PHOTODIELECTRIC EFFECT IN PHTHALOCYANINE

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PHOTODIELECTRIC EFFECT IN PHTHALOCYANINE

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Recently, work on the study of the photodielectric effect (p.d.e.) has been developed; this effect consists in the fact that, upon optical excitation of a substance, its complex resistance changes. Measurements carried out on inorganic semiconductors have made it possible to obtain very interesting information concerning electronic phenomena in a solid, in particular those connected with local states ([1–4]). It is believed that the p.d.e. can be used as one of the methods for detecting traps and studying their properties ([5]). In a number of cases, measurement of the p.d.e. can provide more information than the study of photoconductivity under direct current. Another advantage of this research method is that it belongs to the class of contactless methods, and measurement of the p.d.e. can be carried out on powdered objects.

Earlier, the p.d.e. in organic semiconductors was observed by I. A. Akimov and E. K. Putseiko ([6]). Experiments carried out by us also showed that some organic semiconductor compounds exhibit the p.d.e. In the present work, the results of an investigation of the p.d.e. in phthalocyanine–one of the most widely studied organic semiconductors ([7–10])–are presented.

Layers of phthalocyanine obtained by sublimation of the substance in vacuum onto a quartz plate, on which a semitransparent platinum electrode had first been deposited, were investigated. The second electrode was an aluminum layer deposited on the phthalocyanine. The layers were illuminated with focused white light from an incandescent lamp passing through a heat filter. The intensity of the incident energy, hereafter taken as 100%, was 1.2 mW/mm^2. The investigations were carried out in a vacuum of 10^{-5}–10^{-4} mm Hg at room temperature. For measurements of capacitance and the tangent of the dielectric-loss angle, an audio generator, a bridge for measuring small capacitances, a wideband amplifier, and an oscilloscope as a null indicator were used.

Upon illumination of the phthalocyanine layers, a considerable increase in the capacitance of the sample C was observed, reaching, at the illumination levels used, 25–30% of the dark value. With increasing frequency f of the alternating

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

field, the effect decreased, so that at high frequencies the limiting value of C in the light, independently of the illumination level, was the value of the dark capacitance. The nature of the frequency dependences of C in the dark and under illumination is presented in Fig. 1. We note that in the coordinates $\lg \Delta C$–$\lg f$ (ΔC is the increase in capacitance at a given illumination level), the experimental data lie on a straight line with slope 2. Figure 1 also shows the frequency dependence of the tangent of the dielectric-loss angle D, which, as is evident, follows the simple relation

$$D \sim 1/f.$$

The tested capacitor, obtained by successive deposition on the metal surface of a dielectric layer (in the present case, phthalocyanine) and a second metallic layer, is essentially a capacitance shunted by the dark or light resistance of phthalocyanine. Therefore, the equivalent circuit of the capacitor may be represented in the form of a parallel-connected capacitance C_p, determined by polarization of the substance due to bound charges, and conductance σ, the magnitude of which

which depends on the concentration of free carriers in it. The experimental results also support such an equivalent circuit. Indeed, C and D for such a circuit are determined by the expressions

$$C = \sigma^2/4\pi^2 f^2 C_p + C_p, \tag{1}$$

$$D = \sigma/2\pi f C_p, \tag{2}$$

and it is seen that the experimental dependences of the logarithms $\Delta C = C - C_p$ and D on $\lg f$ agree with the calculated ones.

Fig. 1. Dependence of the capacitance C (1-4) and of the tangent of the dielectric-loss angle D (5-7) on frequency. 1 –in the dark; 2, 5 –at an intensity of the incident light of 19%; 3, 6 –at 57%; 4, 7 –at 100%.

Fig. 2. Theoretical dependences of the capacitance on frequency for the adopted equivalent circuit: a –when illumination changes C_p; b –when illumination changes σ. An increase in the curve number corresponds to an increase in the intensity of the incident light.

Under illumination, both C_p and the conductivity may change. In the first case one speaks of a photoelectric dielectric effect (PDE) of the first kind. The character of the curves of the frequency dependence of the capacitance C for different intensities of the incident light is shown for it in Fig. 2a. For a PDE of the second kind, when the change in C and D upon illumination is associated exclusively with the photoconductivity of the substance, i.e., with a change in σ, this family of curves has a substantially different form (Fig. 2b). Since C_p in this case does not change, the curves $C(f)$ for different illumination values have one limiting value, equal to C_p. Thus, from the character of the frequency dependences of C, constructed for different values of the intensity of the incident light, one can distinguish PDEs of the first and second kinds.

Comparison of the results of measurements of the frequency characteristics for phthalocyanine layers (Fig. 1) with the theoretical dependences ((1), (2), and Fig. 2) shows that in the present case we are dealing with a PDE of the second kind. This made it possible for us to use the PDE method to study the electrical characteristics of the material, usually determined from direct-current measurements. The dependences of the PDE on the intensity of the incident light and on the field strength were found, and the specific dark conductivity of phthalocyanine was calculated.

Since for the adopted equivalent circuit D proves to be proportional to σ, then, for a PDE of the second kind, the dependence of the increment of D under illumination (ΔD_ϕ) on the intensity of the incident light must have the same character as the dependence of the photoconductivity $\Delta\sigma_\phi$, namely, it must be: $\Delta D_\phi \sim L^n$. As is seen from Fig. 3, the experimental results

fit the indicated dependence well; moreover, the slope of the straight lines in the frequency interval covered (0.35–10 kHz) does not depend on frequency. The value $n = 0.9$, which corresponds to the values of n usually observed for the lux-ampere dependence of the photoconductivity of phthalocyanine ([7]).

The results of measurements of the dependence of the capacitance and loss tangent on the voltage across the capacitor are shown in Fig. 4. Attention is drawn to the sharp increase of D for phthalocyanine in the dark, which follows the exponential law $D = D_0 \exp \alpha V$. Taking (2) into account, it may be assumed that at the field strengths used Ohm' s law is not obeyed and the increase in electrical conductivity occurs according to Poole' s law. Estimates of the layer thicknesses and of the field strength E showed that such a course of the dependence of D on V corresponds to $E > 10^4$ V/cm, which indeed lies outside the usually indicated ohmic region ([11]). It is of interest that for ΔD_ϕ a considerably weaker dependence on field strength is observed than for D in the dark. This indicates that the observed increase in dielectric losses and, consequently, in electrical conductivity is caused by an increase in the concentration of charge carriers ([12]).

Fig. 3. Dependence of ΔD_ϕ on the intensity of the incident light L at different frequencies:

Figure 3 and Figure 4 graphs

Figure 3: Figure 3 and Figure 4 graphs

1—0.35 kHz; 2—0.5; 3—1.5; 4—4; 5—7; 6—10 kHz

Fig. 4. Dependences of D in the dark (1), ΔD_ϕ (2, 3), and ΔC (4, 5) on voltage. Curves 2 and 4 are for an incident-light intensity of 25%, and 3 and 5 for 57%

The specific conductivity of phthalocyanine in the dark, determined from equation (2) with allowance for the geometry of the capacitor, is $10^{13}\ \Omega^{-1} \cdot \text{cm}^{-1}$, which agrees with literature data ([7], [13]).

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Note: Figure translations are in progress. See original paper for figures.