaction mixture is indeed the necessary condition for the reduction of Au^{3+} ions with hydroxylamine).

In the second series of experiments, the enlargement of gold hydrosol particles was performed in the presence of HAuCl_4 and NH_2OH in accordance with the scheme described above. The TEM data show that, in the first 2 min of reaction, the diameters of nanoparticles did not vary too much. However, after 10 min enlargement, the sizes of gold particles increased by more than an order of magnitude and varied from 300 to 600 nm. The consequent addition of a fresh portion of HAuCl_4 solution to the hydrosol and the proceeding of a reaction in the following 3 min do not, in practice, influence the size of such large metal particles.

Thus, our results qualitatively agree with Natan *et al.* data [23] and demonstrate that, using the reduction of Au^{3+} ions with hydroxylamine, one can substantially enlarge the sizes of initial gold hydrosol particles.

As was demonstrated by the analysis of works [23, 27–29], the necessary condition for the preparation of continuous colloidal metal films by the enlargement procedure is the preliminary formation of a sufficiently dense monolayer of seeding nanoparticles on the substrate surface. Consequently, one should know the adsorption kinetics of gold hydrosol nanoparticles on the surfaces of glassy polymers (PS, PVP). The adsorption kinetics was earlier studied in detail [22] by the atomic force microscopy and quartz crystal microgravimetry. It was established that, within a wide range of coverage, this process is controlled by the diffusion of nanoparticles from the solution bulk to the polymer surface. Note that, analogous conclusion was drawn in [12, 13, 21] where the authors also studied the adsorption of colloidal gold particles on various substrates.

The next step of this work consisted in the study of possible enlargement of gold hydrosol particles preliminarily adsorbed on the surfaces of poly(2-vinylpyridine) and polystyrene.

The Enlargement of Nanoparticles in Monolayer Ensembles on the PVP Surface

To perform experiments, we chosen the samples that significantly differ in contact time between a polymer and a hydrosol and, hence, in the degree of surface coverage with the Au nanoparticles.

Figure 2 shows the AFM images of the surfaces of PVP films (with corresponding cross sections) after 10 min (sample 1) and 1 h (sample 2) of nanoparticle adsorption.

Note first that the sizes (heights) of Au particles adsorbed on the PVP surface turned out to be, on the average, slightly smaller than those of initial sol determined by electron microscopy. We believe that the possible reason for this effect can be the plasticization of the PVP surface layer by the dispersion medium of hydrosol resulted in a decrease of its T'_g to room (and lower) temperature and, hence, in the embedding of gold nanoparticles in a polymer to some depth already at the adsorption stage. This assumption is confirmed by the fact that, as the adsorption time increases from 10 to 60 min, the height of particles over the PVP surface decreases. Indeed, an increase in the time of contact between a polymer and a sol can enhance the effect of plasticization and promote the embedding of Au nanoparticles to a larger depth. The results obtained are in good agreement with the data reported in [16, 20] where the possibility of swelling was mentioned and, presumably, of even some dissolution of PVP in an aqueous medium [16].

Note that, visualizing the sample surface with the AFM technique, we should not forget some restrictions of this method. In particular, at a high surface density of metal nanoparticles, when the interparticle distance does not exceed the radius of cantilever tip (which is equal to 15–20 nm and often even larger), it is practi-

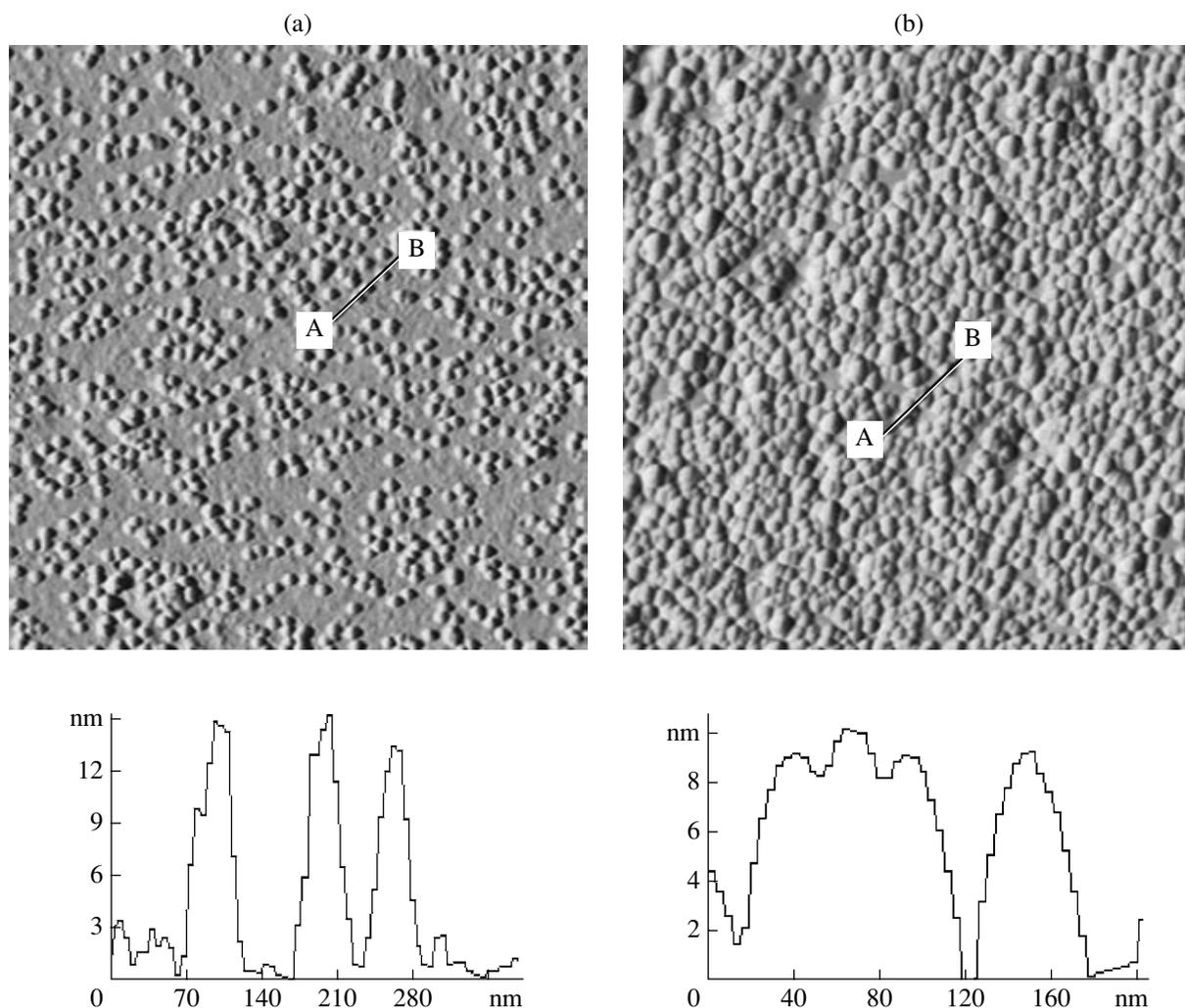


Fig. 2. The AFM images of the surface of poly(2-vinylpyridine) after the adsorption of gold hydrosol particles for (a) 10 min and (b) 1 h. Corresponding cross sections of the surface relief are shown below. The scan area is $2 \times 2 \mu\text{m}^2$.

cally impossible to derive reliable information on the particle height over the polymer surface. The reason for this is in the fact that the probe cannot penetrate between the particles to the substrate and completely “resolve” the picture. In this case, the analysis of obtained AFM images leads to slightly underestimated (compared to real) values of the height of nanosized objects.

The part of samples used in our experiments is characterized by a comparatively high degree of coverage of the PVP surface with seeding nanoparticles; therefore, in principle, it is necessary to take into account both effects described above.

In order to reveal which of these effects play the key role, we performed special experiments on the deposition of gold nanoparticles onto the silicon wafers covered with very thin PVP adsorption layers. The swelling of PVP adsorption layers upon contact with the hydrosol (if ever occurs), cannot lead to any noticeable nanoparticle embedding. According to the analysis of

the AFM images, in this case, the height of particles over the substrate surface is virtually independent of the time of contact between the surface and the hydrosol, i.e., of the density of nanoparticle packing. In addition, it appeared that, upon scanning the surfaces of such samples in contact mode, gold nanoparticles are easily shifted by the cantilever tip that does not take place in the case of their deposition onto “thick” (1–2 μm) PVP films. Therefore, one can state that the aforementioned decrease in the height of Au nanoparticles measured with atomic force microscope is caused by their partial embedding in the PVP surface layer devitrified due to plasticization; i.e., particles are mechanically fixed in a polymer already at the stage of adsorption.

Let us pass now to the results obtained directly upon the enlargement of Au nanoparticle ensembles on the PVP surface. According to experiments, the exposure of PVP film with deposited gold hydrosol particles to mixed aqueous HAuCl_4 and hydroxylamine solution leads to a noticeable particle enlargement. However, the

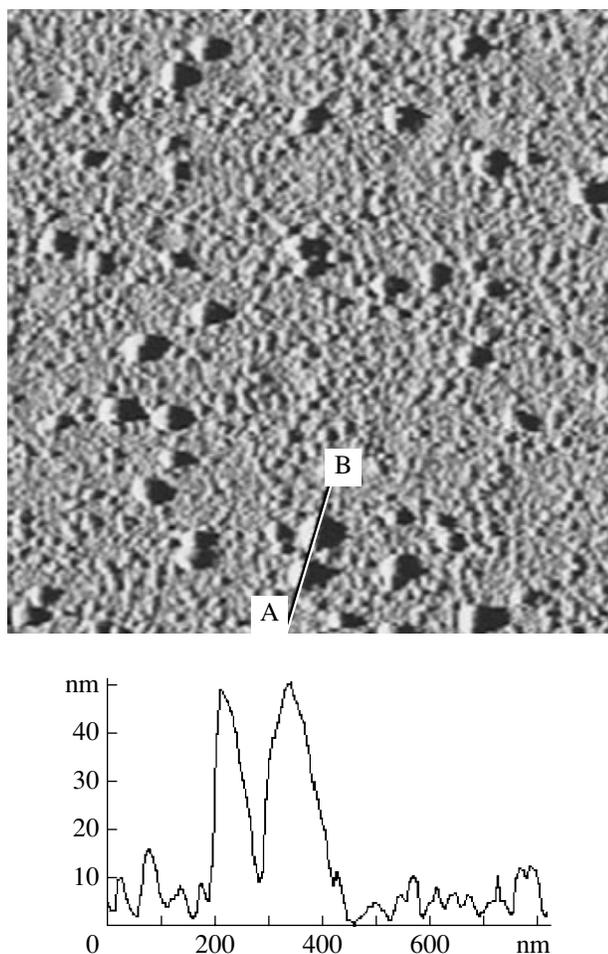


Fig. 3. The AFM image of nanoparticulate gold film prepared by the dipping of sample 1 in the solution of $\text{HAuCl}_4/\text{NH}_2\text{OH}$ mixture for 9 min and cross section of the surface along the AB line. The scan area is $2 \times 2 \mu\text{m}^2$.

structure of forming colloidal metal film in this case strongly depends on the packing density of the initial nanoparticle monolayer.

Figure 3 shows the AFM image of nanoparticulate Au film resulted from the dipping of sample 1 in the mixed $\text{HAuCl}_4/\text{NH}_2\text{OH}$ solution for 9 min and the corresponding cross section of the surface relief. It is seen that, after 9-min enlargement, the part of metal nanoparticles has the size equal approximately to 50 nm (note that the particles of similar size were also obtained in [23]). At the same time, considerable amount of particles whose diameters are even somewhat smaller than the initial value is present on the sample surface.

In our opinion, this is explained by the fact that, at low coverages of the PVP surface, two processes can proceed simultaneously. First, this is the enlargement of previously adsorbed nanoparticles. Second, the nucleation and growth on the polymer surface of new particles forming the fraction with smaller sizes than initial

hydrosol. Indeed nitrogen atoms constituting the PVP pyridine groups possess lone-pair electrons. Therefore, they can rather actively interact with various metals (including gold) by the mechanism of the formation of coordination bond and serve as additional nucleation sites in the reduction of Au^{3+} by hydroxylamine.

To verify this assumption, we performed the following experiment. A bare (with no nanoparticles) PVP sample was dipped in water for 9 min; the second similar sample, in the mixed $\text{HAuCl}_4/\text{NH}_2\text{OH}$ solution. It turned out that typical relief with the 2–3 nm heights of spherical asperities was developed on the surface of polymer film stored in such a mixture (Fig. 4b). The morphological changes of PVP surface cannot be attributed to its swelling in a reaction mixture, because the exposure of analogous sample to pure water does not lead to significant changes of its surface structure (see Fig. 4a). Hence, we can conclude that the monolayer of gold particles with the sizes of up to 3 nm is really formed on the polymer surface. More detailed study of such an unusual process of “direct” synthesis of gold nanoparticle ensembles on the PVP surface will be the subject of forthcoming publication.

Let us turn now to the results obtained upon the enlargement of particle ensemble formed on the PVP surface during 1-hour adsorption. Figure 5 presents the AFM image of nanoparticulate Au film obtained after 9-min dipping of sample 2 in the solution of $\text{HAuCl}_4/\text{NH}_2\text{OH}$ mixture and the corresponding cross section of surface relief. In this case, the mean particle size after the enlargement equals 16–20 nm that is much smaller than for sample 1. Seemingly, in a given system, a reasonably uniform growth of adsorbed nanoparticles takes place; as was demonstrated by the analysis performed using a FemtoScan-001 program, their total number remains practically constant. Evidently, this follows from much higher surface coverage with the particles after 1-h adsorption.

The analysis of the AFM images taken after various enlargement times (5–25 min) demonstrated that gold particles grow most noticeably in the first 10–15 min of reaction (see Fig. 6); then, the “thickness” of colloidal metal film almost does not vary. Note that, in these experiments, we used particles with a diameter of 16 ± 6 nm.

Chloroauric acid is present in a reaction mixture in considerable excess; therefore, the observed drastic retardation of particle growth does not follow from the consumption of Au^{3+} ions. The result obtained, first, can be an artifact due to the incorrect estimation of nanoparticle sizes, because the cantilever tip cannot pass between the particles (we mentioned earlier such a possibility). Second, the nanoparticle surface can be passivated (“poisoned”) by the PVP molecules during the reaction. Indeed, it is possible, in principle, that polymer macromolecules can go into the reaction mixture due to dissolution [16] (or their fragments due to swelling) with subsequent adsorption on the nanoparti-

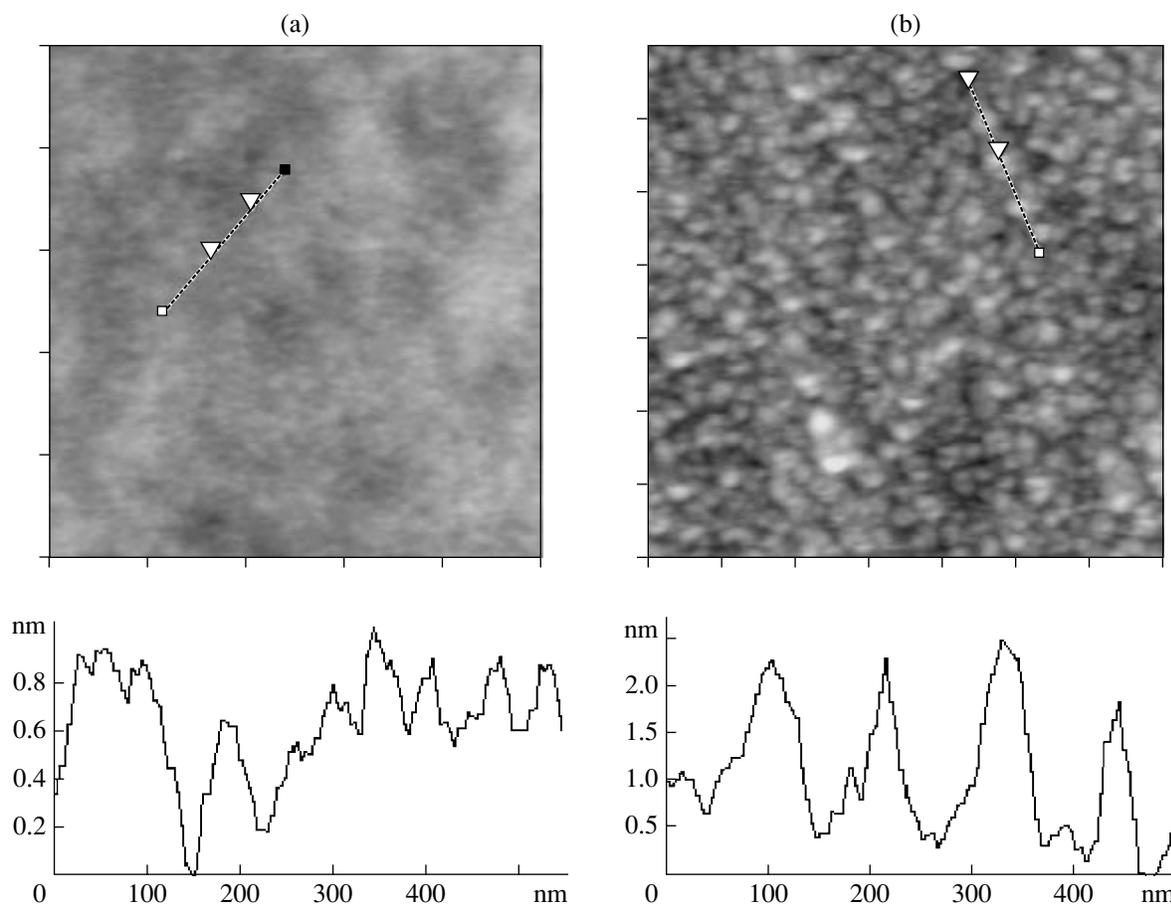


Fig. 4. The AFM images of the surfaces of bare (with no nanoparticles) PVP films after their dipping in (a) water and (b) the solution of $\text{HAuCl}_4/\text{NH}_2\text{OH}$ mixture for 9 min and the corresponding cross sections of the surface relief. The scan area is $2 \times 2 \mu\text{m}^2$.

cle surface. This problem will be treated in more detail in our next communication.

The Enlargement of Nanoparticles in Monolayer Ensembles on the Surfaces of Polystyrene and Its Mixtures with Oligomeric Homologue

The AFM images of the surfaces of PS-234 and its mixtures with oligomeric PS-5 covered with adsorbed gold hydrosol particles (time of adsorption is 2 h) are shown in Fig. 7.

Above all, the attention is attracted by the fact that the coverage of PS surface with nanoparticles is much lower than when using PVP as a substrate. Since the adsorption kinetics of hydrosol particles is identical for both polymers [22], the observed effect is explained, probably, by the weak interaction between nanoparticles and PS; because of this, their significant part is “washed off” from the surface of the sample during its withdrawal from the hydrosol.

As shows the analysis of the AFM images presented in Fig. 7, even an insignificant amount (2 vol %) of added PS-5 leads to such a noticeable decrease in the T_g' of

high-molecular-weight matrix that metal nanoparticles embed in a polymer to 2–3 nm already at room temperature (Fig. 7b); an increase in the PS-5 content to 5 vol % is accompanied by an increase in the thickness of devitrified surface layer and, correspondingly, in the depth of nanoparticle embedding (Fig. 7c).² Evidently, this effect is explained in the segregation (adsorption) of low-molecular-weight component at the boundary with the air.

The results obtained allow us to draw two main conclusions. First, metal nanoparticles deposited onto the PS-234 film containing insignificant amount of oligomeric PS-5 appeared to be fixed in a matrix surface layer already after the exposure of a sample at room temperature. Second, the incorporation (into high-molecular-weight matrix) of even small amount of the second component that can segregate at the air–polymer interface is a promising procedure for controlling T_g' .

Let us discuss now the results of experiments on the enlargement of gold nanoparticles in the ensembles on

² We remind to the reader that, according to [37], the glass transition temperature of the surface layer of PS with a molecular mass of 270 000 is equal to 40–50°C.

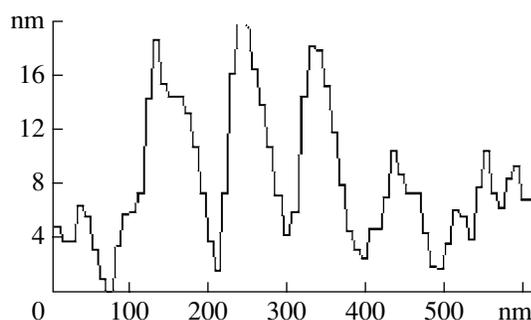
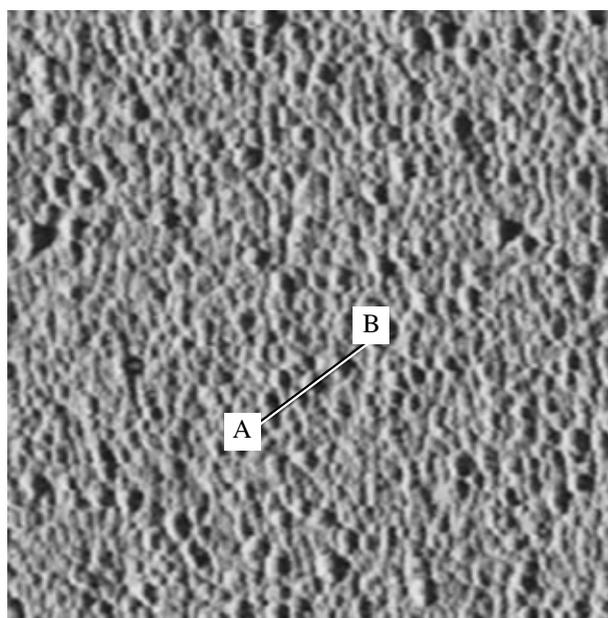


Fig. 5. The AFM image of nanoparticulate gold film prepared by the dipping of sample 2 in the solution of $\text{HAuCl}_4/\text{NH}_2\text{OH}$ mixture for 9 min and the cross section of surface relief along the AB line. The scan area is $2 \times 2 \mu\text{m}^2$.

the surfaces of initial PS-234 and mixtures based on this polymer.

Note that, to fix nanoparticles in the surface layer of high-molecular-weight PS, prior to enlargement, the samples were annealed for 1 h at 60°C ; i.e., within the range between “surface” and “bulk” glass transition temperatures [37]. Such a thermal treatment should result in a noticeable embedding of nanoparticles in the surface layer of glassy PS [37]. Indeed, as follows from the data shown in Fig. 8a, after the heating under aforementioned conditions, particles embed in PS, on the average, to 3–4 nm.

Figure 8 shows 3D images of the PS-234 surface with deposited nanoparticles taken after (a) the annealing of a system for 1 h at 60°C and (b) its subsequent exposure in the solution of $\text{HAuCl}_4/\text{NH}_2\text{OH}$ mixture for 9 min. Corresponding cross sections of surface relief are shown at the right-hand side of this figure.

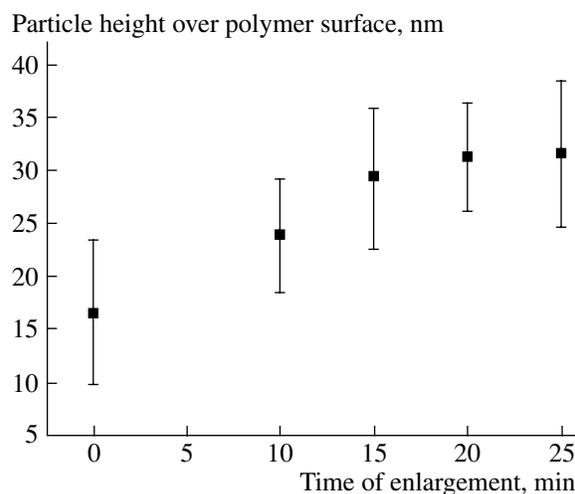


Fig. 6. The kinetics of the enlargement of Au nanoparticles on the PVP surface.

The AFM data presented in Fig. 8b testify that the sizes of sol particles “incorporated” into the PS surface layer are increased approximately to 50 nm in the course of enlargement process. However, in contrast to the PVP/Au nanoparticles system, all metal particles that are present on the surface grow fairly uniformly during the reduction of Au^{3+} ions with hydroxylamine; new particles are not formed in this case. Seemingly, this can be associated with a much higher chemical inertness of PS as compared to PVP.

Analogous results were obtained also upon the enlargement of nanoparticle ensembles on films prepared from the PS-234 mixtures with its oligomeric homologue PS-5.

In conclusion, we discuss the results of preliminary experiments on studying the lateral conductivity of colloidal gold films formed on the PVP surface by the enlargement of particles in the mixed solution of chlorauric acid and hydroxylamine.

It was shown above that, upon the exposure of the monolayer ensemble of gold hydrosol particles, which is formed on the PVP surface after 1-h adsorption, to aqueous solution containing $\text{HAuCl}_4/\text{NH}_2\text{OH}$ mixture, nanoparticles grow almost uniformly. In this case, according to the AFM data, most of the polymer surface appeared to be covered with metal already after 9 min of reaction. It can be assumed that contacts can arise between gold particles in the course of enlargement; first, single contacts are formed and then their number steadily increases. At a certain stage of enlargement, this can lead to the emergence of conductive channels in the forming “two-dimensional” structure (nanoparticulate film) of a metal.

Results of these experiments demonstrated that the resistance of initial system, i.e., bare (with no nanoparticles) PVP film with sputtered gold electrodes, was higher than $100 \text{ k}\Omega$. This value decreased to $\approx 10 \text{ k}\Omega$

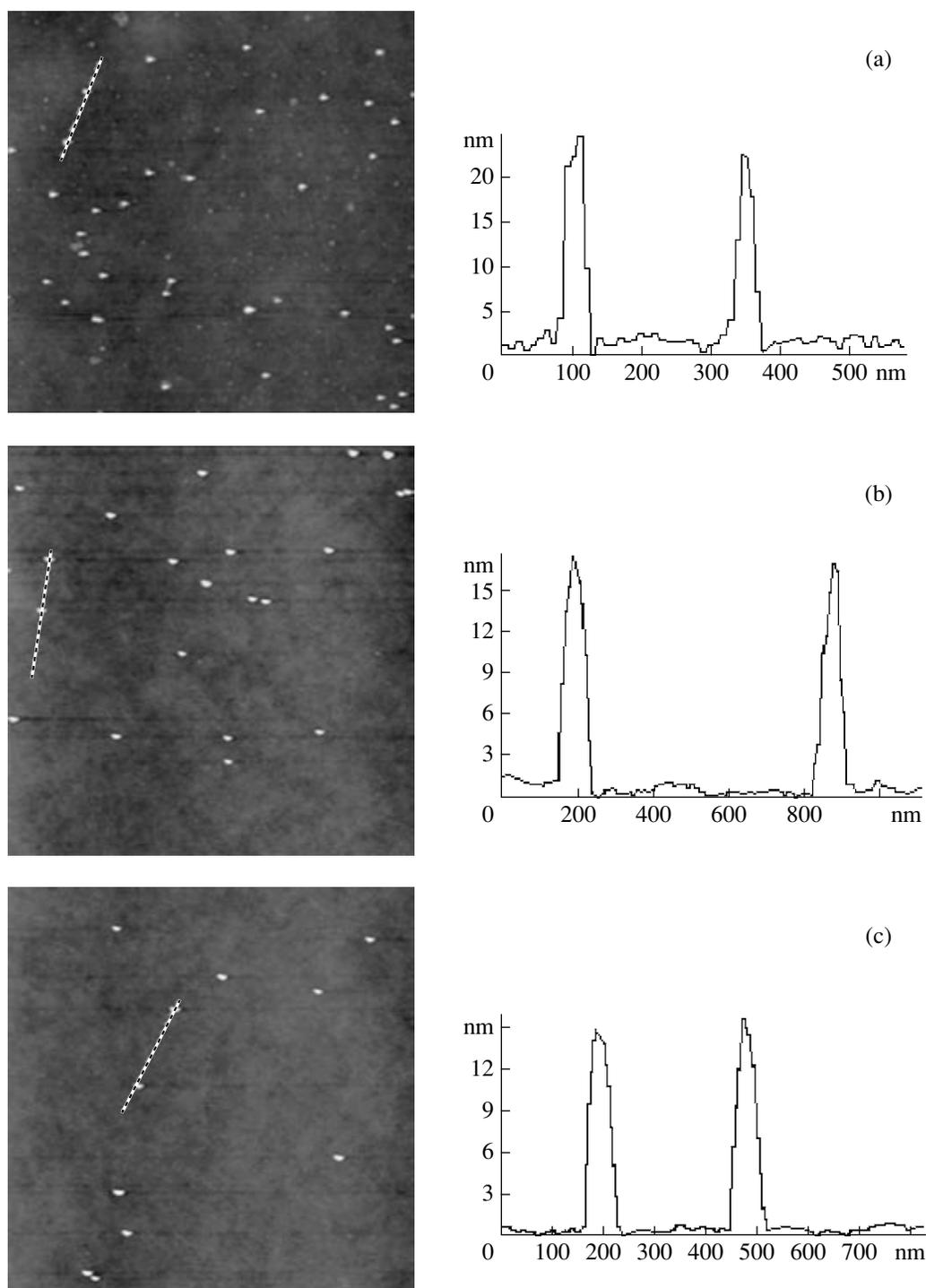


Fig. 7. The AFM images and the corresponding cross sections of the surfaces of PS-234 and its mixtures with PS-5 oligomer covered with adsorbed gold nanoparticles after the sample exposure at room temperature: (a) PS-234, (b) 2 and (c) 5 vol % of PS-5. The scan area is $2 \times 2 \mu\text{m}^2$.

after the formation of the adsorption layer of gold hydrosol particles (sol concentration is 10^{12} ml^{-1} , adsorption time is 1 h). The enlargement of nanoparticles in such a layer for 5 min decreased the resistance to about 5 k Ω ; after the reaction for 9 min, i.e., upon the formation of structure shown in Fig. 5, to $R \approx 3.5 \text{ k}\Omega$.

With allowances made for the resistivity of pure gold ($2 \times 10^{-8} \Omega \text{ m}$) and the geometry of studied samples (the width of interelectrode gap and the particle diameter taken as the film thickness), the resistance value mentioned above (3.5 k Ω) formally corresponds to the presence of conductor from solid Au with the

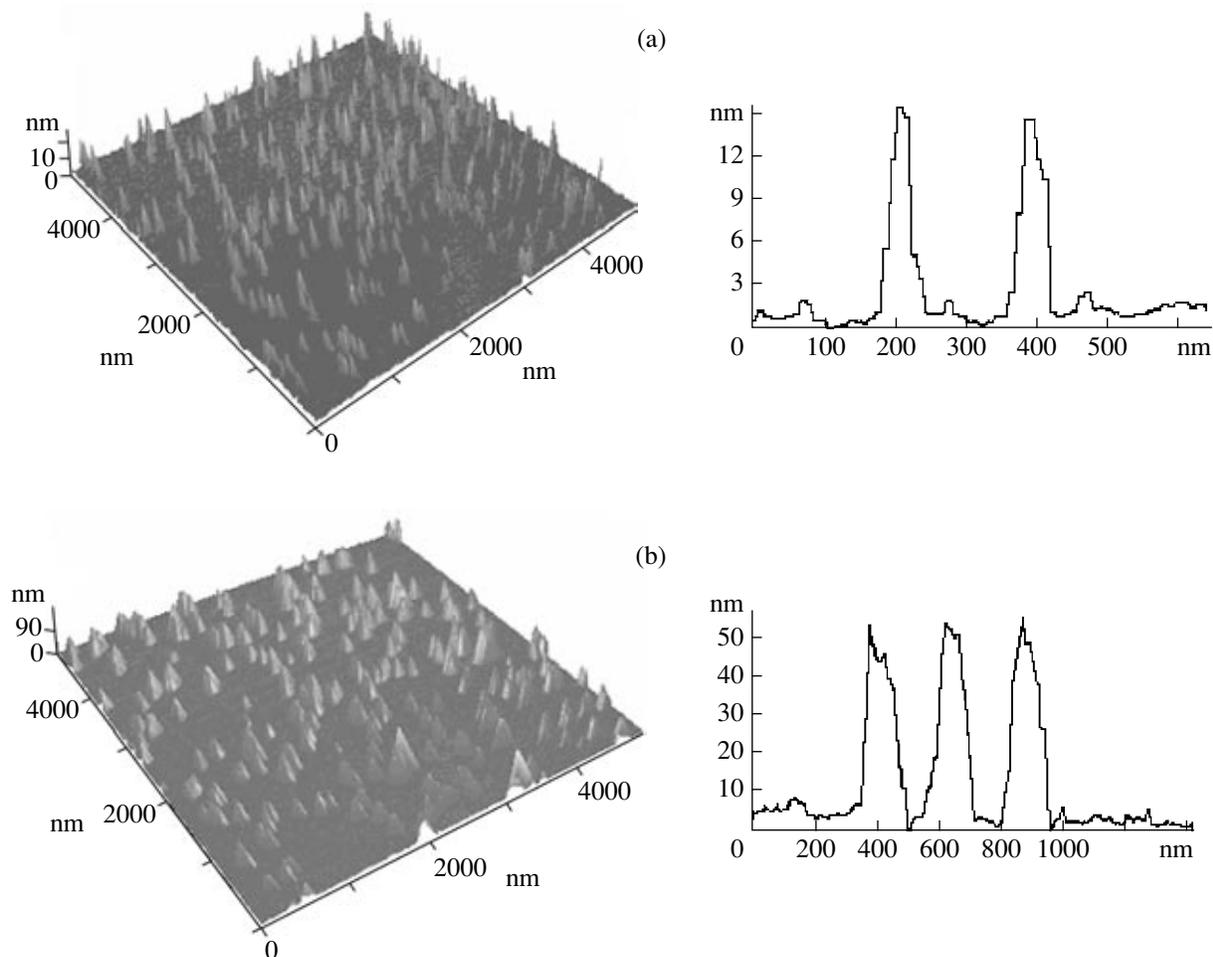


Fig. 8. The AFM 3D images of the surfaces of PS-234 surface with adsorbed gold hydrosol particles after (a) the annealing of a system at 60°C for 1 h and (b) consequent exposure in the solution of $\text{HAuCl}_4/\text{NH}_2\text{OH}$ mixture for 9 min and the corresponding cross section of the surface relief.

width of about 0.2 μm between the electrodes. The result obtained testifies that, after the 9-min enlargement of hydrosol particles adsorbed on the PVP surface, “two-dimensional” structure characterized by the presence of the channels of lateral conductivity is actually formed; however, its properties are far from those of “continuous” film of colloidal gold. It is evident that, to prepare such a film, one should increase the duration of the stage of particle enlargement.

CONCLUSIONS

The process of the enlargement of gold hydrosol particles adsorbed on the PVP surface in aqueous solution containing the mixture of HAuCl_4 and hydroxylamine was studied. It was shown that the character of this process depends on the packing density of initial nanoparticle monolayer. At a sufficiently high surface coverage, a uniform growth of all particles takes place, whereas, at low coverage, both the enlargement of adsorbed particles and the formation and growth of new

particles are observed. The proposed explanation of these effects is based on the account of possible coordination of Au^{3+} ions with nitrogen atoms constituting the PVP pyridine groups.

It was shown that, in the case of PS, adsorbed particles of gold hydrosol can be enlarged after their preliminary “incorporation” into the polymer surface layer by the annealing of a system at a temperature below T'_g but above T'_g .

Using high-molecular-weight PS as an example, it was demonstrated that, in principle, it is possible to decrease T'_g by the addition of small amounts of oligomeric homologue.

We performed tentative experiments on the study of the conductivity of colloidal gold films prepared by the enlargement of gold particles adsorbed on PVP from the hydrosol. It was demonstrated that contacts providing the formation of conductive channels arose between nanoparticles in the course of their enlargement.

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REFERENCES

1. Lyon, L.A., Pena, D.J., and Natan, M.J., *J. Phys. Chem.*, 1999, vol. 103, p. 5826.
2. Maxwell, D.J., Emory, S.R., and Nie, S., *Chem. Mater.*, 2001, vol. 13, p. 1082.
3. Roldughin, V.I., *Usp. Khim.*, 2004, vol. 73, p. 123.
4. Pattabi, M., Rao, K.M., Sainkar, S.R., and Sastry, M., *Thin Solid Films*, 1999, vol. 338, p. 40.
5. Kovacs, G.J. and Vincett, P.S., *J. Colloid Interface Sci.*, 1982, vol. 90, p. 335.
6. Stepanov, A.L., Abdullin, S.N., and Khaibullin, I.B., *J. Non-Cryst. Solids*, 1998, vol. 223, p. 250.
7. Zaporozhtchenko, V., Strunskus, T., Behnke, K., *et al.*, *J. Adhes. Sci. Technol.*, 2000, vol. 14, p. 467.
8. Sato, T., Hasko, D.G., and Ahmed, H., *J. Vac. Sci. Technol.*, 1997, vol. 15, p. 45.
9. Doron, A., Joselevich, E., Schlittner, A., and Willner, I., *Thin Solid Films*, 1999, vol. 340, p. 183.
10. Kooij, E.S., Wormeester, H., Brouwer, E.A.M., *et al.*, *Langmuir*, 2002, vol. 18, p. 4401.
11. Bhat, R.R., Fisher, D.A., and Genzer, J., *Langmuir*, 2002, vol. 18, p. 5640.
12. Schmitt, J., Machtle, P., Eck, D., *et al.*, *Langmuir*, 1999, vol. 15, p. 3256.
13. Zhu, T., Fu, X., Mu, T., *et al.*, *Langmuir*, 1999, vol. 15, p. 5197.
14. Liu, Y., Wang, Y., and Claus, R.O., *Chem. Phys. Lett.*, 1998, vol. 298, p. 315.
15. Jiang, C., Markutsya, S., and Tsukruk, V.V., *Langmuir*, 2004, vol. 20, p. 882.
16. Malynych, S., Luzinov, I., and Chumanov, G., *J. Phys. Chem., B*, 2002, vol. 106, p. 1280.
17. Li, W., Xu, R., Wang, L., *et al.*, *Mol. Cryst. Liq. Cryst. Sci. Technol., A*, 1999, vol. 337, p. 185.
18. Kim, B., Tripp, S.L., and Wei, A., *J. Am. Chem. Soc.*, 2001, vol. 123, p. 7955.
19. Swami, A., Kumar, A., Selvakannan, P.R., *et al.*, *J. Colloid Interface Sci.*, 2003, vol. 260, p. 367.
20. Kunz, M.S., Shull, K.R., and Kellock, A.J., *J. Colloid Interface Sci.*, 1993, vol. 156, p. 240.
21. Shull, K.R. and Kellock, A.J., *J. Polym. Sci., Part B: Polym. Phys.*, 1995, vol. 33, p. 1417.
22. Sukhov, V.M., Dement'eva, O.V., Kartseva, M.E., *et al.*, *Kolloidn. Zh.*, 2004, vol. 66, p. 539.
23. Brown, K.R. and Natan, M.J., *Langmuir*, 1998, vol. 14, p. 726.
24. Brown, K.R., Walter, D.G., and Natan, M.J., *Chem. Mater.*, 2000, vol. 12, p. 306.
25. Jana, N., Gearheart, L., and Murphy, C.J., *Langmuir*, 2001, vol. 17, p. 6782.
26. Wei, Z., Mieszawska, A.J., and Zamborini, F.P., *Langmuir*, 2004, vol. 20, p. 4322.
27. Brown, K.R., Lyon, L.A., Fox, A.P., *et al.*, *Chem. Mater.*, 2000, vol. 12, p. 314.
28. Musick, M.D., Pena, D.J., Botsko, S.L., *et al.*, *Langmuir*, 1999, vol. 15, p. 844.
29. Hrapovic, S., Liu, Y., Enright, G., *et al.*, *Langmuir*, 2003, vol. 19, p. 3958.
30. Meltzer, S., Resch, R., Koel, B.E., *et al.*, *Langmuir*, 2001, vol. 17, p. 1713.
31. Rivas, L., Sanchez-Cortes, S., Garcia-Ramos, J.V., and Morcillo, G., *Langmuir*, 2001, vol. 17, p. 574.
32. Kim, J.H., Jang, J., and Zin, W.-C., *Langmuir*, 2000, vol. 16, p. 4064.
33. Keddie, J.L., Jones, R.A., and Cory, R.A., *Faraday Discuss. Chem. Soc.*, 1994, vol. 98, p. 219.
34. Meyers, G.F., DeKoven, B.M., and Seitz, J.T., *Langmuir*, 1992, vol. 8, p. 2330.
35. Kajiyama, T., Tanaka, K., and Takahara, A., *Polymer*, 1998, vol. 39, p. 4665.
36. Satomi, N., Takahara, A., and Kajiyama, T., *Macromolecules*, 1999, vol. 32, p. 4474.
37. Rudoy, V.M., Dement'eva, O.V., Yaminskii, I.V., *et al.*, *Kolloidn. Zh.*, 2002, vol. 64, p. 823.
38. Tichroeb, J.H. and Forrest, J.A., *Phys. Rev. Lett.*, 2003, vol. 91, p. 016 104.
39. Zhang, Y., Zhang, J., Lu, Y., *et al.*, *Macromolecules*, 2004, vol. 37, p. 2532.
40. Zhang, X., Tasaka, S., and Inagaki, N., *J. Polym. Sci., Part B: Polym. Phys.*, 1999, vol. 38, p. 654.
41. Tanaka, K., Takahara, A., and Kajiyama, T., *Macromolecules*, 1997, vol. 30, p. 6626.
42. Rudoy, V.M., Bol'shakova, A.V., Dement'eva, O.V., *et al.*, *Struktura i dinamika molekulyarnykh sistem* (Structure and Dynamics of Molecular Systems), Kazan: Kazan. Gos. Univ., 2004, issue 11, pt. 3, p. 44.
43. Hariharan, A., Kumar, S.K., and Russell, T.P., *Macromolecules*, 1990, vol. 23, p. 3584.
44. Wattenbarger, M.R., Chan, H.S., and Evans, D.F., *J. Chem. Phys.*, 1990, vol. 93, p. 8343.
45. Kajiyama, T., Tanaka, K., and Takahara, A., *Macromolecules*, 1998, vol. 31, p. 3746.
46. Zsigmondy, R., *Kolloidchemie*, Leipzig, 1931.
47. Filonov, A.S. and Yaminskii, I.V., *Rukovodstvo pol'zovatelya paketa programmogo obespecheniya dlya upravleniya skaniruyushchim zondovym mikroskopom i obrabotki izobrazhenii "FemtoScan-001". Versiya 2.16* (A Guide for the User of the Software for Controlling Scanning Probe Microscope and Image Processing "FemtoScan-001". Version 2.16), Moscow: Tsentr Perspektivnykh Tekhnologii, 1999.