Morphology of the Dithionylpyrrole Langmuir-Blodgett Films and their AFM Modification

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The dithionylpyrrole LB films surface morphology was found to change drastically with varying the number of monolayers, subphase and the type of substrate used. The AFM modification of LB films was carried out by different methods, namely, by increasing the force on cantilever in semicontact mode, and applying the voltage (5 V, 10 V) between the tip and the substrate in contact mode. The shape of the nanostructures is strongly dependent on the LB film morphology and formation methods.

1. Introduction

Recently, considerable interest has been growing in the nanostructure fabrication on organic Langmuir-Blodgett (LB) films by various scanning probe techniques [1, 2, 3]. The LB method provides the possibility of growing ultrathin films with controlled thickness and ordered molecular orientation from a variety of organic materials. SPM has proved to be a powerful tool not only for imaging, but also for modifying the LB film surface with nanometer-scale resolution.

In this paper the dithionylpyrrole LB films surface morphology was investigated by multimode SPM Solver P47 (NT-MDT, Moscow) and different methods for their controlled and reproducible modification with AFM were considered.

2. Experimental procedures

The $\alpha\alpha' - \beta$-hexadecyldithionylpyrrole LB films were prepared by usual LB

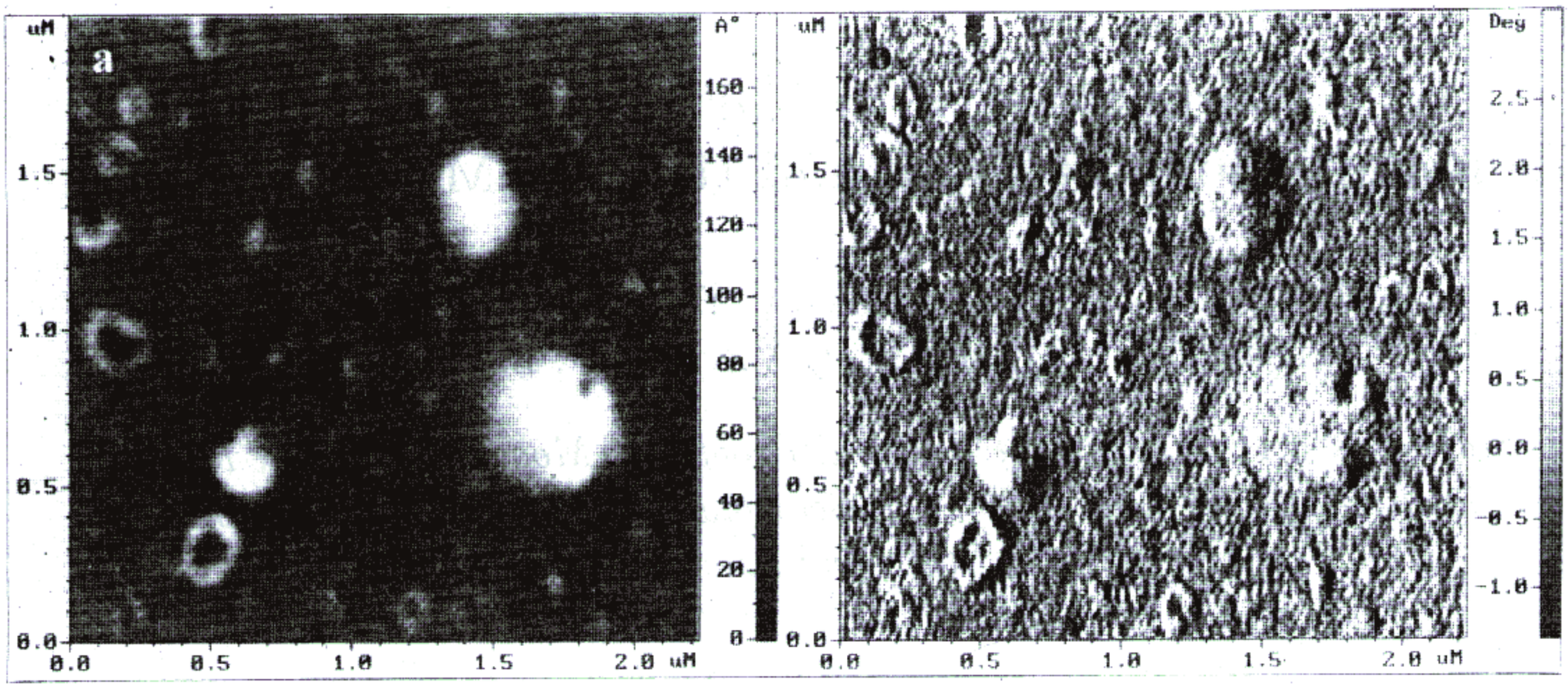

Figure 1. AFM image (semicontact mode; panel (a) – height, panel (b) – phase) of the 3 monolayer dithinylpyrrole LB film deposited on mica from the $Fe(NO_3)_3$ subphase.

technique. The films were deposited onto freshly cleaved HOPG and mica at a deposition speed of 6.7 mm/min and surface pressure of $\sim$ 35 mN/m if the $FeCl_3$ subphase was used, and at a deposition speed of 17 mm/min and surface pressure of $\sim$ 40 mN/m if the $Fe(NO_3)_3$ subphase was used. Since all the films were of the Y-type, those deposited on mica had odd number of layers (3, 5, 7) and the films formed on the HOPG showed even number of layers (2, 4, 6).

Investigations of the dithionylpyrrole LB films surface morphology and their nanomodification were performed with SPM Solver-P47 (NT-MDT, Moscow).

3. Results and discussion

The morphology of the LB films was found to change drastically with varying the number of monolayers, subphase and the type of substrate. Fig. 1 gives an AFM image of three monolayer LB films deposited on mica from $Fe(NO_3)_3$. Three distinct features are observed here: the first one is the islands with curved boundaries, similar to fractals; the second one is numerous large grains; the third one is the presence of tore-like clusters made of grains.

Since the energy of interaction between the amphiphilic molecules and the subphase differs from that between the amphiphilic molecules and the substrate surface, during the film deposition the equilibrium between the liquid expanded (LE) and liquid condensed (LC) phases could vary and results in the grain formation. The grains connect with each other to form islands. For hydrocarbon

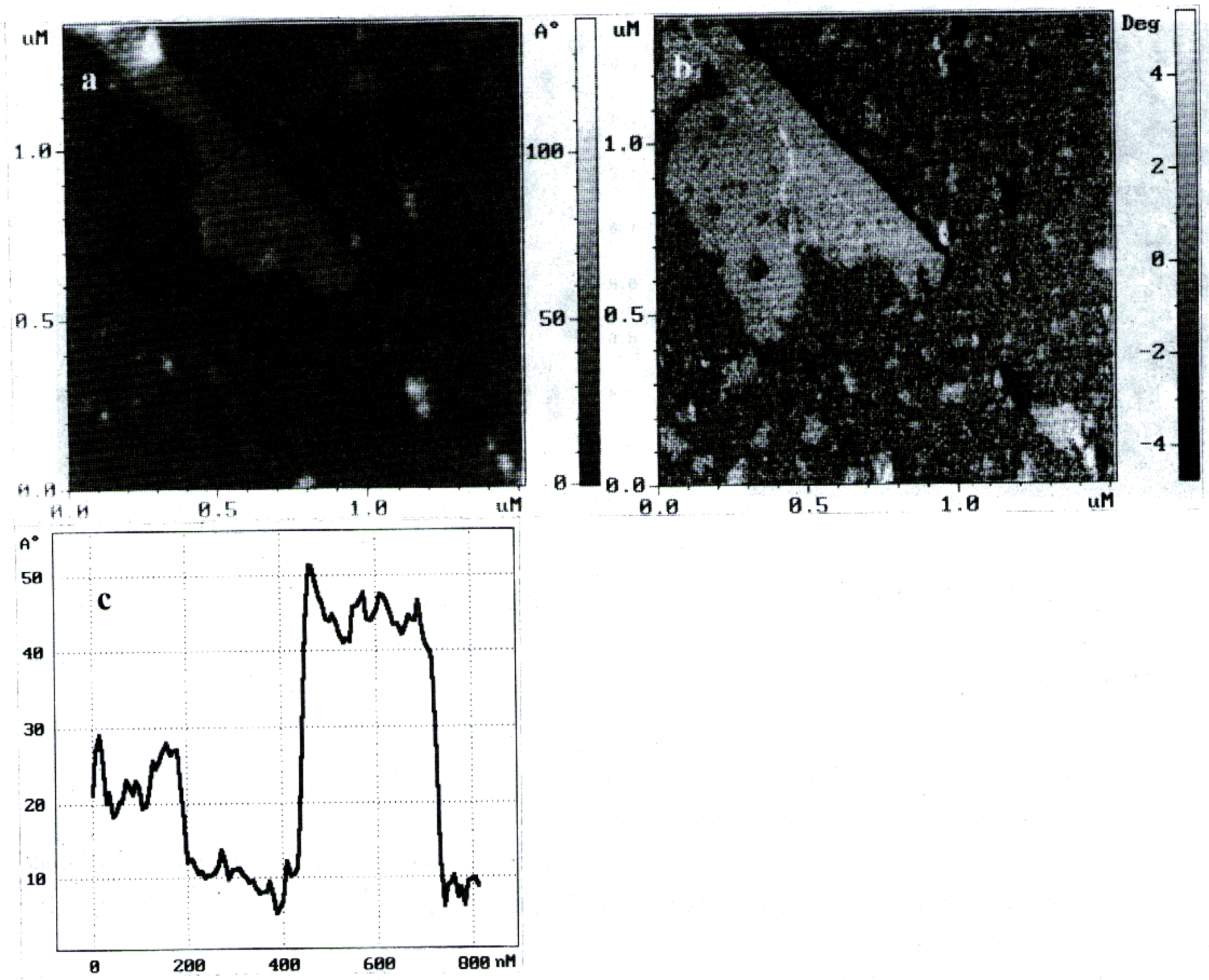

Figure 2. AFM image (semicontact mode; panel (a) – height, panel (b) – phase) of the 3 monolayer dithinylpyrrole LB film deposited on mica from $FeCl_3$ subphase. Plotted in panel (c) is the profile along the lines cutting through the film showing the height difference between 3 monolayers.

chains the entropy effects become pronounced, which leads to the fractal geometry of the islands.

The large grains shown in Fig. 1 are likely to represent either $Fe(NO_3)_3$ crystals originated from the adhesion of the subphase drops on the film surface, or the clusters split off from the film during the process of its formation at the meniscus from the boundary of the Langmuir layer formed on the subphase surface. Their size varies from 60 nm to 200 nm and the height from 5 nm to 17 nm. In this case they are likely to be centers of formation of liquid crystal phase of the LB film. From the comparison of the mean-square surface roughness of the islands of the liquid crystal phase surrounding these large grains ($S_q = 0.5$

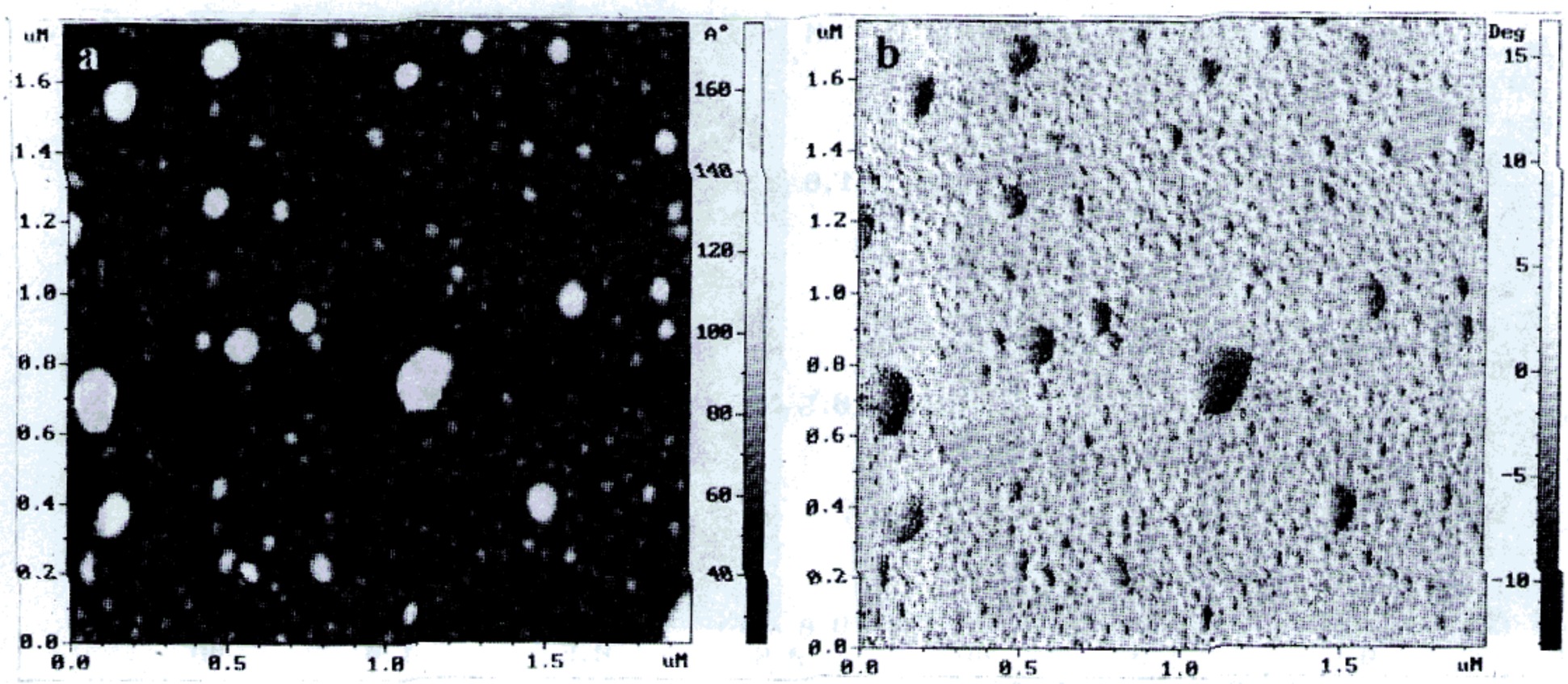

Figure 3. AFM image (semicontact mode; panel (a) – height, panel (b) – phase) of the 7 monolayer dithinylpyrrole LB film deposited on mica from the $FeCl_3$ subphase.

nm) and the islands of the fractal shape ($S_q = 1.5$ nm) one can draw a conclusion that a more smooth surface belongs to the first LC phase.

As seen from Fig.1, the formation of tore-like clusters from the grains is also possible. The external tore diameter is 150–200 nm, the internal 50–100 nm, and the height 8–10 nm.

It is the phase sensitivity not only to the surface relief but also to the surface properties, namely, to adhesion and local hardness that we used to investigate the nature of large grains as well as to elucidate the mechanism of the LB film formation. From a rather homogeneous phase image with no contrast (Fig. 1) we could conclude that the observed grains are clusters made of the amphiphilic molecules of dithienylpyrrole.

Fig. 2 gives an AFM image of three monolayer LB films deposited on mica from the $FeCl_3$ subphase. A clear contrast seen in the phase image allows us to infer that two mechanisms of the LB film formation exist: the first one is the molecular (classical) mechanism forming smooth film coatings and the second one is the cluster mechanism when the separation of a small island from the film occurs at the meniscus with its subsequent adsorption on the substrate. It was found that the morphology of three monolayer LB films deposited on mica from $FeCl_3$ subphase changes drastically. The film is island-like without any tore clusters and possesses a small number of large grains.

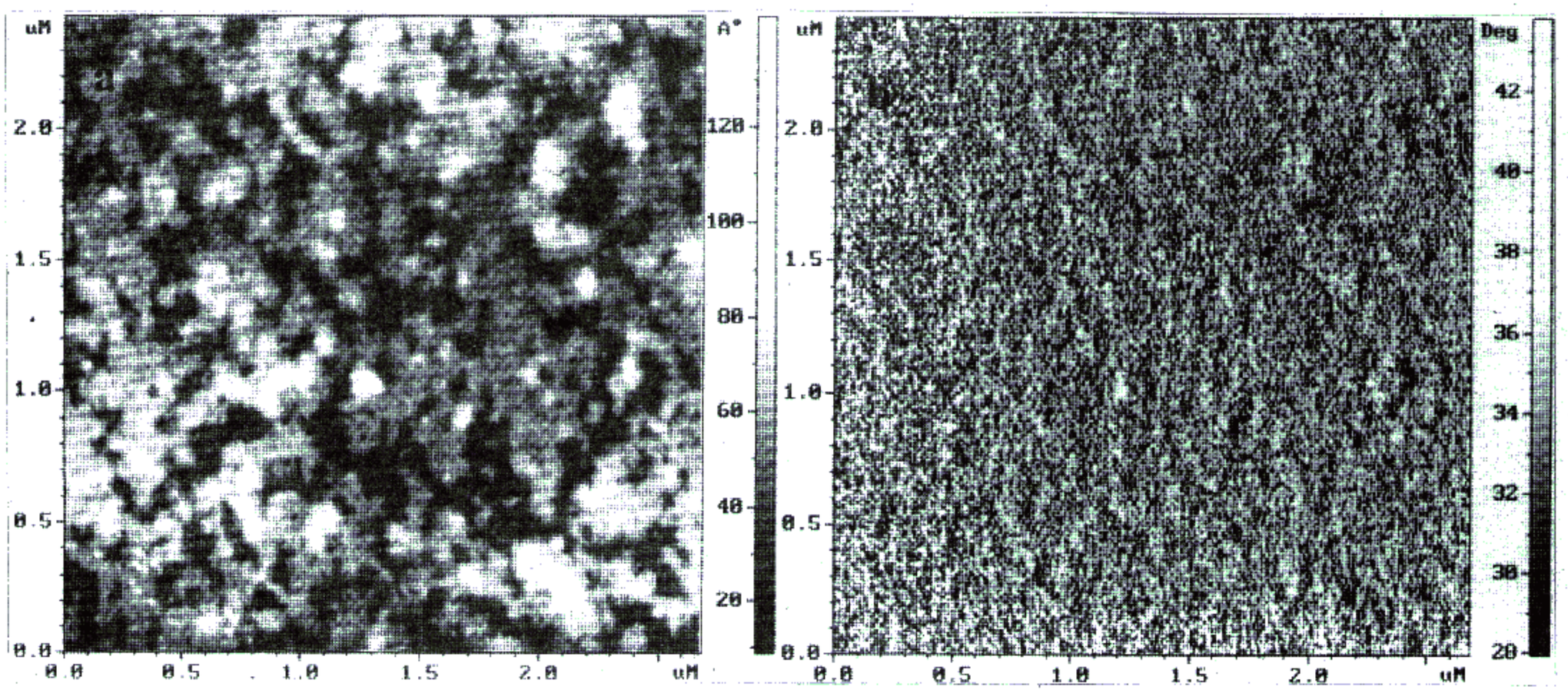

Figure 4. AFM image (semicontact mode; panel (a) – height, panel (b) – phase) of the 6 monolayer dithinylpyrrole LB film deposited on HOPG from the $FeCl_3$ subphase.

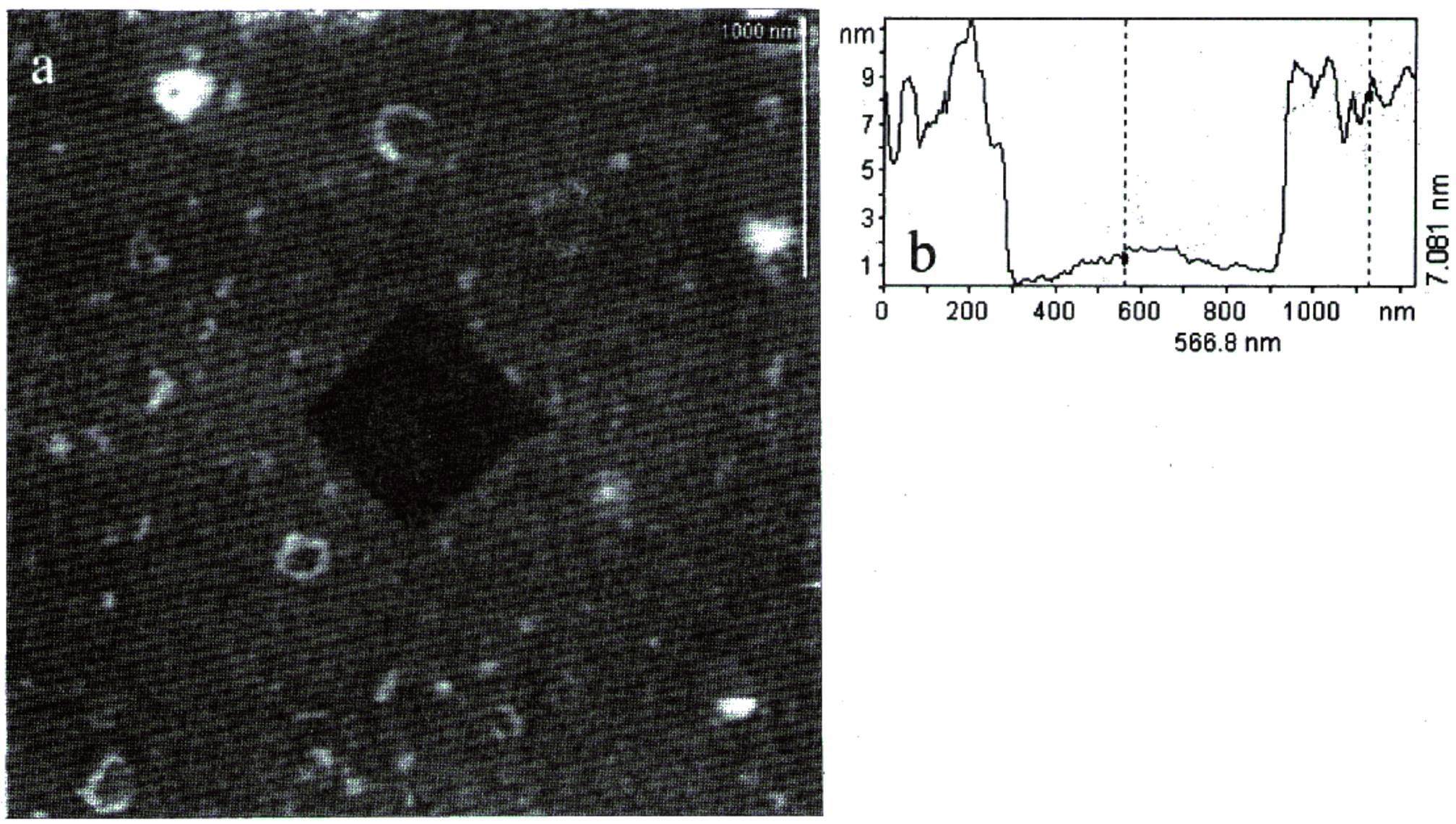

Figure 5. AFM image (semicontact mode; panel (a) – height) of the 3 monolayer dithinylpyrrole LB film deposited on mica from the $Fe(NO_3)_3$ subphase; panels (b) – profile along lines cutting through written square hole.

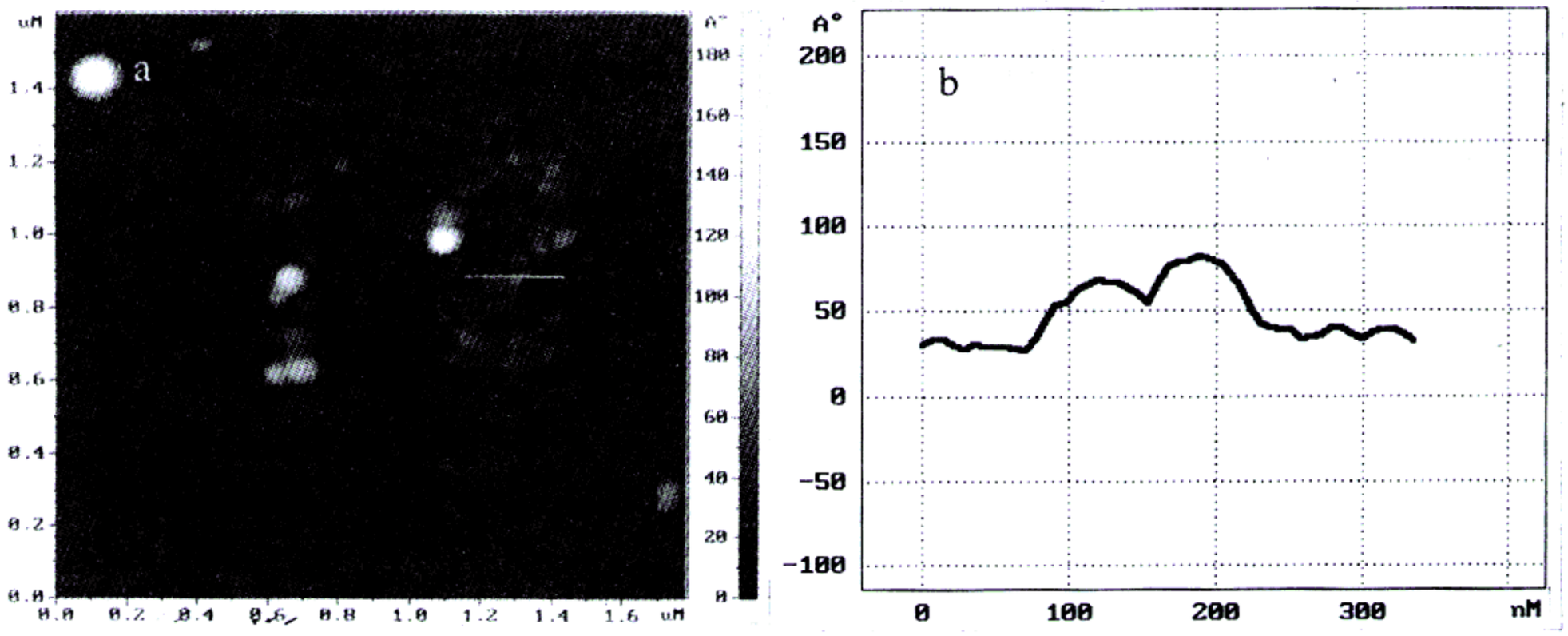

Figure 6. AFM image (semicontact mode; panel (a) – height) of the 7 monolayer dithinylpyrrole LB film deposited on mica from the $FeCl_3$ subphase with written figures "1" and "2"; panel (b) shows the profile along the lines cutting through the written figure "2".

With increasing number of monolayers the morphology of LB films varies dramatically. This is most vividly seen in films deposited from the $FeCl_3$ subphase.

Fig.3 shows an AFM image of seven monolayer LB film deposited on mica from the $FeCl_3$ subphase. Even with a visual inspection of the image, the film roughness is seen to be much greater than a molecular size. The grain structure of the film is quite distinct with the grain size varying from tens to hundreds of nanometers. The LB films deposited on mica from the $Fe(NO_3)_3$ subphase demonstrate no substantial change in their morphology as the number of monolayers increases.

Fig.4 shows an AFM image of the six monolayer LB film deposited on graphite from the $FeCl_3$ subphase. The films formed from the $FeCl_3$ subphase consist of randomly connected islands with curved boundaries, similar to fractals. Inside the islands one could clearly see the hole-like defects 18–50 nm in diameter. Their appearance seems to be due to the growth kinetics of the film, namely, fast process of coalescence of small islands into the large ones. With increasing number of monolayers the morphology of LB films deposited on graphite from the $FeCl_3$ subphase practically does not change.

The investigations carried out on the LB films by SPM methods have demonstrated high mobility of the LB films with a tendency for restructuring mainly in the process of formation.

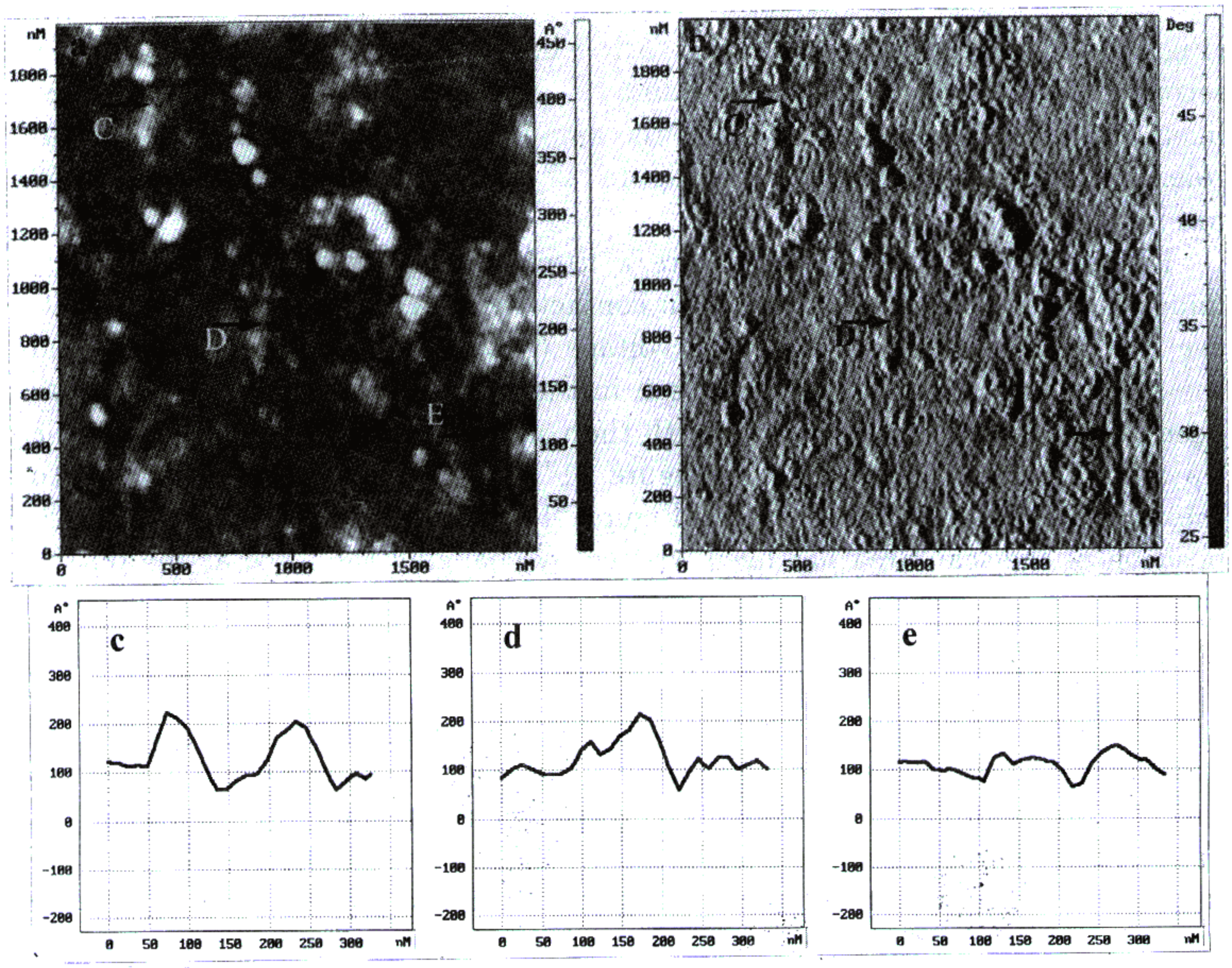

Figure 7. AFM image (semicontact mode; panel (a) – height, panel (b) – phase) of the 6 monolayer dithinylpyrrole LB film deposited on HOPG from the $FeCl_3$ subphase with written figures "1", "1", "1"; Panles (c), (d), and (e) show the profiles along lines cutting through the formed figures.

Three and seven monolayer LB films deposited on mica and six monolayer LB film deposited on graphite had been chosen for their controlled AFM modification. In the AFM image (Fig. 5(a)) a well defined square hole 610×610 nm in size can be clearly seen which has been formed by increasing the force to 70 nN. Similar structures can be formed in an regular. Yet, contamination of the AFM probe by the film material could lead to formation of irregular holes and, correspondingly, to destruction of periodicity.

The modification was performed otherwise (Fig. 6(a)) by simply increasing the force also on the cantilever (Si, $k = 48$ N/m) but the semicontact mode of the AFM operation had been chosen and the tip motion occurred under a preset program. While in the first case we observed the square hole ~ 7 nm in depth

(Fig. 5(b)), roughly corresponding to the height of three monolayers, in the second case the written figures "1" and "2" appeared as convex up and, most likely, have been formed by grains of the amphiphilic molecules of dithienylpyrrole. The dimensions of the written figure "2" were ~ 8 nm in height and ~ 150 nm in width (Fig. 6(b)).

Figures "1", "1", "1" (Fig. 7) are written by AFM with conductive probe under different conditions, namely, in contact mode without applying the voltage and in contact mode with the voltage (5 V, 10 V) between the tip and the substrate. Figure "1", clearly seen in the E-position of the scan area, has been written in the contact mode with the voltage of 10 V applied between the tip and the substrate. The same figure "1" in the D-position obtained with the voltage of 5 V is less distinct. Figure "1" (practically invisible) in the C-position of the scan area has been written by changing the force acting on the cantilever in the absence of voltage. The appearance of figure "1" which is 6–7 nm in depth and 40–50 nm in width in E-position can obviously be interpreted as the destruction of the LB film under the action of the beam of electrons emitted from the tip when a high electric field was applied between the tip and the substrate. When the voltage of 5 V is applied, a partial destruction of the LB film is probably accompanied by its polimerization. The shape of the nanostructures is strongly dependent on the LB film morphology and formation methods. The demonstrated methods are versatile and powerful tools to create complex nanometer-scale structures. In combination with resist techniques and conductive layers, it should be possible to make nanometer-sized circuits.

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