PHOTOASSISTED STM OF PHOTOCONDUCTIVE ORGANIC THIN FILMS

A. E. Pochtenny[1], P. Karageorgiev[2], A. N. Lappo[1]

[1]Belarussian State University of Technology, Minsk, Belarus
[2]Institute of Physics, University of Potsdam, Potsdam, Germany

The films of phthalocyanine and perylene derivatives found an application for solar cells [1,2], light-emitting diodes [2], gas sensors [3]. The improving of such devices can be reached by forming of nanocomposites [4,5]. The determination of correlation between the structure and electrical properties of nanocomposites requires the experimental methods of phase analysis on a nanometer scale.

Photoassisted scanning tunneling microscopy (photoSTM) combines the high spatial resolution of STM with energy selectivity of optical spectroscopy and can be used in nanoscale phase analysis. However, many difficulties restrain the application of photoSTM technique in this area [6]. The main difficult is the heating due to light absorption. The heating causes thermal expansion of STM tip affecting the tunneling gap width. As we have showed in previous reports [7,8], the illumination of organic semiconductors influences on the STM images and local current-voltage characteristics, but remain not clear the contribution of thermal expansion in these effects. We present in this report the photoSTM investigation results of N,N'-bismetyl-perylene-3,4,9,10-tetracarboxylic diimide (perylene pigment PTCDI) and copper phthalocyanine (CuPc) thin films.

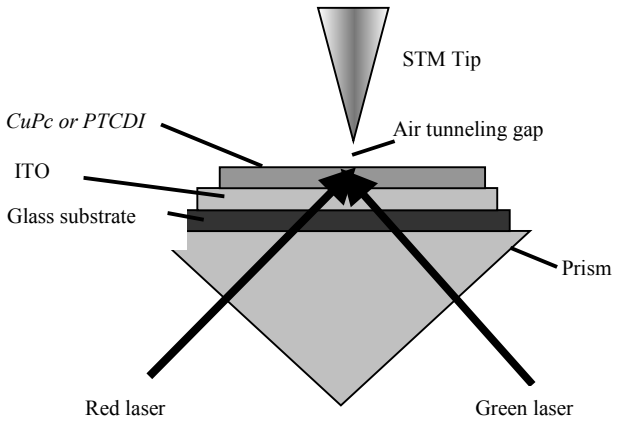

Fig. 1. Experimental setup of photoSTM

The PTCDI and CuPc films with 50 nm in thickness were thermal deposited in vacuum 10^{-2} Pa on the glass substrates with ITO covering at the room temperature. As we reported earlier [9,10], the both types of materials form the grain structured films with grain size in nanometer range. The visible optical absorption spectra were measured by spectrophotometer SPECORD M40 (Carl Zeiss Jena, Germany). The pho-

toSTM setup is shown in Fig. 1 and consists of the ellipsometer ("Multiscop", Optrel GbR, Germany) and the STM ("Explorer™", TopoMetrix Co., USA). The sample is placed on the glass prism and can be illuminated by He-Ne gas laser ("red laser") with wavelength 633 nm and/or by laser diode ("green laser") with wavelength 532 nm (fig. 1). The STM images under on/off light exposure were measured in air in constant current mode. The STM probes were prepared by cutting of Pt / Ir wire with 0.25 mm in diameter.

Fig. 2 shows the visible absorption spectra of PTCDI and CuPc. As the spectra indicates, CuPc absorbs the light with wavelength 633 nm and is practically transparent at the wavelength 532 nm. PTCDI on the contrary absorbs the light with wavelength 532 nm and not absorbs practically the light with wavelength 633 nm. PTCDI and CuPc are the photoconductive materials with photoconductivity spectra similar to absorption spectra. This fact causes the choice of laser wavelength for photoSTM measurements.

Fig. 3 presents the STM images of PTCDI and CuPc film surfaces obtained by switching on/off laser illumination during scanning. It is shown that the absorbed light causes formation of the steps on images, but unabsorbed light not forms such steps. Routine test of the ITO surface without organic films demonstrates the absence of step formation on the STM image at both operating wavelength.

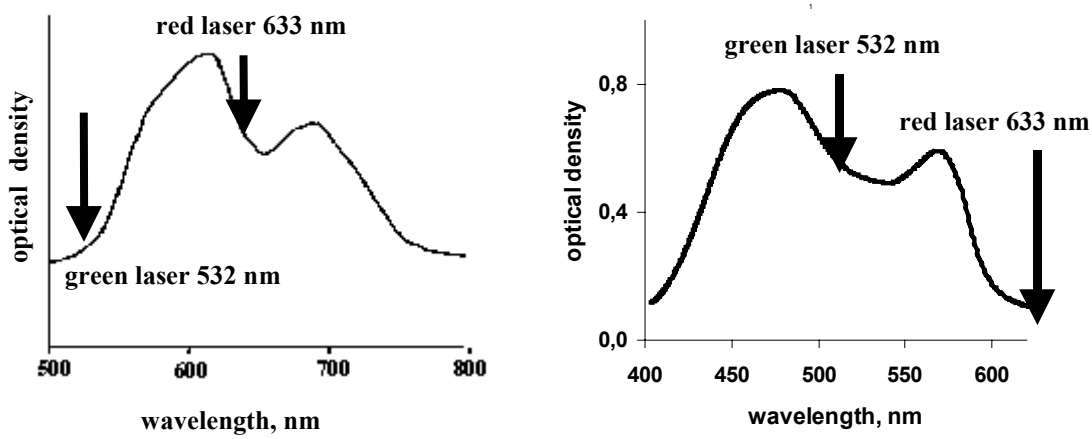

Fig. 2. Absorption spectra of CuPc (on the left) and PTCDI (on the right). The wavelength of red and green lasers is labeled by arrows

The selectivity of photoSTM images (fig. 3) to wavelength evidences of non-thermal nature of step formation because of the Pt/Ir tip absorbs light at both operating wavelength and should be thermal expanded by illumination of both red and green lasers. The same conclusion follows from absence of effect in ITO layer. Therefore, the step formation on the photoSTM images is providing by photoprocesses in PTCDI and CuPc films.

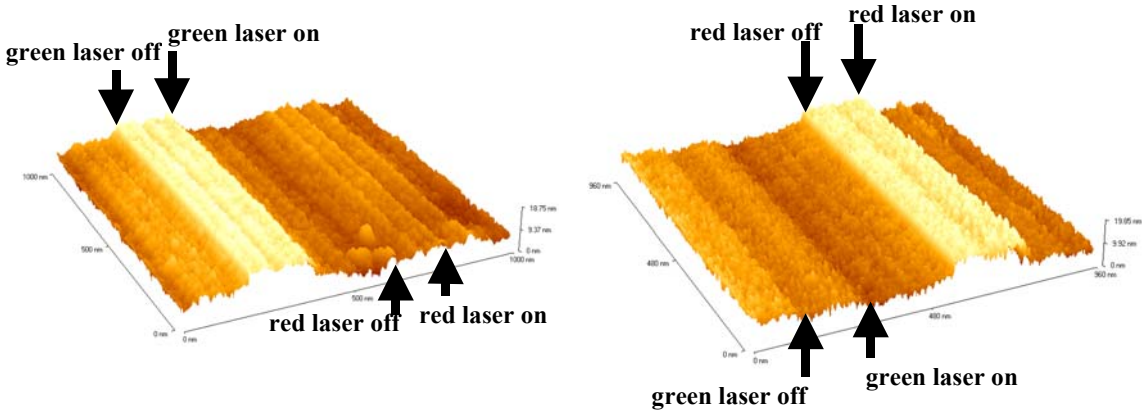

Fig. 3. PhotoSTM images of PTCDI (on the left) and CuPc (on the right) film surface. The illumination was switched on/off during the scanning at the moments labeled by arrows. The scan was obtained at I_t = 8 na, U = 2 V. Scan size is 1000×1000 nm^2

The step formation on photoSTM images can be explained, if take into account high electrical resistance and photoconductivity of PTCDI and CuPc films [8, 11]. The voltage, what defines by STM control circuit, is applied between the conductive ITO layer and STM tip. This voltage distributes between the investigated high-resistance film and tunneling gap, if the film resistance is commensurable to resistance of tunneling gap. The illumination of the film by absorbed wavelength causes the decreasing of film resistance due to photoconductivity effect. The current in film-gap structure increases, therefore, the STM feedback moves STM tip farther from the film surface. This shift of STM tip forms a step on STM image.

The effect of step formation on STM image can be quantitatively described. The voltage U_t on the tunneling gap in case of high-resistance sample is equal to

$$U_t = U - IR, \tag{1}$$

where U is the output voltage of STM control circuit, I is current in the investigated film, R is the electrical resistance of the film. The film and the tunneling gap is electrically connect in series, therefore, tunneling current I_t is equal to current in the film I. Then, the tunneling current in framework of most simple model of tunneling [12] is given by equation:

$$I_t = I_0 \exp\left\{-\frac{2d}{\hbar}\sqrt{2me[V_0 - (U - I_t R)]}\right\}, \tag{2}$$

where I_0 is the pre-exponential factor, d is the tunneling gap width, $\hbar$ is the Planck's constant, m is the electron mass, e is the electron charge, eV_0 is the tunneling barrier height (the mean value of film and tip workfunction in case of STM).

The tunneling gap width from Eq.2 is given by

$$d = \frac{\hbar \ln(I_0/I_t)}{2\sqrt{2meV_0\left[1 - \frac{U}{V_0} + \frac{I_t R}{V_0}\right]}}. \tag{3}$$

Therefore, the step height on the photoSTM image is equal to:

$$H = d_l - d_d = \frac{\hbar \ln(I_0/I_t)}{2\sqrt{2meV_0}} \left\{ \frac{1}{\sqrt{1 - \frac{U}{V_0} + \frac{I_t(R-\Delta R)}{V_0}}} - \frac{1}{\sqrt{1 - \frac{U}{V_0} + \frac{I_t R}{V_0}}} \right\}, \quad (4)$$

where d_l is the tunneling gap width at the scanning under illumination, d_d is the tunneling gap width at the scanning without illumination, ΔR is the change of film resistance as a result of illumination.

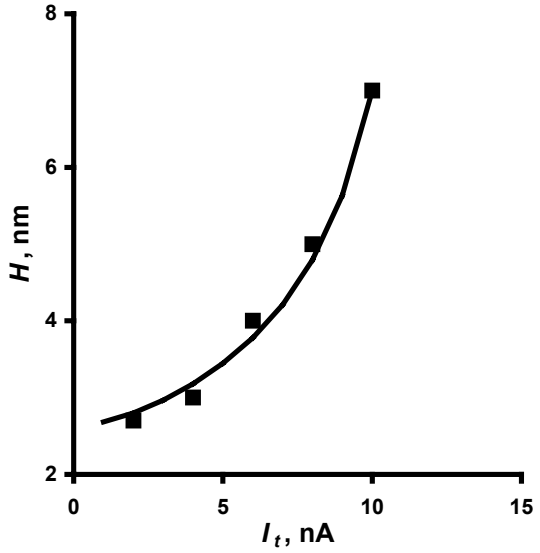

Fig. 4. Dependence of step height on the tunneling current for the photoSTM image of CuPc film surface. Points show the experimental data, full line is the calculation by Eq. 4

Fig. 4 shows that the calculation according to Eq. 4 is in agreement with experimental data for CuPc film. The numerical values of parameters for calculation are: I_0 = $0.82 \cdot 10^3$ A, eV_0 = 4.5 eV, R = 10 MΩ, ΔR = 51 MΩ, U = 4 V (output voltage of STM).

Thus, illumination influences selectivity on the STM images of PTCDI and CuPc film surfaces. Light with wavelength corresponded to absorption area of film material causes the step formation on the STM image. It is shown that these steps are providing by photoprocesses in investigated films but not by thermal expansion of STM tip or by photoprocesses in substrate. The effect is explained subject to high electrical resistance and photoconductivity of the films. It is proposed the simple theoretical model, which is confirmed by experimental step height dependence on the tunneling current. The selectivity of step formation to light wavelength allows using this effect for nanoscale phase analysis of composite films.

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