

Changes in Adsorption and Optical Properties near the Phase Transition of Super Thin Vanadyl Phthalocyanine Langmuir Films

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Abstract—Structural transition in thin vanadyl–phthalocyanine films deposited by Langmuir technology was studied in detail with the help of the vacuum adsorption and optical spectroscopy techniques. The reversible structural transition observed only in super-thin Langmuir films is accompanied by nonreversible changes during heating. This transformation of the film having defects and amorphous regions occurs during the film transition from a metastable state to a more stable one that is characterized by a lower free energy.

Key words: Langmuir–Blodgett films, phthalocyanine, phase transition, adsorption, light adsorption spectrum.

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INTRODUCTION

The Langmuir–Blodgett films are a convenient modeling object for the study of low dimensional systems; they are also a promising material for the creation of structures for molecular electronics. Films for which a radical change in the properties of a phase transition occurs in a narrow temperature range are the most interesting. Currently, the ferroelectric [1] and magnetic [2] Langmuir films have been synthesized. In the previous publications using the examples of the semiconductor–metal [3, 4] and ferroelectric–paraelectric [5] phase transitions we demonstrated the close relationship between the adsorption–desorption properties of solids and the change in the symmetry of their crystal structure during phase transformation. Based on the performed cycle of research the method of detection of structural phase transitions, which consists in the study of the adsorption of molecules at various temperatures, was proposed. The passing of the temperature of the structural phase transition is accompanied by a sharp increase in the number of adsorbed molecules. However, the proposed method does not allow one to make any conclusion about the nature of the phase transition. To solve this problem we need to use additional methods. Therefore, in this work the problem was the detection of phase transitions in vanadyl–phthalocyanine films and the study of the optical properties of the Langmuir films near the phase transition temperature.

MEASUREMENT METHODS

In this work we used modified vanadyl–phthalocyanine films $\text{PcVO}(\text{R}_4)$, where $\text{R} = \text{SO}_2\text{NHC}_{18}\text{H}_{37}$. The $\text{PcVO}(\text{R}_4)$ films were obtained using Langmuir–Schaefer technology at room temperature by the removal of their monolayers from a water surface at a surface pressure of 5–12 mN/m and a pH of 6.0. This method allows one to obtain films of the X-type on one side of the substrate. As the substrates for the samples in the adsorption measurements, quartz resonators with a frequency of 5 MHz were used, on which films with thicknesses of 5, 10, and 15 monolayers were deposited. The measurement of the number of adsorbed molecules N_a was carried out by the method of “piezo-resonance quartz balance” [6]. The active area of the geometric surface of the Langmuir film on the resonator was $\sim 0.3 \text{ cm}^2$. The sensitivity of the method for the adsorption was 6×10^{12} molecules. The uncertainty in the N_a measurement was determined by the measurement accuracy of the adsorbate vapor pressure and was no more than 5%. The temperature of the samples was measured using a platinum resistance thermometer and maintained with an accuracy of $\pm 0.5 \text{ K}$. The sample was kept for a day in a vacuum $\sim 10^{-5} \text{ Pa}$ in order to obtain a standard surface of the film before the measurement of adsorption isotherms.

As in the previous work, the adsorbate consisted of water molecules. In [1, 5] we showed that the adsorption of most molecules on a Langmuir films leads to their swelling, i.e., during the process of adsorption the area of the free surface of adsorbents changes. There-

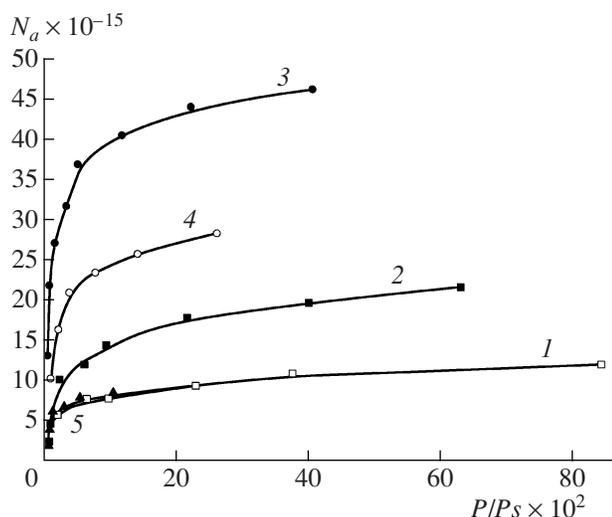


Fig. 1. The adsorption isotherms of water molecules on the film $\text{PcVO}(\text{R}_4)$. The temperature of measurements T , K: (1) 283; (2) 303; (3) 313; (4) 323; (5) 343. The thickness of the film is 5 monolayers.

fore, in the present work we did not normalize the number of adsorbed molecules on the area of the sample surface.

For the optical measurements we used $\text{PcVO}(\text{R}_4)$ films with a thickness of 5, 10, and 15 monolayers obtained under similar conditions on glass and quartz substrates. Absorption spectra were investigated on a Shimadzu UV-3600 UV-VIS spectrophotometer in air using a specially constructed thermal unit, which allowed us to set and control the temperature of the sample with an accuracy of ± 1 K.

RESULTS AND DISCUSSION

Let us consider the results of adsorption measurements. As an example, Fig. 1 shows the adsorption isotherms of water molecules on a $\text{PcVO}(\text{R}_4)$ film at several measurement temperatures. The values of N_a in the figure are given without taking surface roughness into account. The time necessary to establish the adsorption equilibrium, as in the case of other Langmuir films [1, 5], did not exceed 30 minutes for all pressures and temperatures used. The adsorption isotherms were fully reversible. Their shape was similar to the form of the isotherms that we observed in [1, 5]. As shown in Fig. 1, the adsorption increased quite abruptly (at the same value of p/p_s , where p is the pressure of the adsorbate vapors and p_s is the pressure of the saturated adsorbate vapors) with the increase of the measurement temperature up to $T = 313$ K and then decreased. Similar adsorption isotherms of H_2O molecules at different measurement temperatures were obtained for the films $\text{PcVO}(\text{R}_4)$ containing 10 and 15 monolayers.

Based on the data obtained from the adsorption measurements we plotted the dependence of the num-

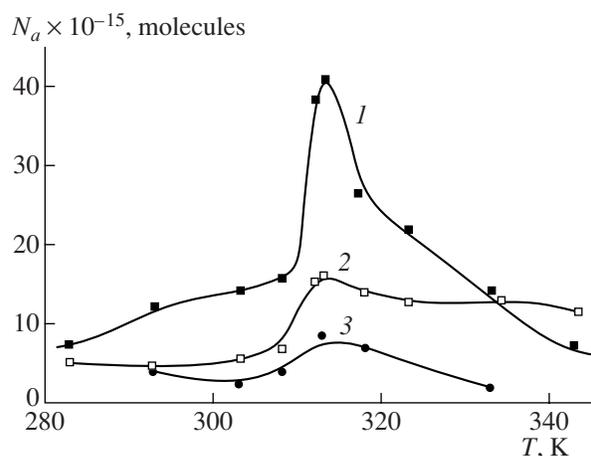


Fig. 2. The dependence of the number of adsorbed water molecules on a $\text{PcVO}(\text{R}_4)$ film with a thickness of 5 (1), 10 (2) and 15 (3) monolayers on the temperature. The relative water vapor pressure $p/p_s = 0.1$.

ber of adsorbed molecules H_2O on temperature for $\text{PcVO}(\text{R}_4)$ films containing different numbers of monolayers (Fig. 2). The pronounced maximum observed for all samples at a temperature of $T = 313$ K indicates the process of the structural phase transition at this temperature. Indeed, the increase in the number of adsorbed molecules with increasing temperature cannot be explained by assuming that the area of the sample at which the adsorption occurs remains constant. Gas pressure on the adsorbent can lead to structural changes in a film, especially in a film having capillaries [7]. In our case, these capillaries are significant gaps between the molecules of PcVO . Weak bonds between the molecules of molecular crystals can be destroyed under the adsorbate pressure. The capillaries will expand, resulting in increased space being available for the adsorbate molecules. The filling of micropores by the adsorbate molecules has a volumetric character [8]. Restructuring of the film at the phase transition facilitates the access of the adsorbate molecules to the adsorbent and leads to an increased adsorption capacity. After the completion of the structural phase transition in the film its adsorption capacity decreases.

Figure 2 shows that with increasing film thickness, the increase of its adsorption capacity at the temperature of the phase transition becomes less pronounced, i.e., with the increase of the number of layers of the Langmuir film the phase transition is suppressed. Such “surface” phase transitions were also observed by us in the Langmuir films of polymers [1]. The “surface” character of the detected phase transition is apparently related to the fact that in a film with a small number of layers the process of restructuring is easier to accomplish.

Let us consider the absorption spectra of the Langmuir $\text{PcVO}(\text{R}_4)$ films. In Fig. 3, for example, the spectra for samples with the thickness of 10 and 15 layers is

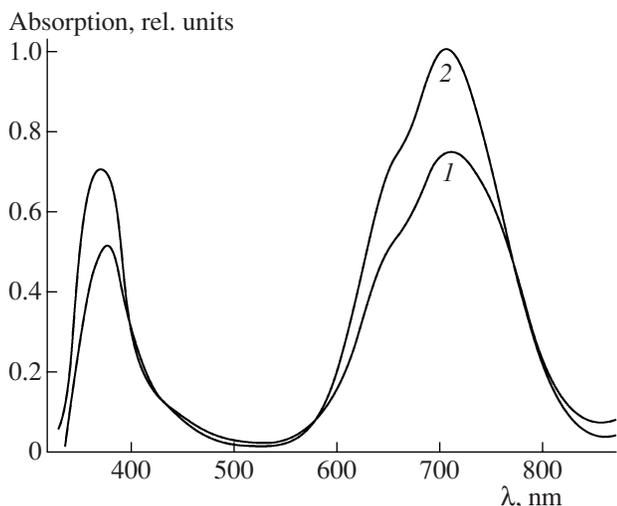


Fig. 3. The absorption spectra of PcVO(R_4) films with a thickness of 10 monolayers (1) and 15 monolayers (2) at $T = 296$ K.

shown. The absorption spectrum has two major peaks near $\lambda_1 = 370$ nm (“S-band”) and $\lambda_2 = 705$ nm (“Q-band”) (Fig. 3). These absorption bands are usually attributed to the electronic transitions between twice degenerate levels of the higher occupied (HOMO) and lower unoccupied (LUMO) molecular orbitals formed by the system of conjugated π -bonds of the central ring in the molecules of phthalocyanines. The position of these peaks is similar to that in data from the literature on PcVO films obtained by vapor deposition on the quartz substrate [9]. Our measurements for the films of different thickness showed that the amplitude of absorption was directly proportional to the thickness of the film.

The absorption peak with a maximum at the wavelength λ_2 has a complicated form (Fig. 3). Therefore, to determine the structure of this peak, an approximation of its shape in the range of wavelength 500–900 nm was performed using the sum of two Gaussian curves. As a result of this analysis it was found that the peak with the maximum at $\lambda_2 = 705$ nm consists of lines with the maxima at $\lambda_{21} = 651$ nm and $\lambda_{22} = 705$ nm. The appearance of a small amplitude absorption peak at λ_{21} was associated with vibron repetition of the long wavelength maximum λ_{22} in [10–12]. Note that with increasing film thickness a relative increase in the peak λ_{21} is observed (from 0.08 of the amplitude of the peak λ_{22} at the film thickness of 10 monolayers to 0.15 at the film thickness of 15 monolayers). The relative value of the λ_{21} peak of the Langmuir films PcVO(R_4) was somewhat lower than for the films deposited from the vapor [9]. This difference can be attributed to the greater regularity of the Langmuir films compared to the deposited ones.

Let us consider on the dependence of absorption spectra on temperature. The absorption spectra were measured in the temperature range 290–340 K, i.e., at

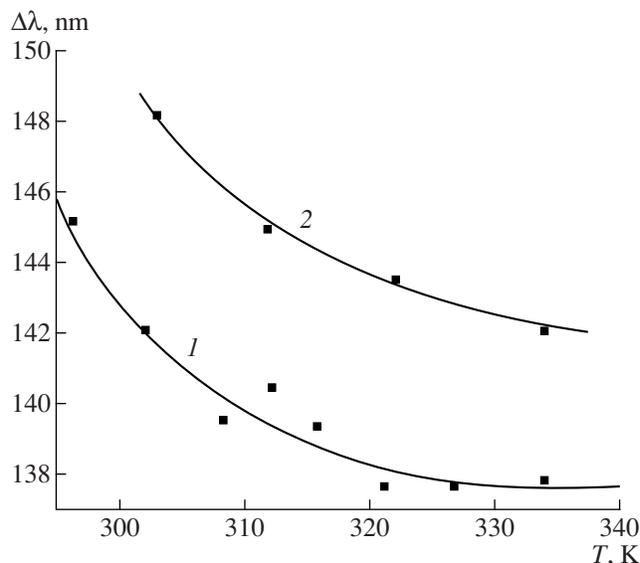


Fig. 4. The temperature dependence of the half-width of the spectral absorption line ($\lambda_{22} = 705$ nm) for a PcVO(R_4) film with a thickness of 10 monolayers (1) and 15 monolayers (2).

temperatures both above and below the detected structural phase transition ($T = 313$ K). In this temperature range the line with the absorption maximum at $\lambda_1 = 370$ nm remained unchanged, and the half-width of the line $\lambda_2 = 705$ nm decreased by about 10%. This narrowing of the spectrum is determined by the most intense peak λ_{22} , while its vibron repetition λ_{21} does not change. The dependence of the half-width of the absorption line for the peak λ_{22} is presented in Fig. 4.

The results of the study of absorption spectra of films with different thickness are consistent with the data of adsorption measurements. The change of the absorption line has a “surface” character, i.e., the effect of the narrowing is reduced from 8.0 ± 0.4 nm for the films with 10 monolayers to 6.0 ± 0.4 nm for the 15 monolayer ones. Ultrathin films have a large number of defects and amorphous regions due to the existence of a transitional layer film-substrate. Therefore, in the ultrathin films with defects, the process of restructuring is easier to accomplish.

The effect of the narrowing of the absorption line at λ_{22} was partly irreversible. The reversible part of the effect is apparently related to a structural phase transition. Typically, the high temperature phase is more symmetric and, therefore, more ordered. However, the Langmuir films have a certain number of defects and amorphous regions. Under these conditions metastable structures inevitably arise in a film. Heating of the sample facilitates the transition of these structures to a more stable state characterized by lower energy. And the film in general is becoming more ordered, which is reflected in the irreversible narrowing of the absorption spectrum band after the “annealing” of defects.

CONCLUSION

Thus, in the present work an attempt was made to describe the “surface” phase transition we found in PcVO(R₄) films. The comparison of adsorption data and optical measurements showed that with an increase in temperature we are dealing with two simultaneously occurring processes: a reversible structural phase transition (observed only in ultrathin films) and irreversible changes in the defective areas induced by the heating of the sample. Such a transformation of the films having defects and amorphous regions occurs during the transition from the metastable state to a more stable one characterized by a lower value of free energy.

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