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THE INFLUENCE OF NEAR-SURFACE CHARGES ON THE LIGHT-INDUCED CHANGE IN THE CONTACT POTENTIAL DIFFERENCE OF SEMICONDUCTORS

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In papers (1) an original method was proposed for determining the ratio of the hole and electron conductivities excited by light in crystallophosphors; for this purpose it is necessary to measure the dependence of the photoconductivity and of the light-induced change in the contact potential difference Δ (c.p.d.)$_{\mathrm{sv}}$ on the intensity of the exciting light. Considering Δ (c.p.d.)$_{\mathrm{sv}}$ as the result of diffusion of electrons and holes nonuniformly generated by sufficiently intense and strongly absorbed light, the authors obtained a relation between the stationary value Δ (c.p.d.)$_{\mathrm{sv}} - \varphi_0$ and the photoconductivity σ_ϕ:

$$\varphi_0 = -\frac{kT}{e} Z \ln \sigma_\phi + \mathrm{const},$$

where $Z = (\sigma_{\mathrm{d}} - \sigma_{\mathrm{e}})/(\sigma_{\mathrm{d}} + \sigma_{\mathrm{e}})$; σ_{d} and σ_{e} are the hole and electron components of the photoconductivity. In practice, one plots the dependence of Δ (c.p.d.)$_{\mathrm{sv}}$, in units of kT/e, on the natural logarithm of the light intensity; the slope of the resulting straight line determines the quantity αZ, where α is the exponent in the dependence of the photoconductivity on illumination. Experimental verification of the method (1-3) on certain crystallophosphors revealed a very serious difficulty. Thus, at high light intensities, in some specimens there was observed the appearance of a slower component with a sign opposite to that of the principal component of Δ (c.p.d.)$_{\mathrm{sv}}$ (“antipolarization”). Several hypotheses were proposed concerning the nature of “antipolarization” ; however, they were not tested experimentally, and, all the more, they remained unaccounted for in the method under consideration.

In our preceding work (4) we experimentally confirmed another point of view concerning the nature of the condenser photo-emf and Δ (c.p.d.)$_{\mathrm{sv}}$, namely that two components are to be recognized in them. The first component is due to the diffusion of current carriers nonuniformly generated by light, and

Fig. 1

Figure 1: Fig. 1

the second to the drift of these carriers in the field of the near-surface charge. These data indicate the one-sided nature of the approach to Δ (c.p.d.)$_{\text{sv}}$ in ([1]), since, in deriving the working formulas of the method, the initial field in the semiconductor was set equal to zero, whereas it may be not only an external field but also the field of the near-surface charge; thus the cause of the appearance of the drift term in Δ (c.p.d.)$_{\text{sv}}$ was eliminated.

The present work is devoted to clarifying the influence of near-surface charges on the formation of Δ (c.p.d.)$_{\text{sv}}$, and also to seeking ways of eliminating this influence. Measurements of Δ (c.p.d.)$_{\text{sv}}$ were carried out on the apparatus described in ([5]); the photoconductivity was measured under constant illumination with an EMU-4 direct-current amplifier. The objects of the investigation were the semiconductors ZnS, CdS, TlJ, and Se, polycrystalline preparations of which, made in the form of a paste in alcohol,

were applied to the fixed electrode of the dynamic capacitor and dried. Some samples were obtained by sublimation in a vacuum of 10^{-5} torr. The magnitude and sign of the near-surface charge were varied by means of continuous illumination with monochromatic light or by adsorption of gases.

It was established that near-surface charges alter the spectral distribution of Δ (c.p.d.)$_{\text{light}}$, and, owing to the presence of a shift of the drift-component spectrum relative to the diffusion-component spectrum toward longer wavelengths, these changes are more significant in the region of the semiconductor absorption edge.

Fig. 1. Kinetics of the rise and decay of Δ (c.p.d.)$_{\text{light}}$ for CdS annealed in air at 500°, as a function of oxygen pressure in different regions of spectral sensitivity, and also in the full light of an SVD-120 mercury lamp.
1 –760 torr; 2 –1 torr; 3 –10^{-2} torr

In the region of the absorption fall-off of the semiconductor. In the depth of fundamental absorption, the diffusion term predominates in Δ (c.p.d.)$_{\text{light}}$, while the drift term can change the magnitude, but not the sign, of Δ (c.p.d.)$_{\text{light}}$. This assertion, based on our numerous experiments, explains the correctness of determining the type of photoconductivity from the sign of Δ (c.p.d.)$_{\text{light}}$ and of the condenser photo-emf in this spectral region by many authors. The long-wavelength boundary of Δ (c.p.d.)$_{\text{light}}$ is not a characteristic quantity, since it depends substantially on the presence, magnitude, and sign of the near-surface field. On the long-wavelength absorption edge, when the near-surface charge is sufficiently large, the drift term begins to play the principal role in Δ (c.p.d.)$_{\text{light}}$, which makes it possible to apply the dynamic-capacitor method to the study of surface phenomena. Thus, when the sign of the near-surface charge is opposite to the sign of the predominant light-generated current carriers, i.e., when the drift and diffusion components have different signs, Δ $(\text{c.p.d.})_{\text{light}}$ can change sign on going from the region of fundamental absorption to the region of weak absorption (the "sign-reversal" phenomenon). If the signs of both components are the same, then in the spectrum of Δ $(\text{c.p.d.})_{\text{light}}$ a noticeable "tail"is observed on the long-wavelength side, due to the drift term.

A change in the spectral distribution of Δ $(\text{c.p.d.})_{\text{light}}$ caused by a near-surface charge for an organic semiconductor—the dye auramine O—has already been reported in work (4). An analogous phenomenon is also observed on polycrystalline CdS samples, preliminarily annealed in air to 500°. In high vacuum, a clearly expressed "sign reversal" is observed in the spectrum of Δ $(\text{c.p.d.})_{\text{light}}$, indicating the presence of a positive near-surface charge on the illuminated surface of CdS. Unannealed samples do not exhibit a "sign reversal" in vacuum. The positive near-surface charge in vacuum is apparently associated with sulfur defects that arise during annealing (analogously to ZnS (6)). With increasing oxygen pressure, the long-wavelength maximum decreases and then disappears altogether. This indicates the disap-

bringing the positive near-surface charge to zero or even forming a negative near-surface charge, which is possibly associated with adsorption on the CdS surface of negative oxygen ions.

Table 1

Semiconductor	Curve number in Figs. 2 and 3	$(\alpha Z)_{\text{meas}}$	α	Semiconductor	Curve number in Figs. 2 and 3	$(\alpha Z)_{\text{meas}}$	α
TlJ	1	0.63	0.68	CdS	7	0.56–1.1	0.7
ZnS—Cu	2	1.04	1.0	CdS	8	0.61	0.7
CdS	3	0.7—0.3	0.69	CdS	9	0.03	–
Se	4	0.62	1.0	CdS	10	0.32	–
TlJ	5	0.6—1.25	0.7	CdS	11	0.24	–
TlJ	6	0.68	0.7				

It was further found that the drift term has slower kinetics of establishment and disappearance of Δ $(\text{c.p.d.})_{\text{sv}}$ than the diffusion term. In Fig. 1 the kinetic curves are compared for a polycrystalline CdS layer annealed to 500°, with various near-surface charges. It is interesting that the character of the kinetic curves for $\lambda = 578$ mμ

Fig. 2. Dependence of Δ $(\text{c.p.d.})_{\text{sv}}$ on the intensity of the exciting light. 1—TlJ (sample No. 1), $\lambda = 430$ mμ; 2—ZnS—Cu, $\lambda = 313$ mμ; 3—CdS, $\lambda = 365$ mμ;

Fig. 2. Dependence of Δ (c.p.d.)$_{\text{sv}}$ on the intensity of the exciting light.

Figure 2: Fig. 2. Dependence of Δ (c.p.d.)$_{\text{sv}}$ on the intensity of the exciting light.

Fig. 3

Figure 3: Fig. 3

4—Se, $\lambda = 580$ mμ; 5 and 6—TlJ (sample No. 2, sublimated), $\lambda = 430$ mμ; 7 and 8—TlJ (sample No. 3, sublimated), $\lambda = 430$ mμ. Curves $1, 2, 5, 6, 7, 8$ were measured in vacuum, 10^{-2} torr; curves 3 and 4, in air.

(mainly drift) is the same regardless of the sign of Δ (c.p.d.)$_{\text{sv}}$ and differs sharply from the character of the kinetic curves for $\lambda = 313$ mμ (mainly diffusion). In the spectral region where both components are present in appreciable amounts, and all the more so when the samples are excited by unresolved light, the relaxation of Δ (c.p.d.)$_{\text{sv}}$ is of considerable complexity.

It was further established that the presence of a drift term affects the form of the dependence of Δ (c.p.d.)$_{\text{sv}}$ on the intensity of the exciting light. In this case three experimental situations may arise: a) the near-surface field is absent, and Δ (c.p.d.)$_{\text{sv}}$ is determined only by the diffusion term; b) the sign of the near-surface charge is opposite to the sign of the majority carriers of the photocurrent, and the drift term is subtracted from the diffusion term; c) the sign of the near-surface charge coincides with the sign of the majority carriers of the photocurrent, and the two terms are added. For situation a), a logarithmic dependence of Δ (c.p.d.)$_{\text{sv}}$ on the illumination is characteristic. Possibly curves $1, 2, 4, 6, 8$ of Fig. 2 belong to this case-

I note. In situation b) the drift term can reduce the experimentally measured values $(aZ)_{\text{meas}}$ down to zero (curve 3 in Fig. 2, curves 9 and 11 in Fig. 3, Table 1). Conversely, in situation c) the drift term increases $(aZ)_{\text{meas}}$, making them even larger than unity* (curves 5 and 7 in Fig. 2). From what has been said it follows that the ratios of the electron and hole components of the photoconductivity of some phosphor crystals, determined in $(1, 2)$, may differ substantially from the true values, since there is no certainty that they are not distorted by the near-surface field. It has been established that "antipolarization" is a particular case of the drift term in situation b).

Fig. 3. Dependence of Δ (c.p.d.)$_{\text{sv}}$ on the intensity of the exciting light for CdS annealed in air at 500°, $\lambda = 450$ mμ, vacuum 10^{-5} torr

Two ways are emerging for eliminating the drift component from Δ (c.p.d.)$_{\text{sv}}$, so that the method (1) may be applied to the remaining diffusion component. The first way is based on the difference in the relaxation times of the two components (see Fig. 1), and the second on the possibility of changing the near-surface charge by external factors (illumination, etc. (4)).

The case of a p-type semiconductor with a negative near-surface charge is represented by curves 5 and 7 in Fig. 2. In Δ (c.p.d.)$_{\text{sv}}$ for curve 5, both the fast components and the slow ones (5 min), mainly associated with the motion of photocurrent carriers in the near-surface field, are included. In Δ (c.p.d.)$_{\text{sv}}$ for curve 6, only the fast ($<$ 10 sec) components are included. Similar results can also be obtained by additional "red" illumination, which promotes the dissipation of the near-surface charge (4) (curves 7 and 8). In this case the dependence of the photocurrent on the illumination of the additional illumination does not change, and $a = 0.7$.

Another possible case—a negative near-surface charge on an n-type semiconductor—is presented in Fig. 3, on which the following quantities were measured: on curve 9, the stationary value of Δ (c.p.d.)$_{\text{sv}}$; on curve 11, the same with "red" illumination, $\lambda = 620$ mμ; on curve 10, the maximum overshoot of Δ (c.p.d.)$_{\text{sv}}$. The absence of growth of Δ (c.p.d.)$_{\text{sv}}$ on curve 9 testifies to the large magnitude of the near-surface charge, the influence of which could not be completely eliminated even by intense "red" illumination (curve 11). This is also indicated by the excessively small value of $(aZ)_{\text{meas}}$ in this case and by the form of the relaxation curves.

The method (1) must be checked for the case of absence of a near-surface charge; however, at present there is no criterion that would make it possible to reliably establish in which case the drift term in Δ (c.p.d.)$_{\text{sv}}$ can be neglected or whether it has been eliminated altogether.

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* According to (1), $aZ \leqslant 1.0$ when $a \leqslant 1.0$.