Scanning force microscopy visualization of adsorption from liquids

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Adsorption of residual impurities from liquid media on various substrates was studied by scanning force microscopy. A new express method for controlling the purity of liquids was suggested.

Key words: scanning force microscopy, adsorption, molecular films.

Progress in studying clean surfaces by scanning force microscopy[1,2] makes it possible to study many real physicochemical processes on a solid surface, *e.g.*, friction[3] and adhesion,[4,5] and structures and conformations of biological systems[6] with subnanometric spatial resolution. The recent application of scanning force microscopy for studying phenomena on a liquid—solid state interface is of doubtless interest.[7,8,9] The control of the purity of a substrate and the liquid is significant for studies in liquids. Even insignificant impurities in the liquid can be adsorbed on a substrate or an object studied and can substantially affect surface processes. The appearance of an adsorbate on the solid surface can result in a change in the adhesion between solid states and change of the permeability of filters, including biological membranes. The use of pure liquids and elimination of side processes are of practical significance. For example, adsorption of impurities on clean substrates at various stages of lithography, using solutions and pure liquids, decreases the yield of microelectronic production. The use of pure liquids is also important in the technology of application of molecular Langmuir—Blodgett films, which are promising materials for modification of properties of solid state surfaces.

The high sensitivity of scanning force microscopy makes it possible to study adsorption of a substance on a solid surface from solutions with an extremely low content of impurities and to study the initial stages of adsorption: formation of nuclei, clusters, and islands of films.

In this work, scanning force microscopy is used for studying adsorption of impurities from pure solutions (distilled water, hydrochloric acid) on the surface of freshly cleaved graphite and mica.

Experimental

Distilled water (20 μL) was applied to the surfaces of freshly cleaved highly oriented pyrolytic graphite and freshly cleaved mica with surface areas of 10×10 mm^2. Water droplets were evaporated in an atmosphere of dry nitrogen for 2 h. In some experiments, 20 mg of 37 % hydrochloric acid (analytically pure grade, Merck) was applied to the graphite surface for comparison. Two min after application hydrochloric acid was removed by centrifuging. The graphite and mica surfaces were preliminarily cleaned by the method of interlayer cleavage in air. Images were obtained on a Nanoscope-2 microscope, using industrial probes with tips of Si_3N_4 (Digital Instruments, USA). The mechanical rigidity of a cantilever was 0.06 N m^{-1}.

When the images were mathematically treated, only deduction of mean slope was used, and the other methods (averaging, median filtration, and other), which can distort original patterns, were not used.

Results and Discussion

Impurities are adsorbed on the mica surface from distilled water to form both rigid structures, *i.e.*, stable, strongly bound, and surface structures than can be easily deformed and shifted. Rigid forms of the adsorbed substance appear in the images as stable light protrusions (Fig. 1, *a*). Mild forms of the adsorbed substance are shifted during scanning and can be observed in the negative contrast at the edge of the frame, using a larger scale. Shifting of the "mildly" adsorbed substance can be retarded on rigid protrusions, and then it also appears in the negative contrast. In our experiments, the adsorbed substance is shifted mainly toward the direct scan. If parameters of the direct and reverse scans differ, for

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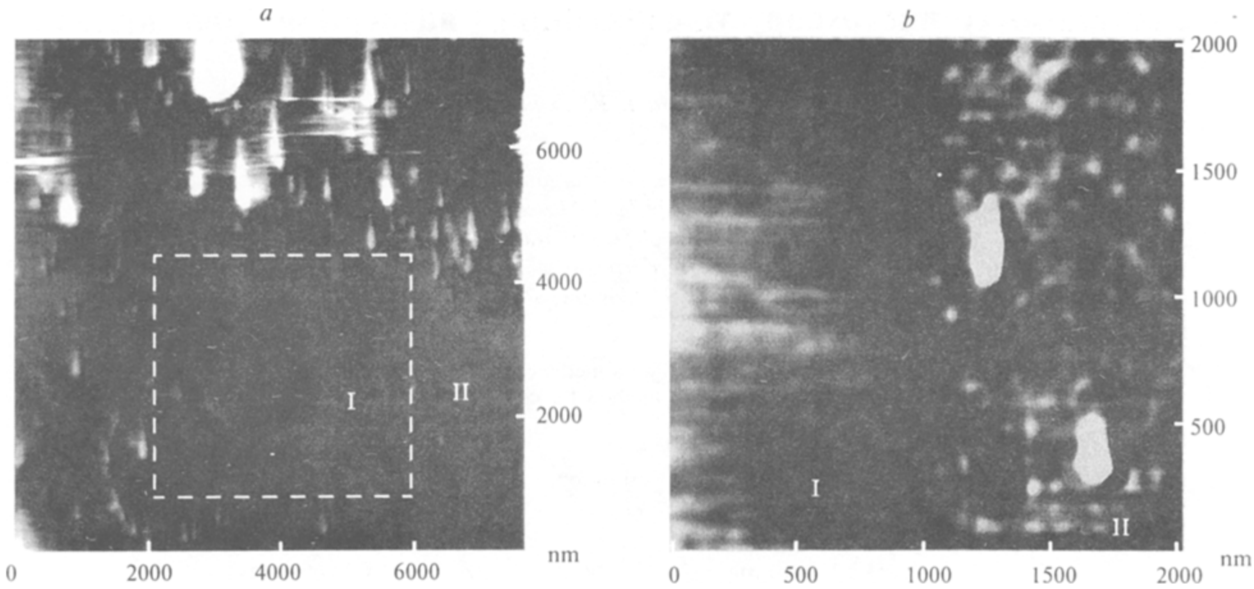

Fig. 1. *a.* Image of the mica surface with traces of the adsorbate. Multiple scanning was performed over region I. The size of the frame was 7.7×7.7 μm^2. *b.* Image of the boundary of the scanning area. Multiple scanning was performed over region I localized to the left in the image.

example, due to different rates of movement of the tip, the adsorbed substance can shift predominantly to one edge of the frame. If then the sizes of the frame are enlarged in such a way that the initial scanning area (I) is localized in the central part, a cleaned region can be distinguished in the first magnified pattern, and traces of the shifted adsorbed substance can be observed. Weakly adsorbed impurities are removed due to scanning, and the mica surface becomes clean. The fragment of the boundary of the cleaned region is presented in Fig. 1, *b*. In the left part of the frame the adsorbate film is removed due to multiple scanning. It is present in the right part, and this results in an increase in roughness. When the window is 1 μm^2, the scatter of amplitudes of the heights for the clean region ranges from 0.8 to 1.4 nm, and the mean square value changes from 0.15 to 0.2 nm. For the contaminated region the ranges of these parameters are 2.5 to 3 nm and 0.3 to 0.4 nm, respectively.

The image of the pyrolytic graphite surface after evaporation of distilled water is presented in Fig. 2, *a*. The measurements were carried out in the constant force mode (F ~2×10^{-8} N). Pyrolytic graphite has a polycrystalline structure, sizes of individual crystallites are 1 to 10 μm. Broken chemical bonds near defects, for example, steps on the surface, favor the formation of initial adsorption centers. The experiments performed show that adhesion between the protrusions formed by the adsorbed substance and the graphite surface is small, and the adsorbate can be removed by the probe of the microscope at the value of the normal force not higher than 10—30 nN.

When the same region of the graphite surface is visualized by the scanning force microscope, insignificant differences are seen in several first images subsequently obtained. These differences disappear, as a rule, after 3—10 repeated scans. This is explained by the fact that an easily deformed adsorbed substance is present on the graphite surface. Surface structures formed by this substance are plastic, adhesion between them and the substrate is small, and these structures can be easily removed by the action of the tip of the force microscope. A prolonged scanning allows one to completely remove "mild" forms of the adsorbed substance and obtain images of the cleaned region stable in time and without noise. The detailed image of the boundary of the area undergone multiple scanning is presented in Fig. 2, *b*. The probe of the microscope was repeatedly moved in the region of the surface localized in the right part of Fig. 2, *b* due to which the surface was cleaned. The unremoved adsorbate film is well observed in the left part of the frame. The topography of its surface is not uniform. The scatter in amplitudes of heights for the clean region is 0.8 to 1.4 nm, and the mean square value is 0.15 to 0.2 nm, while for the contaminated regions these values are 2.5—3 nm and 0.3—0.4 nm, respectively, at the size of the window of 1 μm.

The experiments on visualization of the film formed on the graphite surface due to evaporation of 37 % hydrochloric acid also testify in favor of the shift of the adsorbed substance by the probing tip of the force microscope. Hydrophobic surfaces in aqueous media undergo considerable mutual attraction due to which nonpolar compounds at first are accumulated near the

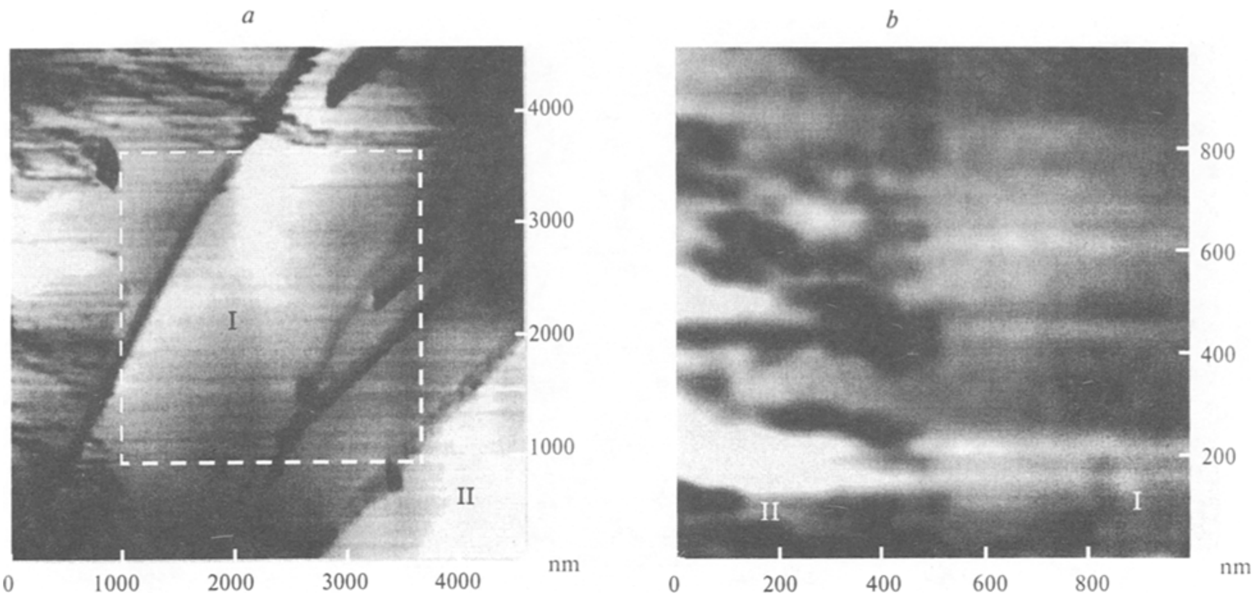

Fig. 2. *a*. Image of the pyrolytic graphite surface with traces of the adsorbate. Region I is the area of multiple scanning. *b*. Image of the boundary of the scanning area. Multiple scanning was performed over region I.

graphite surface and precipitated on the graphite substrate after evaporation of the liquid. Therefore, it should be expected that films of the adsorbed substance mainly consist of nonpolar organic substances. Adhesion between such films and the graphite substrate should be weak, and this is confirmed by visualization by scanning force microscopy. A smooth region of clean graphite (Fig. 3) corresponds to the region of initial multiple scanning, and it is well observed in the larger frame. The graphite surface is cleaned from the adsorbate layer due to a prolonged scanning. The mean thickness of the adsorbed layer is ~3 nm.

The 7×7-μm^2 image of the fragment of the two-component film consisting of a mixture of equal molar portions of eicosylamine $Me(CH_2)_{19}NH_2$ and docosane diol $HO(CH_2)_{22}OH$ is presented in Fig. 4, *a*. The film was applied onto the mica surface according to the Langmuir—Blodgett method at the pressure of 30 mN m^{-1}. The first monolayer of the film completely covers the mica surface. Islands of the second layer are localized on the first layer. There are small regions on some of these islands, which correspond to the third layer. The first layer forms a rigid covering, which remains undistorted upon scanning. The second and third layers give stable images, although there are insignificant shifts of the third layer over the second layer caused by the action of the probing tip of the force microscope. A dark area appears at the boundary of the first smaller frame on going to the second larger frame (Fig. 4, *b*) and disappears in next patterns. It can be assumed that the appearance of the dark region is explained by shifting the adsorbed substance during scanning over the smaller frame. It can be observed on going to the larger frame that dark regions appear and again disappear at boundaries of new frames.

A scanning force microscope allows one to obtain unique information on the distribution of the adsorbed substance over the substrate surface. When the adsorbed substance exists in the rigid nondeformed form, this

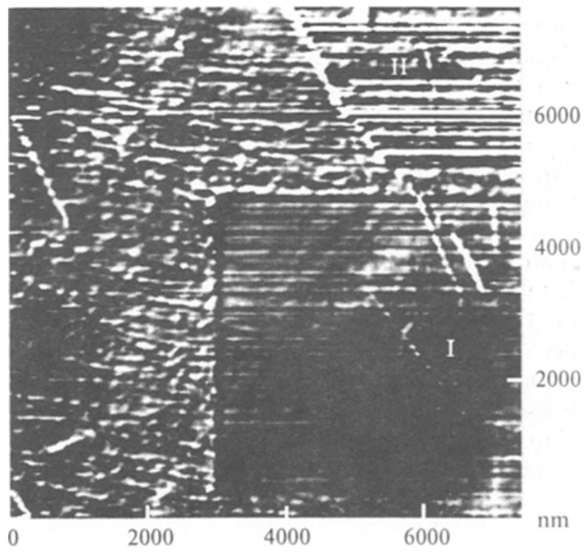

Fig. 3. Image of the graphite surface with the film of the adsorbate. The film of the adsorbate was removed with the tip of the scanning force microscope in the area of multiple scanning I.

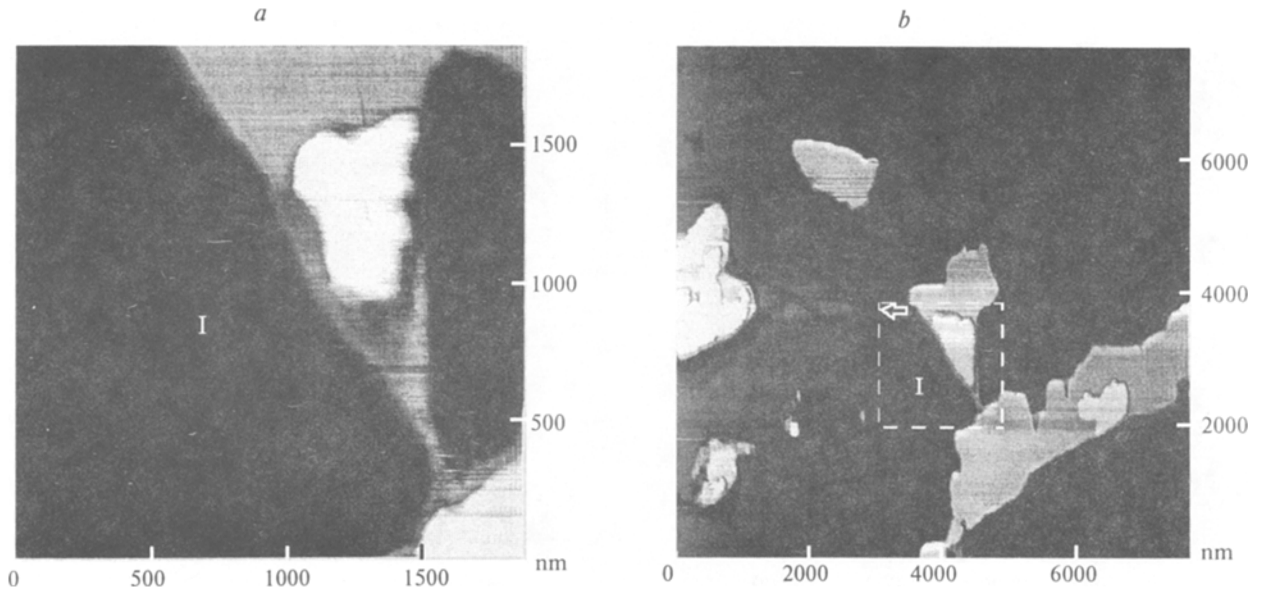

Fig. 4. *a.* Image of the fragment of the two-component Langmuir—Blodgett film. The size of the frame is 2×2 μm^2. *b.* The adsorbate was condensed near the left boundary of the frame due to scanning over region I (see Fig. 4, *a*). The arrow indicates the place of localization of the adsorbate.

method makes it possible to estimate the volume of the adsorbed phase.

It is considerably more difficult to follow the behavior of a weakly adsorbed substance. The existence of a thin film of the adsorbed substance can be determined, for example, by visualization of its edge formed due to partial removal of the film.

The possibility of visualization of the shifted adsorbate on the images with negative contrast (as dark regions corresponding to hollows) can be explained in terms of the following model notions. The topographies presented in Figs. 1—4 are obtained in the constant force mode. In this case, for homogeneous materials light areas on the image correspond to elevations on the surface, and dark regions correspond to hollows. The correspondence is not so unambiguous for heterogeneous materials.

Let us consider the case of a planar sample, whose central and peripheral parts consist of different substances. Let us assume that each of the substances is characterized by the value of the Hamaker constant (H), which determines the force interaction between the tip and planar surface. Then the expression for the interacting force F between the planar surface removed by distance Z from the tip and the tip with a radius of curvature R can be written in the form

$$F = -\frac{HR}{6(Z)^2}. \qquad (1)$$

If H takes different values at different regions of the surface, equal interacting forces between the tip and substrate for different regions are possible only upon their unequal mutual removal. Then a seeming relief can appear on the surface of a sample heterogeneous in composition. In fact, let us consider a sample with the planar surface (Fig. 5), whose central and side parts are presented by different materials (different constants H_i). Depending on the ratio between constants H_2 and H_1, an elevation ($H_1 < H_2$) or a hollow ($H_1 > H_2$) can appear in the pattern of the sample. Although a more rigid approach is based on integration of pair interactions over all volumes of the probe and sample, the calculation of the force interaction by Eq. (1) gives quite reliable results. Additional interactions, for example, capillary forces that appear for thin liquid films, can result in the appearance of the seeming relief. The value of capillary

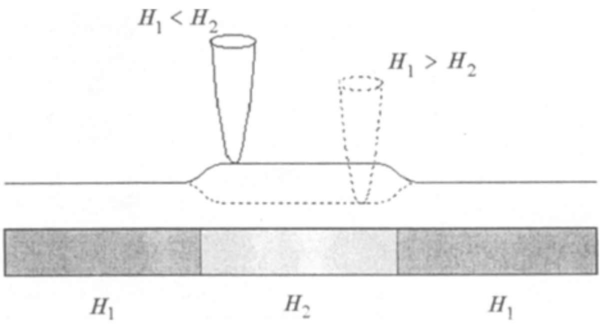

Fig. 5. Profile of movement of the probe of the scanning force microscope above the geometrically smooth surface of the sample of heterogeneous composition.

forces is determined by the coefficient of surface tension γ, radius R of the tip, and distance D between the tip and the sample:

$$F = -\frac{4\pi R\gamma\cos\theta}{1+\frac{D}{d(P)-D}}, \qquad (2)$$

where θ is the contact angle, P is the relative humidity, and $d(P) = -(1.08 \text{ nm})\cos[\ln(P)]$.[10]

The additional capillary forces from the viscous adsorbate layer can be a possible reason for the appearance of negative contrast. When an adsorbate is present, additional lateral forces (forces of friction) can result in parasitic bends of the cantilever, which also can result finally in the appearance of contrast. The previous measurements by a friction scanning force microscope[11] indicate that coefficients of friction differ for two-component films applied onto the smooth substrate surface.

The shift of the "mild" form of the adsorbed substance during scanning, which is observed by scanning force microscopy, allows one to suppose that a similar shift of the adsorbate occurs in the regime of scanning tunneling microscopy. Various anomalous images appear, when pyrolytic graphite is measured in air by tunneling microscopy.[12] Multiple scanning of the same area often result in the transformation of anomalous images into typical images of the lattice, whose sizes correspond to the parameters of the unit cell of graphite (0.246 nm and 0.144 nm). In fact, the shift of the adsorbate layer results in the appearance of the clean graphite surface, and the adsorbate is removed from the tunnel gap. After this the adsorbate cannot affect tunneling processes. As shown previously,[13] additional channels and conditions for electron tunneling can appear in films adsorbed on substrates, including monolayer coverings artificially applied onto the graphite surface, which results in anomalous images of film—substrate systems. A shift of an adsorbate in images can be directly registered by a force microscope, while in a scanning tunneling microscope the process of removal of an adsorbate can be indirectly observed by the qualitative change in the pattern from anomalous to typical.

Determination of insignificant admixtures in the bulk liquid is a difficult problem. However, when admixtures are precipitated onto substrates, the high sensitivity of scanning force microscopy allows one to quantitatively analyze concentrations of admixtures. The correct selection of used substrates with specified chemical properties provides the conditions for selectively analyzing admixtures.

The sensitivity of the method can be evaluated in the following way. Let n be the surface concentration of molecules of the adsorption layer (the number of molecules per unity surface of substrates), h is the initial thickness of the liquid layer (before evaporation). If N measurements obtained by the scanning microscope registered N molecules, the averaged value (one molecule per frame) can be considered as the criterion of the sensitivity of the method. When the pattern of the surface is plotted by the typical value of 400×400 points, a single molecule can be distinguished for a frame size of 100 nm. Then let us assume that the size of a molecule is $1\times1\times1$ nm^3, and 16 points take part in displaying a molecule. This corresponds to the surface concentration n of $\sim10^{10}$ molecules/cm^2. This gives the volume concentration of $\sim10^{-8}$ %, when the initial thickness of the liquid layer h = 1 mm. The evaluation of sensitivity presented above is not quite strict, because it does not take into account various factors of adsorption. For example, adsorption can result in the formation of large clusters, detection of which can be highly improbable. The method suggested is close to the widely used method for determination of the purity of evaporated water by studying traces on clean glass. It is noteworthy that the best examples of scientific equipment[14] for determining the purity of water by sedimentation or photometry make it possible to detect bulk volume concentrations of admixtures at the level not higher than 10^{-6} %. The use of a scanning force microscope allows one to increase the sensitivity of observations by several orders of magnitude.

Thus, the possibility of using a scanning force microscope for observation of initial stages of adsorption from pure liquids is shown. It is shown that the "mild" form of the adsorbed substance observed by the force microscope can appear in images in the negative contrast. The surface can be mechanically cleaned under the action of the probing tip.

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