SPM investigations of phase distribution in lead phthalocyanine-perylene derivative composite films

B.A. Gribkov[1], O.M. Stukalov[2], A.E. Pochtenny[3], V.L. Mironov[1], S.V. Gaponov[1], A.V. Misevich[3]

[1] Institute for Physics of Microstructure of RAS, N.Novgorod
[2] Institute of Solid State and Semiconductor Physics of NASB, Minsk
[3] Belarussian State University of Technology, Minsk

During last years organic semiconductors found practical application in organic solar cells and organic LEDs [1]. One possible way to advance the electronic properties of organic semiconductor materials is a doping by another organic or inorganic material [2]. The arrangement of one material in matrix of another one is important characteristic that significantly influence on electronic properties of composite. In this report we analyze possibilities of different SPM techniques for exploring of phase arrangement in photoconductive phthalocyanine–perylene composite films. This pair of materials is of great interest for laminar p-n-junction organic solar cells [3, 4].

The composite films of 20 and 100 nm in thickness (as measured by quartz crystal microbalance) were deposited onto the glass-ceramic substrates with nickel electrode by laser vacuum evaporation of powdered mixture of 1:1 lead phthalocyanine (PbPc) and perylenetetracarbocylic diimide (PTCDI).

Morphology of the films and local electronic properties was investigated using SPM Solver-P47 (NT-MDT). Platinum coated cantilevers were used in conductive probe measurements. Additionally the samples were analyzed by photoassisted STM (photo-STM), in which the gap of Femtoscan-Online STM (ATC, MSU) was illuminated by He-Ne laser light [5]. The STM tips were Pt/Ir wire prepared by cutting. All SPM images were analyzed using FemtoScan-Online program.

AFM topography analysis shows that the film morphology represents big clusters with lateral size up to 1 μm and height up to 100 nm on background of uniform polycrystalline morphology with grain size of 80-120 nm. It should be noted that both PbPc and PTCDI one-component laser evaporated films have typical uniform polycrystalline morphology with grain size 50-100 nm. The same elongated clusters on grain background were observed in perylene-CuPc films by Rudiono et al. [6] using SEM and authors suggested that its formation result from perylene precipitation. Therefore, it is possible to suggest that clusters and grain films are different phases.

To clarify chemical nature of clusters we apply a number of SPM methods that as known can give chemical information. They are commercially available friction (or lateral) force microscopy (LFM) in contact mode, phase imaging in resonant mode, scanning capacitance microscopy (SCM), scanning Kelvin probe microscopy (SKPM) and scanning spreading resistance microscopy (SSRM). Additionally we used the photoassisted STM. All these techniques excluding SSRM and photo-STM does not give us any chemical contrast between clusters and grain film.

SSRM technique (or AFM with conductive tip) allows the local conductivity of the film to be mapped additionally to topography images in contact mode. Fig. 1 represents topography (a) and current images (+5 V on tip) of the composite film of 100 nm in thickness. As seen some places of the film are significantly more conductive than grain film. Moreover, some another grains that not protruded on topography are conductive too. It is known that perylene and its derivatives are more conductive then phthalocyanines. Moreover, perylenes demonstrate n-type conductivity, while phthalocyanines have a p-type. Based on this it can be concluded that conductive areas are PTCDI. Part of conductive areas corresponds to protruded clusters, another one is deep in PbPc material. It should be noted that clusters placed not on

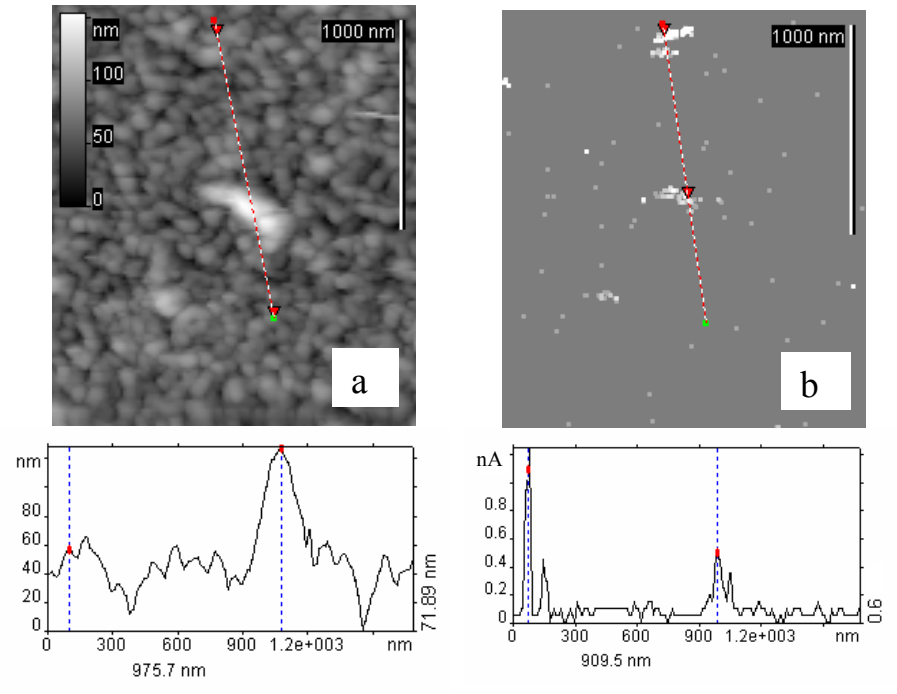

Fig. 1. Topography (a) and spreading resistance (b) images of the composite film PbPc-PTCDI.

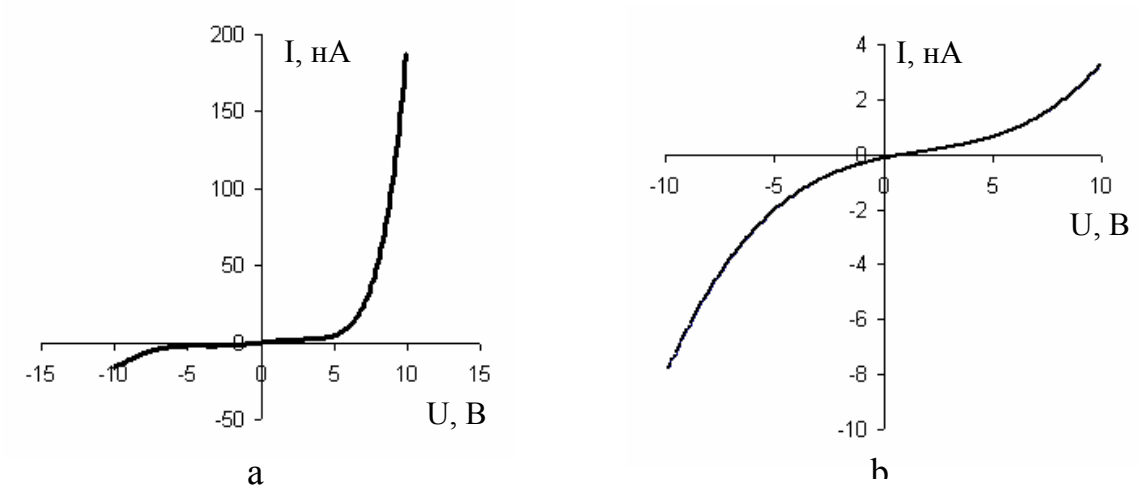

Fig. 2. Typical I-V curves of tip-to-cluster (a) and tip-to-grain film (b) contacts.

PbPc surface (in this case the current will decrease on its) but reach the metal substrate and have electrical contact to it.

The SSRM technique allows the local I-V curves to be measured in different points of the film. The fig.2 represents I–V curves of tip-to-cluster (a) and tip-to-grains (b) contacts. The rectifying behavior of I-V curves are different for clusters and grain film and agree with theoretical concept of electronic properties of contacts of metal-n-type (PTCDI clusters) and p-type (grain film) semiconductor.

Therefore, local I-V curves of tip-to-surface contacts additionally to mapping of contact currents can be used for identifying the nature of material on surface.

Early we found [5] that the photo-STM technique allows the local photoconductivity of phthalocyanine and its spectral dependence to be mapped with high resolution. In present study the aim is to demonstrate possibility of this technique for identification of material in composite films. The used He-Ne laser light is significantly absorbed by PbPc and not

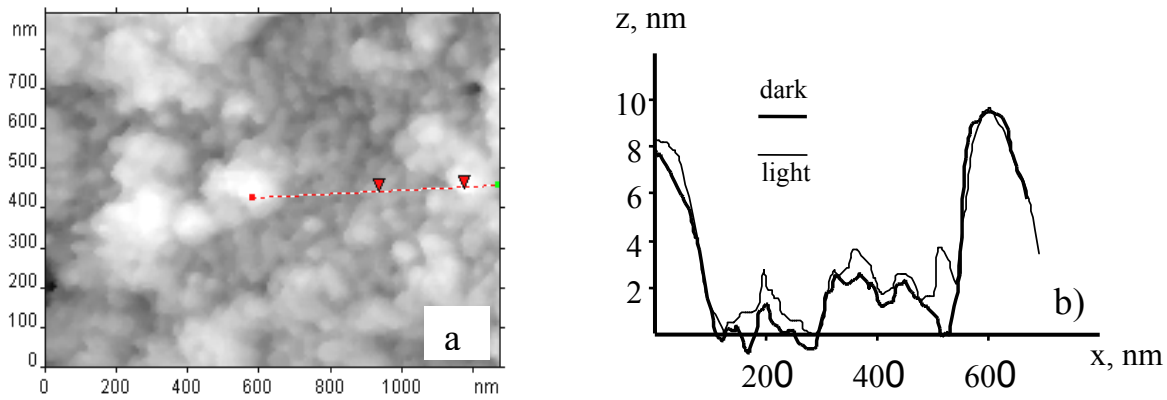

Fig. 3. a) – dark STM image of surface of the composite film PbPc-PTCDI, b) – profiles of the same area of dark and light STM images.

absorbed by PTCDI material. Most reproducible STM-images were obtained for the composite films of 20 nm in thickness.

Typical STM-image is shown on fig. 3a. The film surface contains large areas of clusters and areas of grain morphology like films of 100 nm in thickness. To explore influence of light on tunneling we acquire dark and light STM-images of the same area of film. Light was switch-on in 10-15 min after obtaining of the dark image to minimize photothermal transients in tip. Fig. 3b represents the surface profiles traced through the same area of typical dark (fig. 3a) and light STM-images. It should be noted that light images appear the same as dark ones, and distinction are visible only if height information to be analyzed. As seen height difference between cluster and grain film is decreased with light switch-on. This phenomena is reversible.

If grain film is a PbPc that absorb He-Ne laser light, its resistance decreases due to photoconductivity, overall tunneling current increases in connection with influence of local resistance on tunneling [7], and piezoscanner move tip away from surface to maintain constant tunneling current. If clusters is a PTCDI material that not absorb light, the STM tip go over clusters by the same way as in dark. Therefore height difference between clusters and grain film decreases. And conversely, if grain film is PTCDI material and clusters are PbPc, the height difference will be increase. Thus, grain film consists from PbPc, while clusters are PTCDI material. This agree with measurements of spreading resistance of the composite films of 100 nm in thickness.

Therefore, possibilities of different SPM techniques for local chemical analysis are demonstrated on example of the PbPc-PTCDI composite films. Most reliable results give mapping of spreading resistance, measurements of local I-V curves of contact tip-to-surface and photo-STM techniques.

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