EFFECT OF OXYGEN ON THE PROPERTIES OF BARRIER STRUCTURES OF LEAD PHTHALOCYANINATE IN VARIOUS POLYMORPHOUS MODIFICATIONS

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The change of the short-circuit photocurrent ($I_{sc}$) during the adsorption of $O_2$ was investigated for barrier structures based on PbPc in various polymorphous modifications. The change in $I_{sc}$ is described by the proposed generalized equation of adsorption

$$I_{sc} = A p^{0.5}/(1 + b p^{0.5}),$$

where $p$ is the partial pressure of $O_2$, and $A$ and $b$ are constants. The displacement of the maximum on the frequency dependence of $I_{sc}$ after the introduction of donor gases into the $O_2$ is explained by the formation of a charge-transfer complex of the $\text{PbPc}^\delta-\cdots\text{D}^\delta+$ type.

Films of organic substances, such as phthalocyanines (Pc), are widely used for the manufacture of electrographic structures [1, 2] and have been used in the development of solar cells [1, 3], gas sensors [4], and nonlinear waveguides [5]. A characteristic feature of Pc is the presence of several polymorphous modifications (PM). The optical, photoelectric, and other properties of the various polymorphous modifications differ significantly [1-5].

The aim of the present work was to investigate the effect of polymorphism on the short-circuit photocurrent ($I_{sc}$) and the nature and magnitude of the change in $I_{sc}$ during the adsorption of the acceptor gas (oxygen) and its mixture with the donor gas (ethanol or ammonia vapors) in organic barrier structures based on lead phthalocyaninate (PbPc). The choice of PbPc as a subject for investigation was based on the fact, on the one hand, that it effectively forms donor--acceptor complexes with oxygen, which play an important role in the photogeneration of current carriers [1, 4], and on the other that it is capable of crystallizing in four polymorphous modifications, the content of which can be set by the temperature of the substrate $T_s$ in thermal deposition under vacuum.

The investigated samples were prepared in the form of sandwich structures with barrier upper and ohmic lower electrodes. The sandwich structures were prepared by successive thermal vacuum deposition of a semitransparent lower Au electrode, a film of PbPc with a thickness of 1000 nm at a specific $T_s$ (determined by the polymorphous modification), and a semitransparent upper Ni electrode.

The $I_{sc}$ value arising during excitation by the modulated light of various LEDs was recorded by means of a UNIPAN 237 selective nanovoltmeter. The signal from the output of this instrument was delivered to an ENDIM 621.02 recorder or through a B7E42 digital voltmeter to a computer. A G3-117 oscillator with automatic frequency sweep was used to obtain a modified signal and record the frequency dependence. With unmodulated illumination $I_{sc}$ was recorded directly by a B7E42 digital voltmeter linked to a computer.

According to [6, 7], at $T_s < 300$ K films of $\alpha$-PM are formed, while at $T_s > 430$ K films of the most stable triclinic PM are formed. There are no reliable data on the conditions for the production of films of the monoclinic PM by thermal vacuum deposition. They are produced by the sublimation of PbPc in an atmosphere of nitrogen at lower temperatures than the triclinic PM [1, 6]. The monoclinic PM can therefore be formed during thermal vacuum deposition at $T_s = 320-380$ K.

Our previous investigations [6] showed that the $I_{sc}$ value and its reversible change with the admission of oxygen is significantly larger with illumination of the upper barrier Ni electrode than with illumination of the ohmic lower Au electrode, particularly with illumination by strongly absorbed light. Therefore, only the results obtained during illumination of the upper Ni electrode with the strongly absorbed light of the red LED ($h\nu = 1.56$ eV) will be given below.
Fig. 1. Dependence of $I_{sc}$ on the frequency of the radiation from the red LED for the sandwich structure Au/PbPc/Ni in an atmosphere of oxygen (1), with the presence of 5 ml/liter of ethanol (2) or ammonia (3), and their ratio (2' and 3' respectively).

Fig. 2. Dependence of the $I_{sc2}/I_{sc1}$ ratio at oxygen partial pressures $p = 2 \times 10^4$ and 20 Pa on the modulation frequency of the radiation of the red LED during illumination of the Ni electrode of the barrier sandwich layer based on PbPc for the $\chi$ (1), monoclinic (2), and triclinic (3) polymorphous modifications.

The measured frequency dependence of $I_{sc}$ for all the sandwich layers has the form of an asymmetric curve with a maximum in the region of 500-600 Hz with a sharper drop in the region of higher frequencies (Fig. 1, curve 1). The form of the frequency dependence of $I_{sc}$ depends on the polymorphous modification and hardly depends at all on the partial pressure of oxygen $p$. Therefore, to analyze the effect of the polymorphous modification of the PbPc films on the sensitivity of $I_{sc}$ of the sandwich layer to oxygen the frequency dependence of the $I_{sc2}/I_{sc1}$ ratio, where $I_{sc1}$ is the value of $I_{sc}$ at oxygen partial pressure $p = 20$ Pa and $I_{sc2}$ is the value at $p = 2 \times 10^4$ Pa, was analyzed. The obtained relations for the sandwich layer of the $\chi$, monoclinic, and triclinic films ($T_s = 300, 350, \text{and} 440 \text{K}$ respectively) are shown in Fig. 2. It is seen that in the sandwich layer of the triclinic polymorphous modification increase of $p$ from 20 Pa to $2 \times 10^4$ Pa leads to a substantial increase of $I_{sc}$, while for the $\chi$ polymorphous modification on the other hand it leads to a slight decrease of $I_{sc}$. The sensitivity of $I_{sc}$ of the sandwich layers produced at 350 K (monoclinic PM) was appreciably lower than for the triclinic PM, while the frequency dependence of $I_{sc2}/I_{sc1}$ had a different form (Fig. 2, curve 2). Since changes of the same type are observed if an IR LED ($h\nu = 1.3 \text{ eV}$) is used, the sign of the change of $I_{sc}$ during the adsorption of oxygen does not depend on the energy of the exciting quanta for a given polymorphous modification.

The increase of $I_{sc}$ for the barrier structure during the adsorption of oxygen is due to an increase in the height of the potential barrier ($\gamma$) at the Ni/PbPc interface as a result of the transfer of holes into the volume and the localization of radical-anions $O_2^-$ on the surface [6]. The holes and $O_2^-$ are formed as a result of the dissociation of a charge-transfer complex under the influence of light according to the following scheme:

$$
PbPc^* + (PbPc^+ \cdots O_2^-) \rightarrow PbPc + (PbPc^+ \cdots O_2^-)^* \Rightarrow PbPc + O_2^+ + h^+, \quad (1)
$$

$$
PbPc + h\nu = PbPc^*, \quad (2)
$$

where PbPc* is an exciton; $(PbPc^+ \cdots O_2^-)$ is the charge-transfer complex; $h^+$ is a quasifree hole. The direct excitation of the charge-transfer complex by light was not considered on account of its low effectiveness during irradiation with the light of the red LED, since the absorption region of the charge-transfer complex lies in the region of lowest energies and the