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Study of Surface Recombination in Layers of Organic Dyes–Photoconductors

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It is known that photoconductivity in inorganic semiconductors, as a rule, is observed not over the entire spectral region of absorption, but only in a comparatively narrow region of its long-wavelength part, reaching a maximum at the beginning of the steep rise of the absorption curve ([1]).

In a paper by one of the authors ([2]) it was shown that, for thin layers of trypaflavine (an organic dye) obtained by deposition from solutions and having a comparatively narrow absorption band, the curve of the spectral distribution of photoconductivity depends on the layer thickness. Whereas for the thinnest layers ($\sim$ 20 mμ) a correlation was observed between the spectral curves of optical absorption and photoconductivity, for thick layers ($\sim$ 400 mμ) an anticorrelation occurred, which made it possible for the first time to observe a "maximum" of photoconductivity also on the short-wavelength side of the absorption band. The presence of such an anticorrelation was subsequently shown for layers of a number of other dyes: pinacyanol ([3]), phthalocyanines ([4]), indigo ([5]), and others. If the absorption band has several maxima, then the spectral curve of photosensitivity correspondingly has a complex form. The indicated decrease of the photocurrent may have various causes. One of them may be the light-filter action of the outer part of a thick layer. However, this action obviously plays an insignificant role, since the anticorrelation is observed both under front and rear illumination of the layer (transverse illumination). Another cause may be that, when strongly absorbed light falls on a photoconductor, absorption occurs mainly in a thin surface layer, where, as a result, a high concentration of free current carriers is created. For nonlinear photoconductors this leads to enhanced recombination of carriers, with which the observed phenomenon may be connected. However, a dip in photoconductivity in the region of the absorption maximum also occurs for linear photoconductors. De Vore showed that in this case the phenomenon can be explained if recombination of carriers at the surface of the photoconductor is taken into account ([6]).

Proceeding from the concepts that the decrease of current carriers created by light at a given place in the semiconductor occurs through diffusion into a region of lower concentration, as well as as a result of recombination in the bulk and at the surface, de Vore derived a general formula for the photocurrent arising in

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a semiconductor specimen of thickness l under illumination by monochromatic light transverse to the applied field, for which the absorption coefficient is equal to α:

$$P = \frac{1 - e^{-z}}{1 + \xi \operatorname{cth} \frac{\lambda}{2}} \left[1 + \frac{\xi\lambda \left[\lambda \operatorname{cth} \frac{\lambda}{2} - z \operatorname{cth} \frac{z}{2} \right]}{\lambda^2 - z^2} \right].$$

Here P is the photocurrent referred to a unit of incident energy; Z, ξ, and λ are dimensionless coefficients; $z = \alpha l$ characterizes the light absorption of the layer ($I_{\text{abs}} = I_{\text{inc}}(1 - e^{-z})$); $\lambda = l/(D\tau)^{1/2}$ characterizes the layer thickness, $\xi = S(\tau/D)^{1/2}$ is the ratio of surface recombination to bulk recombination; S is the veloc—

the surface recombination rate; D is the diffusion coefficient of the carriers in the semiconductor, and τ is their lifetime under illumination in the stationary state. De Vore' s formula may be regarded as an expression characterizing the change in photocurrent with a change in the thickness l of the sample for a fixed wavelength of the incident light (α = const). The argument l is contained in the right-hand side, entering into z and λ.

The aim of the present work was to make a quantitative estimate, on the basis of De Vore' s theory, of the surface recombination rate in linear photoconductors —organic dyes—and also to find other quantitative characteristics of photocarriers that determine the photoelectric properties of semiconductors, namely: the lifetime, diffusion coefficient, and mobility of photocarriers in organic semiconductors.

Fig. 1. Spectral curves of the photocurrent, referred to unit incident energy, and of the absorption of solid layers. 1—pinacyanol, 2—trypaflavine; a—P for a thin layer, $-P$ for a thick layer, —absorption spectrum.

For two organic dyes, trypaflavine and pinacyanol, which are linear photoconductors in vacuum ([2,3]), spectral dependences of the photoconductivity were measured under vacuum conditions for layers of different thickness obtained by deposition from solutions. The measurements were carried out on an apparatus described earlier ([5]). The thickness l of the investigated layers was determined from their optical density D_o; for this purpose, using a simple photoelectric photometer assembled by us, the intensity of monochromatic light that had passed through the interelectrode gap before deposition of the layer and the

Fig. 2 and Fig. 3: dependence of photocurrent on dye-layer thickness

Figure 2: Fig. 2 and Fig. 3: dependence of photocurrent on dye-layer thickness

intensity of the light transmitted by the layer were measured over the entire visible region of the spectrum in which the absorption bands of the dye layers are located. Previously, for layers of these dyes deposited on plane quartz plates, the thicknesses and optical densities had been determined independently, which made it possible for us to establish, for each dye, a quantitative relation between these quantities and thereby to determine the value of the absorption coefficient $\alpha = D_o/l \lg e$. The thinnest of the investigated layers had a thickness of 40 mμ for pinacyanol and 19 mμ for trypaflavine, while the thickest were, respectively, 322 and 253 mμ.

The spectral curves of the photocurrent, referred to unit incident energy, for these limiting layer thicknesses, as well as the spectral curves of optical absorption, are shown in Fig. 1. As is seen from the figure, for thin layers the shape of the photocurrent curve reproduces the absorption spectrum of the layer fairly well. For thick layers, however, in the region of the absorption maximum the curve of photoelectric sensitivity exhibits a dip. For layers of intermediate thickness we obtained curves occupying an intermediate position between curves a and .

The photocurrent referred to unit absorbed energy can be found from the formula $i = P/(1 - e^{-z})$. In Figs. 2 and 3 the dots represent the ex–

experimental values of i for pinacyanol and tripaflavin as a function of the dye-layer thickness for three wavelengths corresponding to the edge of the absorption band, its maximum, and a certain intermediate region. The theoretical dependence of i on l in these figures is shown by solid lines. In constructing these curves, to pass from l to z and λ, the experimentally determined values of α^* and the values of $D\tau$ found by fitting were used; these were equal to $1.3 \cdot 10^{-11}$ cm^2 (pinacyanol) and $6.1 \cdot 10^{-11}$ cm^2 (tripaflavin).

Fig. 2. Dependence of the photocurrent, calculated per unit absorbed energy, on the thickness of a pinacyanol layer for wavelengths: 1–720 mμ, 2–660 mμ, 3 –580 mμ

Fig. 3. Dependence of the photocurrent, calculated per unit absorbed energy, on the thickness of a tripaflavin layer for wavelengths: 1–566 mμ, 2–508 mμ, 3 –407 mμ

tripaflavin). The quantity ξ was also determined by fitting and was 5 and 1.3, respectively,** for pinacyanol and tripaflavin. As is seen from the figures, the experimental results and the theoretical curves with these values of the parameters $\xi = S(\tau/D)^{1/2}$ and $D\tau$ agree well with one another. However, it is not possible to determine from this S, D, and τ, since these three quantities enter de Boer's formula only in the form of two products. Therefore we determined the

lifetime by an independent experiment—the study of the photocurrent kinetics with the aid of a taumeter.***

Figure 4 shows oscillograms of the photocurrent in a linear horizontal sweep, obtained when the dye layers were illuminated by rectangular pulses of duration 0.018 sec. It is seen from the oscillograms that the observed photocurrents were sufficiently inertia-free. As shown by the investigation with exponential sweep, the build-up curves and, at the 50% level, the decay curves of the photocurrent are exponentials with times $\tau = 1.1 \cdot 10^{-4}$ sec for pinacyanol and $2 \cdot 10^{-4}$ sec for tripaflavin.**** Knowledge of the value of τ made it possible to determine D and S. Using Einstein' s equation $D = ukT/e$, we determined the mobility u. In this, T was taken to be equal to

* For the wavelengths we selected, the values of α are: for pinacyanol $2.88 \cdot 10^4$ (720 mμ), $1.09 \cdot 10^5$ (660 mμ), and $1.4 \cdot 10^5$ (580 mμ); for tripaflavin: $8 \cdot 10^3$ (566 mμ), $9.6 \cdot 10^4$ (508 mμ), and $2.0 \cdot 10^5$ cm^{-1} (470 mμ).

** We were forced to determine the quantities ξ and $D\tau$ by fitting, since the de Boer equation given above is not solvable with respect to ξ and λ.

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**** For pinacyanol, the presence of $\tau < 0.01$ sec was shown by Nelson (7). Before him, E. K. Pushcheiko, by the condenser method, showed for pinacyanol the appearance of a photo-e.m.f. under monochromatic illumination with frequency 150 cps (8). This testifies to a time of relaxation of the photoeffect substantially less than 0.007 sec. The presence of short times τ of the order of 10^{-3}-10^{-5} sec in organic dyes (phthalocyanines) was established with the aid of a taumeter in (9).

295° K, since the experiments were carried out at room temperature. All calculated quantities are collected in Table 1.

It is seen from this table that, for dyes, the values of the quantities S, D, and u are several orders of magnitude smaller than those usually observed in inorganic semiconductors. The small value of S is possibly connected with the fact

Table 1

Dye	ξ	$D\tau$, cm^2	τ, sec.	S, cm/sec	D, cm^2/sec	u, cm^2/V·sec
Pinacyanol	5	$1.3 \cdot 10^{-11}$	$1.1 \cdot 10^{-4}$	0.16	$1.2 \cdot 10^{-7}$	$4.8 \cdot 10^{-6}$
Trypaflavine	1.3	$6.1 \cdot 10^{-11}$	$2 \cdot 10^{-4}$	0.05	$3 \cdot 10^{-7}$	$1.2 \cdot 10^{-5}$

that the layers studied were obtained by rapid deposition from solutions and had a very smooth surface, characterized by specularly selective reflection. The

Fig. 4. Oscillograms of photocurrents: a—pinacyanol, b—trypaflavine

Figure 3: Fig. 4. Oscillograms of photocurrents: a—pinacyanol, b—trypaflavine

smallness of the quantity S should also explain the experimental fact that even for the thickest dye layers the drop in photocurrent in the region of the absorption maximum never reaches zero, as is usually the case in inorganic photoconductors. The specific conductivity of the layers of the dyes studied, even under intense illumination with a focused beam of light from a 100-watt incandescent lamp, remains small and amounts to 10^{-8}–10^{-10} $\Omega^{-1}\text{cm}^{-1}$. Meanwhile

Fig. 4. Oscillograms of photocurrents: *a*—pinacyanol, *b*—trypaflavine

the lifetime of nonequilibrium current carriers for dyes, as is seen from Table 1, has a value close to the value of τ for inorganic semiconductors, and the quantum yield of the photocurrent is apparently fairly high ([10]). Therefore the small absolute magnitude of the photoconductivity of dyes can be explained by the very low mobility of the carriers. Unfortunately, the literature contains no data on the mobility of carriers in dye layers with which we could compare the values obtained here. The few available estimates of mobilities in anthracene give a large scatter (10^2—10^{-4} cm^2 V^{-1} sec^{-1}) ([11]). The values of u obtained by us are close to the smallest value of the mobility for anthracene, obtained from the measurements of Northrop and Simpson ([11,12]). With the mobility values indicated in the table and lifetimes in the fields used by us, $\sim 10^4$ V/cm, the free path of a carrier in a dye layer is 500–2500 Å.

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