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V. I. Bugrienko, È. M. Denga

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Abstract

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V. I. BUGRIENKO, E. M. DENBGA

DEVIATIONS FROM THE ELECTROPHOTOGRAPHIC RECIPROCITY LAW ASSOCIATED WITH EFFECTIVE DRIFT MOBILITY

(Presented by Academician A. V. Shubnikov, February 9, 1968)

It is known ^(1,2) that the effective drift (e.d.) mobility of carriers μ_D in crystals in the presence of trapping is determined by the microscopic mobility μ_m and by the mean "lifetimes" of a carrier in the trapped state τ_g and in the corresponding allowed band τ_t :

$$\mu_D = \mu_m (1 + \tau_g/\tau_t)^{-1}. \quad (1)$$

Excitation of such crystals by light in their intrinsic absorption band leads to gradual filling of the trapping levels and to a monotonic change in the quantities τ_g and τ_t . For crystals with electron conductivity and with l trapping levels of different types, neglecting recombination, it can be shown that

$$\tau_g^{-1} = \sum_{i=1}^l \frac{m_i}{\sum_{i=1}^l m_i} \gamma_i N_{CM_i}; \quad \tau_t^{-1} = \sum_{i=1}^l \gamma_i M_i \left(1 - \frac{m_i}{M_i}\right); \quad (2)$$

here N_{CM_i} is the effective density of states in the conduction band, reduced to the i -th trapping level ⁽³⁾; $N_{CM_i} = N_C e^{-E_i/kT}$; γ_i is the electron-capture coefficient; m_i/M_i is the degree of filling by electrons of trapping centers of the i -th type; E_i is the thermal activation energy of these centers.

For $\tau_g/\tau_t \gg 1$

$$\mu_D \approx \mu_m \sum_{i=1}^l \frac{m_i}{\sum_{i=1}^l m_i} \gamma_i N_{CM_i} \bigg/ \sum_{i=1}^l \gamma_i (M_i - m_i). \quad (3)$$

Consequently, the e.d. mobility is determined by the concentration of carriers localized on trapping levels and therefore must depend on the intensity and duration of the action of the exciting light: $\mu_D = f(I, t)$. Only in the limiting case, when capture of carriers by trapping levels is negligible ($\tau_g \rightarrow 0$), does the e.d. mobility become a constant quantity $\mu_D = \mu_m$.

Thus, the theory of isopotential curves of the photoelectret state of high-resistance crystals developed in the works of V. M. Fridkin and E. I. Adirovich⁽⁴⁻⁶⁾ requires a natural generalization to the case $\mu_D = f(I, t)$. The kinetics of heterocharge formation in nonmetallic crystals with electron conductivity under the combined action of photoactive light, thermal generation, and an electric field⁽⁷⁾, taking into account the change in the e.d. mobility, must be written in the following form:

$$-\ln \left(1 - \frac{Q(t)}{Q_\infty} \right) = \frac{4\pi q}{\chi} \int_0^t n(t) \mu_D(t) dt. \quad (4)$$

Therefore, the problem of finding the form of the equipotential curves of photopolarization $-\ln(1 - Q(t)/Q_\infty) = \text{const}$ reduces to evaluating the integral in relation (4).

The simplest band scheme of an electronic semiconductor that makes it possible to take into account the change in the effective drift mobility during excitation is a two-local scheme. The kinetics of electronic processes for the initial stages of excitation, assuming weak filling of trapping levels, absence of recombination, and thermal activation of electrons into the conduction band from deep levels,

$$m_i \ll M_i; \quad \gamma_2 m_2 N_{CM_2} = 0 \quad (5)$$

is described by the system of equations

$$\begin{aligned} dn/dt &= \beta k I + \gamma_1 m_1 N_{CM_1} - n(\gamma_1 M_1 + \gamma_2 M_2); \\ dm_1/dt &= -\gamma_1 m_1 N_{CM_1} + n\gamma_1 M_1; \\ dm_2/dt &= n\gamma_2 M_2. \end{aligned} \quad (6)$$

Under the initial conditions $n(0) = n_0$; $m_1(0) = m_{10}$; $m_2(0) = m_{20}$, the system has the solution:

$$n(t) = n_\infty - \exp \left[-\frac{1}{2}(A + 2c)t \right] \left\{ \zeta \operatorname{ch} \frac{\lambda}{2} t - \frac{A\zeta - 2c\xi}{\lambda} \operatorname{sh} \frac{\lambda}{2} t \right\}; \quad (7)$$

$$m_1(t) = m_{1\infty} - \exp \left[-\frac{1}{2}(A + 2c)t \right] \left\{ \xi \operatorname{ch} \frac{\lambda}{2}t + \frac{A\xi + 2\gamma_1 M_1 \zeta}{\lambda} \operatorname{sh} \frac{\lambda}{2}t \right\}; \quad (8)$$

$$m_2(t) = m_{20} = \beta k I t - [m_1(t) - m_{10}] - [n(t) - n_0]. \quad (9)$$

Here

$$A = \gamma_1 M_1 + \gamma_2 M_2 - c; \quad c = \gamma_1 N_{CM_1}; \quad \lambda^2 = A^2 + 4c\gamma_1 M_1;$$

$$n_\infty = \frac{\beta k I}{\gamma_2 M_2}; \quad m_{1\infty} = \frac{\beta k I}{\gamma_2 M_2} \frac{\gamma_1 M_1}{c}; \quad \xi = m_{1\infty} - m_{10}; \quad \zeta = n_\infty - n_0. \quad (10)$$

Taking into account relations (3), (7)–(9), under the simplifying assumptions $n(t) \ll m_1(t)$; $n(t) \ll m_2(t)$; $m_{1\infty} \gg m_{10}$; $n_\infty \gg n_0$, we obtain

$$\frac{4\pi q}{\chi} \int_0^t n(t) \mu_D(t) dt = \frac{c\lambda_m}{(1+\varphi)\gamma_2 M_2} \int_0^t \frac{m_1(t)n(t)}{B + \beta k I t} dt.$$

The notations introduced are

$$\lambda_m = \frac{4\pi q}{\chi} \mu_m; \quad \varphi = \frac{\gamma_1 M_1}{\gamma_2 M_2}; \quad B = n_0 + m_{10} + m_{20}.$$

Finally, from (8) we obtain the following equation of the equipotential curve of the photopolarization process:

$$-\ln \left(1 - \frac{Q(t)}{Q_\infty} \right) = \text{const} = \frac{\lambda_m \varphi \beta k I}{(1+\varphi)(\gamma_2 M_2)^2} \left\{ \ln \left(1 + \frac{\beta k I t}{B} \right) - \sum_{k=1}^5 c_k \exp \left(m_k \frac{B}{\beta k I} \right) \left[\operatorname{Ei} \left(-m_k \frac{B}{\beta k I} \right) - \operatorname{Ei} \left[-m_{k+1} \frac{B}{\beta k I} \right] \right] \right\} \quad (11)$$

Here

$$\begin{aligned} -c_1 &= 1 + \frac{\gamma_1 M_1 + c}{\lambda}; & c_2 &= -1 + \frac{\gamma_1 M_1 + c}{\lambda}; \\ 2c_3 &= 1 - A \frac{\gamma_2 M_2}{\lambda^2} + \frac{c + \gamma_1 M_1}{\lambda}; & 2c_4 &= 1 - A \frac{\gamma_2 M_2}{\lambda^2} - \frac{c + \gamma_1 M_1}{\lambda}; \end{aligned}$$

$$c_5 = A \frac{\gamma_2 M_2}{\lambda^2}; \quad 2m_1 = m_3 = A + 2c - \lambda; \quad 2m_2 = m_4 = A + 2c + \lambda;$$

$$m_5 = A + 2c. \quad (12)$$

In the particular case of weak thermal activation of carriers localized on shallow trapping levels,

$$c \ll \gamma_1 M_1 \approx \gamma_2 M_2,$$

the equation of the isoopaque line is considerably simplified:

$$\ln \left(1 + \frac{\beta k I t}{B} \right) \approx \text{const} \frac{(1 + \varphi)(\gamma_2 M_2)^2}{\varphi \lambda_m \beta k I} + \frac{\beta k I}{B} \left\{ \frac{3\varphi + 2}{2c} + \left(1 + \frac{\beta k I t}{B} \right)^{-1} \left[\frac{\varphi}{2c} \exp \left(-\frac{2ct}{1 + \varphi} \right) - \frac{2\varphi + 1}{c} \exp \left(-\frac{2ct}{1 + \varphi} \right) \right] \right\} \quad (13)$$

In calculating (13), the following relation was used, valid for the asymptotic expansion of the integral exponential function (9):

$$\text{Ei} \left(-m_k \frac{B}{\beta k I} \right) - \text{Ei} \left[-m_k \frac{B}{\beta k I} \left(1 + \frac{\beta k I t}{B} \right) \right] \approx$$

$$\approx -\frac{\beta k I}{m_k B} \exp \left(-m_k \frac{B}{\beta k I} \right) \left[1 - \left(1 + \frac{\beta k I t}{B} \right)^{-1} \exp(-m_k t) \right].$$

Thus, for sufficiently weak intensities of the exciting light, the slope of the isopotential curves of photopolarization turns out to be negative. The physical meaning of the existence of a region $\partial(It)/\partial I < 0$ is that the creation of a heterocharge of a given magnitude proceeds more slowly under exposure to light of low intensity, since the effective mobility of the carriers in the crystal in this case proves to be smaller than under more intense illumination.

Fig. 1 Fig. 2

Fig. 1. Initial stages of charging curves of zinc sulfide photoelectrets. Intensity of the exciting light I (rel. units): 1–100; 2–48.8; 3–29.1; 4–15.1; 5–7.2; 6–2.91; 7–1.5. The dashed line shows the level of dark polarization of the crystal.

Fig. 2. Isopotential curves of the photopolarization process. Solid lines—calculated curves; points—experimental results. The designations of the calculated curves are given in Table 1.

The concepts developed above concerning the form of the isopotential curves of the heterocharge-formation process were tested on single crystals of hexagonal zinc sulfide doped with Ag and Al. The experimental procedure was analogous to that described in work (10), but the charging duration was reduced to 2 min, of which during the last t sec the sample was irradiated with ultraviolet light of various intensities. The charging curves and the corresponding isoopaque lines are shown in Figs. 1 and 2. The samples were insulated from the electrodes by thin films, and the presence in this case of a quasi-neutral region in the charged crystals made it possible to apply, in analyzing the charging curves, the theory of the heterocharge of photoelectrets due to É. I. Adirovich (7). The correspondence of the energy spectrum of electron trapping levels...

trons of the investigated crystals to the two-local band scheme considered above was ensured by special doping and, in addition, was confirmed by the spectral distribution of the photoelectret state, by the S-shaped character of the longitudinal photoconductivity, by the effect of redistribution of carriers over trapping levels ⁽¹⁰⁾, and by the complex kinetics of photodepolarization currents ⁽¹¹⁾.

Table 1

Isopotential curve	Charge magnitude $Q \cdot 10^9$, C/cm ²			
		const	D_1	D_2
I	3	0,1567	$4 \cdot 10^4$	4,5
II	2,5	0,1244	$4 \cdot 10^4$	3
III	1,75	0,0769	$4 \cdot 10^4$	1,6
IV	1,0	0,0305	$3 \cdot 10^4$	0,3
V	0,6	0,0075	$1,15 \cdot 10^4$	0,1

Since only the initial stages of the process of formation of the photoelectret state in previously unexcited crystals were investigated, the relation $\beta kIt/B \ll 1$ could be considered satisfied. The assumption ^(10,11) of multiple sticking of carriers at shallow trapping levels is equivalent to satisfaction of the relation $\varphi \gg 1$. These inequalities make it possible to simplify considerably equation (13) for the isopotential curve.

$$It = \text{const} \cdot D_1/I + D_2 I \zeta(t/D_2); \quad (14)$$

$$\zeta(t/D_2) = 3 + \exp(-t/D_2) - 4 \exp(-t/2D_2);$$

$$D_2 = \frac{\varphi}{2c}; \quad D_1 = \frac{B}{\lambda_m} \left(\frac{\gamma_2 M_2}{\beta k} \right)^2. \quad (15)$$

Table 1 gives, for the indicated charge-density values, the principal parameters of the isopotential curves calculated from formulas (14) and (15). For better agreement with the experimental results, the parameters D_1 and D_2 were selected separately for each curve. The noticeable difference in the values of the parameter D_2 for different isopotential curves is evidently explained by the fact that, in the reasoning given above, no account was taken of geometrical factors, which are significant under conditions of strong absorption of the exciting UV light ⁽⁶⁾, nor of the possibility of ionization of shallow trapping levels by the electric field.

Although the mechanism of deviations from the reciprocity law, based on taking into account the change in the effective drift mobility of the carriers, has been verified only for zinc sulfide photoelectrets, it may be assumed that it will also prove valid for other high-resistance materials widely used in electrophotography. The fact that the effective drift mobility changes during excitation of high-resistance semiconductors is certainly not limited to its influence on the shape of the isopakes of the photoelectret state; for example, with its aid it is possible to explain many processes of the complex kinetics of photoconductivity and the so-called fatigue phenomenon.

It is possible that taking into account the effective drift mobility of electrons will also make it possible to explain, from a single point of view, both branches of the isopake of the photographic process on silver halides, without resorting, in order to substantiate deviations from the reciprocity law in the regions of low and high intensities ⁽¹²⁾, to two different mechanisms.

Odessa Polytechnic Institute

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