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Abstract

Full Text

Physics

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Negative Photodielectric Effect

(Presented by Academician A. A. Lebedev, 5 IV 1960)

1. Photodielectric effect in semiconductors. Gudden and Pohl were the first to observe a change in the dielectric properties of semiconductor materials under irradiation (^{1}), which subsequently received the name photodielectric effect (p.d.e.). At present the occurrence of the p.d.e. is associated with an increase in the concentration of localized or free charge carriers. Following Ryv (^{2}), the p.d.e. caused by localized carriers is called a p.d.e. of the first kind, in contrast to the p.d.e. of the second kind, caused by photoconductivity (free carriers). Despite numerous works devoted to the study of the steady-state dependences of the p.d.e. in crystallophosphors, the basic features of the phenomenon cannot be considered established, and, in particular, it is impossible to point to direct proof of the existence of a p.d.e. of the first kind, which is perhaps the only direct way of studying the properties of localized charge carriers that determine the course of photosemiconductor processes. In view of the above, we studied the steady-state and relaxation regularities of the p.d.e. in a typical photosemiconductor—cadmium selenide. At temperatures above room temperature and at frequencies not exceeding 200 kHz, the observed phenomena can be reduced to uncomplicated photoconductivity (^{3}). Upon deep cooling of the samples, regularities characteristic of a p.d.e. of the first kind were found, including the negative p.d.e. considered below—a decrease in active conductivity under optical excitation.

Fig. 1. Block diagram of the setup for separate measurement of increments of the components of the conductivity of a photodielectric capacitor. *Obr.*—sample, *F. V.*—phase shifter, *U*—amplifier, *F. D.*—phase discriminator, *ÉNO-1* —direct-current oscillograph.

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

2. Experimental arrangement and results. The samples studied were brass disks 30 mm in diameter, onto which a powder of activated cadmium selenide in OK-50 epoxy resin was deposited. The thickness of the active layer of the sample after polishing was about 0.2 mm. Glass plates coated with a transparent conducting layer of tin dioxide served as the upper electrode. The sample was placed in one arm of an alternating-current bridge; with an appropriate choice of the resistances of the bridge arms and diagonal, the signal produced by illumination was proportional to the increment in the conductivity of the sample. The block diagram of the measuring setup shown in Fig. 1 gives an idea of the method of separating the conductivity components. The setup made it possible to study the kinetics of the p.d.e. with a time resolution no worse than 10^{-3} sec. (at a frequency of 100 kHz).

When one component of the conductivity was isolated, the other was suppressed by no less than a factor of 30.

When the sample was cooled in the dark to the temperature of liquid air and subsequently excited with visible light (with a heat-absorbing filter), the active and reactive conductivities changed as shown in Fig. 2. Repeated excitations led to the appearance of relaxation processes illustrated in Fig. 3.

Fig. 2. Increment of the active (G_p) and capacitive (C_p) components of the conductivity of a photodielectric capacitor cooled in the dark (mixture of CdSe powder and OK-50 resin). Weight ratio of the mixture components $1:5$. I—excitation intensity, a—10 sec, b—3 sec. Light source—incandescent lamp, maximum illumination 5000 lux.

Fig. 3. Repeated increments of the active component of the conductivity of a photodielectric capacitor (mixture of CdSe powder and OK-50 resin). Weight ratio of the mixture components $1:5$. Excitation by rectangular pulses; fronts of the pulses are bounded by dotted lines. a—10 sec. Duration of fronts $\sim 10^{-3}$ sec. Light source—incandescent lamp behind a heat-absorbing filter. Maximum illumination 2000 lux. The duration of the dark pause preceding the excitation is indicated above the columns.

The stationary increment of the active conductivity became negative at $-40 \div -50^{\circ}$. The increment of the reactive conductivity was positive in all cases; the transient processes upon switching the light on and off developed monotonically. The most significant result of the experiments described should be regarded as the detected negative increment of the active conductivity of the cooled sample, which had not been observed in previously studied objects. An analogous effect was noted by us in some other semiconductors; it was not observed in zinc-sulfide phosphors. The facts listed indicate the regular character of the negative photodielectric effect and its connection with the semiconductor properties of the substances studied.

3. Discussion of the results. For a qualitative analysis of the results obtained, one may use the two-layer model of the sample shown in Fig. 4. Since in the frequency range under consideration the inequality

$$k = \omega \frac{C + C_0}{\Sigma} \gg 1,$$

where ω is the angular frequency, is certainly valid, the dispersion formulas for the conductivity components of the model considered are simplified and take the form

$$G_p = \frac{C_0^2}{(C + C_0)^2} \Sigma; \tag{1}$$

$$\omega C_p = \omega \frac{C C_0}{C + C_0} + \frac{C_0^2}{(C + C_0)^3} \frac{1}{\omega} \Sigma^2. \tag{2}$$

In the simplest case—when there is uncomplicated photoconductivity—excitation changes only Σ, which makes it possible to determine the photoconductivity characteristics from the p.d.e. data. If, along with photoconductivity, a first-order p.d.e. takes place, Σ and C will be functions of excitation, frequency, and temperature. Restricting ourselves to the linear approximation, the increment of the active component of the conductivity under optical excitation in the general case may be expressed as follows:

$$dG_p = \left[1 - \frac{2}{k} \frac{d(\omega C)}{d\Sigma} \right] G_p \frac{d\Sigma}{\Sigma}. \tag{3}$$

Assuming $C \approx C_0$, the condition under which dG_p becomes negative can be written

$$\frac{d\Sigma}{d(\omega C)} < \frac{2}{k} \cong \operatorname{tg} \delta = \frac{\Sigma}{\omega C}, \tag{4}$$

where $\operatorname{tg} \delta$ is the tangent of the loss angle.

The active conductivity may be represented as the sum of ohmic and relaxation (Debye) conductivities

Fig. 4. Equivalent circuit of a photodielectric capacitor used in the calculations. C and C_0 are the capacitances of the semiconductor and passive dielectric, respectively; Σ and Σ_{om} are the total and ohmic electrical conductivities of the semiconductor; Y is the complex conductivity of the equivalent circuit.

Figure 4: Fig. 4. Equivalent circuit of a photodielectric capacitor used in the calculations. C and C_0 are the capacitances of the semiconductor and passive dielectric, respectively; Σ and Σ_{om} are the total and ohmic electrical conductivities of the semiconductor; Y is the complex conductivity of the equivalent circuit.

$$\Sigma = \Sigma_{\text{om}} + \Sigma_{\text{deb}} = \Sigma_{\text{om}}(n_c) + \frac{C_s(n_t) - C_\infty}{1 + \omega^2\theta^2}\,\omega^2\theta, \tag{5}$$

where n_t and n_c are the concentrations of localized and free current carriers; Σ_{om} is the ohmic conductivity; C_s and C_∞ are the capacitances of the semiconductor at zero and very high frequencies; θ is the relaxation time of carriers at the localization levels under consideration. The capacitance of the semiconductor is expressed as

$$C = C_\infty + \frac{C_s(n_t) - C_\infty}{1 + \omega^2\theta^2}. \tag{6}$$

Fig. 4. Equivalent circuit of a photodielectric capacitor used in the calculations. C and C_0 are the capacitances of the semiconductor and passive dielectric, respectively; Σ and Σ_{om} are the total and ohmic electrical conductivities of the semiconductor; Y is the complex conductivity of the equivalent circuit.

The excitation functions here will be only n_t and n_c. Considering one localization level, inequality (4) may be represented in the form

$$\frac{d\Sigma_{\text{om}}}{d(\omega C_s)}(1 + \omega^2\theta^2) + \omega\theta < \operatorname{tg}\delta. \tag{7}$$

It is not difficult to see that for $k > 1$ the increment of the capacitive conductivity is always positive. At low temperatures, when the ohmic conductivity is small, the decrease in the active conductivity under optical excitation should be regarded as the result of the filling of shallow traps (small θ). The filling of deep traps (large θ) from this point of view should lead to an increase in the active conductivity. The unfreezing of traps and the appearance of carriers in the conduction band weakens inequality (7) and, ultimately, changes its sign. It is natural to assume that, upon excitation of cadmium selenide cooled in the dark, deep traps are filled first, which manifests itself in an increase in the active conductivity; the subsequent filling of shallow traps leads to a predominant growth of the capacitance and, consequently, to a decrease in the active conductivity of the sample. The appearance of a spike after the dark pause in Fig. 3 indicates that in the dark there is slow emptying of deep traps. The second spike upon switching off the light, increasing with the frequency and duration of the dark pause preceding the excita-

can be interpreted as the result of the emptying of shallow traps. Deeper levels are emptied more slowly, which leads to a predominance of the positive increment in the first phase of relaxation and to a slow decrease of this increment in the second. The origin of the small negative excursions preceding the transition to the stationary level of the active conductivity (Fig. 2), and of its growth when the light is switched off (Figs. 2 and 3), requires clarification. It may be assumed that they are connected with photoconductivity that appears only at high excitation levels or in the initial stages of relaxation.

It is easy to see that, under the assumptions made, an increase in frequency should lead to a decrease in the absolute value of the negative increment of the active conductivity and to its passage through zero. For the transition point in the absence of ohmic conductivity, the condition $\omega\theta = \operatorname{tg}\delta$ is valid. In the frequency range used by us, this transition was not observed, although a frequency decrease of the increment of the active conductivity was observed. The presence of shallow traps in cadmium selenide is confirmed by the work[4], whose authors established the existence in the related semiconductor CdS of polarizing centers with an activation energy of 0.02 eV.

If the probability of repeated capture is considered large, then the concepts of thermal electronic polarization[5] do not contradict our observations. The mechanism of losses in the case of deep trapping levels, not emptied by heat, is apparently associated with the overcoming of internal barriers, the depth of which cannot be identified with the depth of the levels under consideration[6]. It is not excluded that at high concentrations of trapping centers the relaxation polarization is associated with tunneling transitions of carriers without ejection into the conduction band.

Thus, the negative photo-dielectric effect unambiguously indicates the existence of relaxation polarization of current carriers localized at shallow trapping levels.

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