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Changes in the surface morphology of organic films under the action of laser radiation

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The results of an experimental study of the desorption of organic molecular fragments from perylene derivatives upon changes in film surface morphology under the influence of laser radiation are presented. A combined analysis of laser-stimulated desorption and atomic force microscopy data allowed us to establish patterns in the changes in the morphology and composition of the desorption flux from the film surface. The dependences of the film surface topography on the composition of the desorption mass spectra of organic molecular fragments and adsorption coating particles are obtained. It is shown that the spectral composition and desorption intensity of molecular fragments can be used to assess the surface morphology of organic films.

Keywords: organic films, surface morphology, mass spectra, fragment desorption, laser radiation.

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1. Introduction

Films of perylene derivatives 3,4,9,10-perylene-tetracarboxylic acid dianhydride (PTCDA) and N,N'-Bis(benzyl)-3,4,9,10-perylene-tetracarboxylic diimide ($PTCDI(C_7H_7)_2$) having n-type conductivity are widely used in various optoelectronics devices [1,2], which are often multi-layered structures applied sequentially [3]. At the same time, the quality of each subsequent applied layer, in particular, depends on the condition of the surface of the previous one. Modification of the surface properties of thin-film organic materials can be carried out by acting from the side of the substrate [4,5] or acting directly on the surface of the film itself with an ion beam [6] or more environmentally friendly laser radiation (LR) [7]. In any case, the study of the surface condition of the already applied layer is an important stage in the implementation of multilayer structures. The variety of existing direct and indirect methods for monitoring the condition of the morphology of the surface allows choosing the best option in each specific case. In particular, *in situ* it is convenient to study the morphology of the sample surface using a scanning electron microscope [8]. However, the authors of Ref. [8] used a chip to estimate the thickness of the sample. In the case of the implementation of the *ex situ* variant, atomic force microscopy (AFM) is the most popular method for studying surface morphology, which is often used to confirm the reliability of measurements made by other methods. A technique for optical estimation of the thickness of layered crystals α-In_2Se_3 using Raman spectroscopy is presented in Ref. [9]. In this case, the thickness estimates of the samples obtained from atomic force microscopy data were used as calibration. AFM measurements of the surface of $PTCDI(C_7H_7)_2$ films were performed in this study before and after each stage of laser pulse irradiation in order to compare the mass spectra of desorption stream particles.

We used LR in the field of film absorption to prepare the surface for the next coating. The process of irradiation of LR films is accompanied by desorption of particles from the surface [7]. In this case, it is relevant to identify the relationship between the spectral composition and intensity of the desorption flow components and the state of the film surface topography after laser irradiation. The solution to this problem made it possible to assess the condition of the surface during laser treatment to correct the film modification process.

2. Techniques used

Films of perylene derivatives, $PTCDI(C_7H_7)_2$, were formed under vacuum conditions 10^{-5} Pa from a Knudsen cell onto the surface of gallium arsenide (111), indium phosphide (100), and SiO_2 plates coated with metal film (Au, Ag). The morphology and thickness of the sprayed films were controlled by AFM methods using an NTEGRA-Aura NT MDT scanning probe microscope. NSG01/Au cantilevers with a needle radius of 6–10 nm without coating were used. As a result of calibration of the device, the lateral resolution was several nanometers, and the normal to the surface was 0.1 nm. The thickness of the obtained films was 80–120 nm.

The irradiation of the film surface was carried out by the radiation of the second harmonic of a neodymium laser LTPCH-7 with wavelength of $\lambda_2 = 532$ nm pulse duration 10^{-8} s. The first harmonic $\lambda_1 = 1064$ nm falls into the transparency region of films of perylene derivatives, but

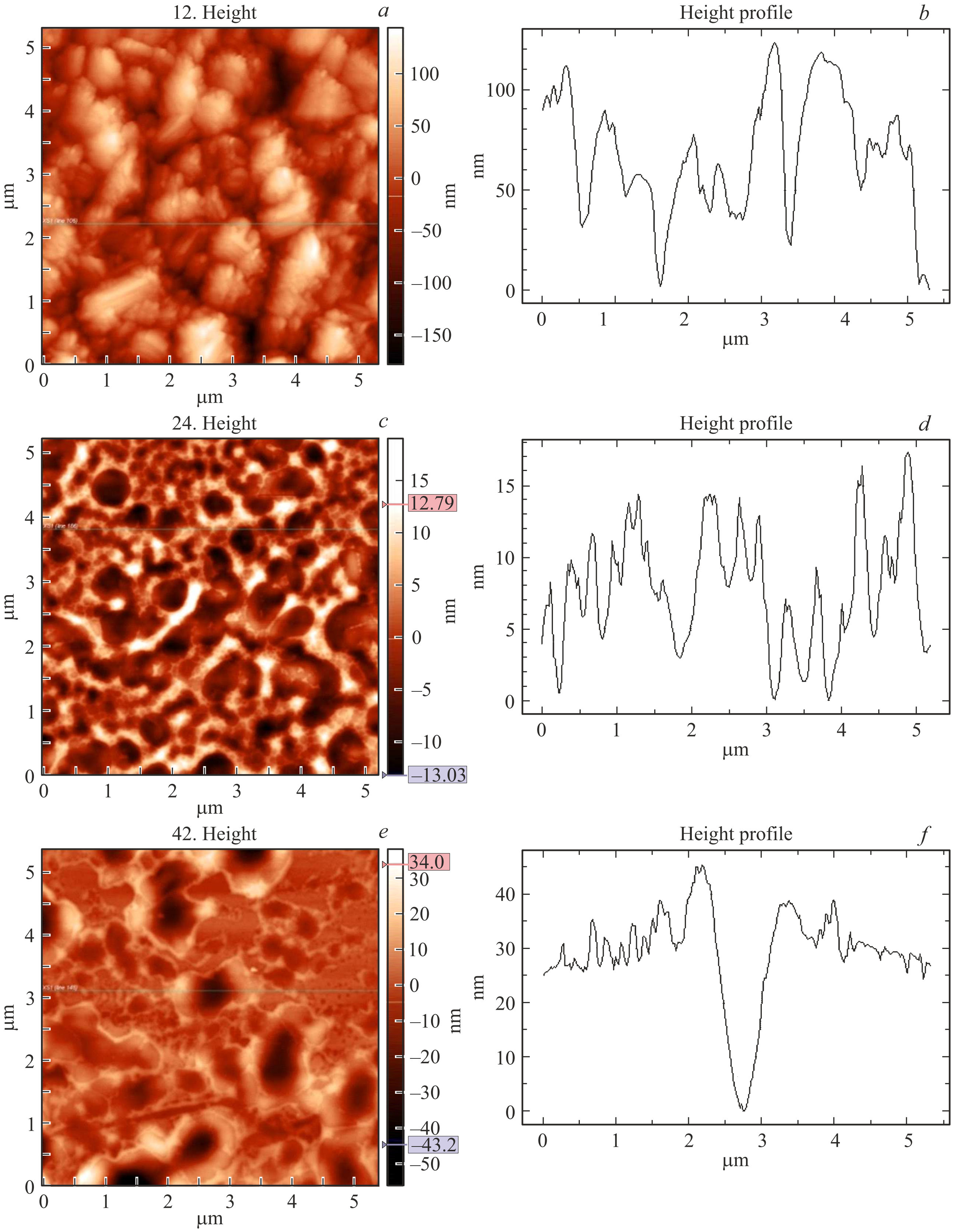

Figure 1. AFM image and surface profiles of film PTCDI $(C_7H_7)_2$: *a, b* — view of the original film; *c, d* — after surface modification by laser radiation; *e, f* — beginning of film destruction and the appearance of a whole (backbone) molecule in the mass spectra.

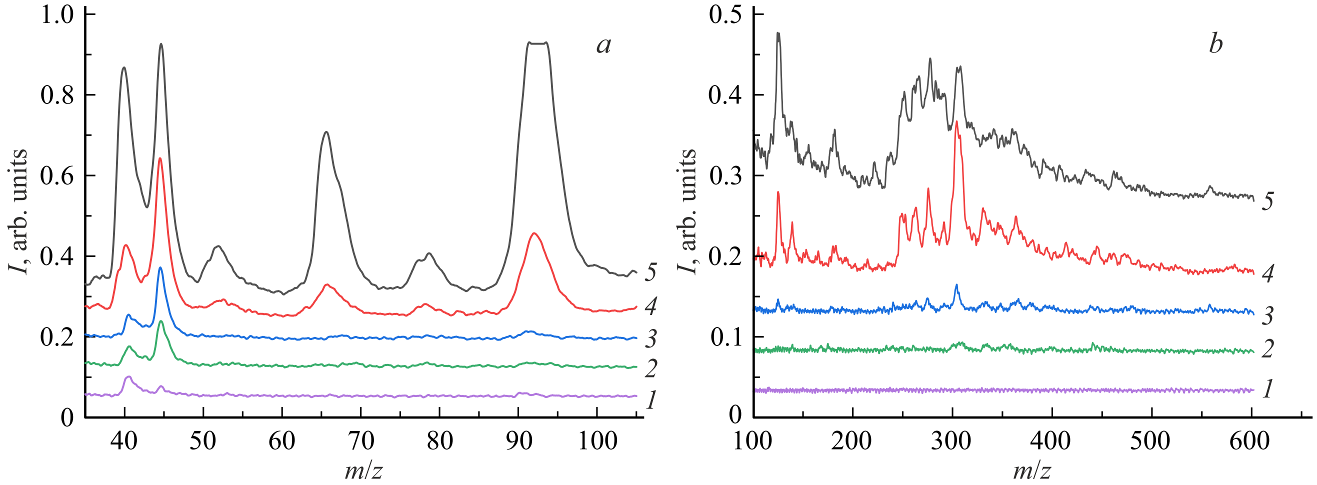

Figure 2. Mass spectra of light (a) and heavy (b) fragments of molecules desorbed from the surface of the PTCDI(C_7H_7)$_2$ film by laser radiation with wavelength $\lambda_2 = 532$ nm with increasing intensity LR (curve *1* — minimum intensity, curve *5* — maximum intensity).

into the absorption region of a part of the substrates used. The pulsed irradiation technique allows *in situ* to study desorption products at each stage of modification of the film surface [7].

3. Experimental results and discussion

The possibilities of laser-stimulated modification of organic films with mass spectral analysis of the accompanying desorption flow of particles from the surface are presented using the example of organic PTCDI(C_7H_7)$_2$ films with a thickness of 120 nm.

Figure 1, a shows an AFM image of the initial PTCDI(C_7H_7)$_2$ film, at the initial stage of the irradiation procedure. The unevenness of the non-irradiated surface reaches 100 nm in places and is comparable to the film thickness of 120 nm (Figure 1, b). At the initial stage of synthesis, islands are formed and then this structure develops. In this case, annealing must be carried out before applying the next layer. Irradiation in the transparency region ($\lambda_1 = 1064$ nm) leads to heating of the substrate and modification of the film occurs on the substrate side, and as practice has shown, there is an increase in the unevenness of the film surface. This option is used if it is necessary to increase the specific area of contact with the deposited film.

When the wavelength of the laser radiation changes ($\lambda_2 = 532$ nm), absorption is carried out by the film itself and the morphology of the surface of the irradiated part changes (Figure 1, c). As can be seen from Figure 1, d the surface profile became more even and amounted to 12 nm. In this case, the desorption stream consists of light (Figure 2, a, curves *2* and *3*) and heavy fragments (Figure 2, b, curves *2* and *3*) of organic molecules, shown for convenience in separate figures. According to the intensity of the peak $m/z = 44$ of the mass (CO_2), it is possible to evaluate the condition of the surface and select an option according to the desired type of AFM image and surface profile. A relatively weak peak of the perylene backbone of the $m/z = 248$ ($C_{20}H_4$) molecule with two CO molecules appears in the spectra of heavy masses (this is $m/z = 304$). The whole molecule $m/z = 570$ is not yet visible, but $m/z = 44$ has grown from the carbonyl part of the molecule (Figure 2, a, curve *3*).

The next increase in LR intensity leads to the appearance of fragments of the molecule $m/z = 91$ (C_7H_7)$_2$ and $m/z = 124$ ($C_{10}H_2$) (Figure 2, curves *4*). The rate of desorption $m/z = 304$ of masses and satellites $m/z = 248$, 276, 332, 360, and 479 increased significantly (Figure 2, b, curve *4*). All these fragments are molecules with different amounts of CO from the carbonyl part [10]. In the light mass spectrum, an increase in radiation intensity is manifested by a sharp increase in $m/z = 44$ and $m/z = 91$ masses at once (Figure 2, a, curve *4*). Individual sections expand and deepen on the surface, which is reflected in the AFM image (Figure 1, e). As can be seen from Figure 1, f the depth of individual dips reaches 40 nm. Apparently, the surface temperature under the influence of LR is not the same in the focal region or the thermal conductivity of the irradiation area is different. A further increase in the intensity of LR leads to a sharp increase in all the listed masses and the appearance of fragments of the backbone of the molecule and substituents. It should be noted that the surface temperature, according to our estimates, did not exceed 450 K, which is far from the temperature of stoichiometry violation [9]. The temperature was estimated by measuring the kinetic energy of the desorption flow particles according to the method proposed in Ref. [11].

A comparative analysis of topographic measurements of surface areas of PTCDI(C_7H_7)$_2$ films before and after exposure to radiation with a wavelength of $\lambda_1 = 532$ nm showed that starting from a certain threshold value of the power density, the film surface is leveled. This process is accompanied by the desorption of fragments of molecules, which are isolated from the general desorption stream for a more detailed study. When particles of the adsorption coating appear in the mass spectra, the film profile does not change. Significant changes occur with the appearance of fragments of molecules weighing 91, 124, and 304 in the spectra. The surface of the film is leveled and the profile unevenness becomes about 8 nm. A further increase in the irradiation intensity leads to the appearance of dips, which is reflected by the appearance in the mass spectra of fragments of C_7H_7 substituents and the backbone of the $C_{20}H_8$ molecule. This is the threshold for the destruction of the film, because then there is an intensive desorption of these and other fragments of molecules.

4. Conclusion

The surface morphology of vacuum-deposited films of $PTCDI(C_7H_7)_2$ perylene derivatives has been studied by AFM at various stages of laser-stimulated modification. At each stage, the composition of the desorption flow from the surface accompanying the laser pulse irradiation process was measured. The connection of the surface topography with the spectral composition of desorbed particles is established and it is shown that the composition and intensity of the fragments of molecules reflect the surface condition. Comparison of the mass spectra of the fragments with the AFM images made it possible to assess the state of the morphology of the film surface from the observed mass spectra of the fragments of molecules directly during the modification of the film surface.

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Conflict of interest

The authors declare that they have no conflict of interest.

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