EFFECT OF AN ELECTRIC FIELD, ILLUMINATION, AND ADSORBED MOLECULES ON THE SPECTRA OF CAPACITOR PHOTO-EMF IN TlJ, AgBr, ZnO

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Abstract

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PHYSICS

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EFFECT OF AN ELECTRIC FIELD, ILLUMINATION, AND ADSORBED MOLECULES ON THE SPECTRA OF CAPACITOR PHOTO-EMF IN TlJ, AgBr, ZnO

(Presented by Academician A. N. Terenin, February 1, 1965)

In a previous paper ([1]), using various low-resistance and high-resistance semiconductors, it was shown that many properties of the capacitor photoeffect can be explained by assuming that the photo-emf in a capacitor is determined by diffusion of free carriers of one sign, upon which is superimposed the photoconductivity of current carriers in the field of near-surface charges. The magnitude and sign of the near-surface charge in the experiments were varied by gas adsorption, an external electric field, constant illumination, and photochemical action.

In the present work these studies are continued on TlJ, AgBr, and ZnO.

Experimental procedure. Sublimed or powder-like semiconductor layers 0.001 to 0.01 cm thick, placed between mica spacers, were introduced into a vacuum capacitor cell with both electrodes semitransparent. The arrangement of the apparatus for measuring the photo-emf is described in ([2]). A double quartz monochromator DMR-2 was used to measure the spectra. Constant illumination ([3]) from the second monochromator could be applied from the front or rear side. A constant voltage of up to ± 2 kV could be applied from a battery to the capacitor cell (below, the polarity on the front electrode is indicated). The spectral curves were referred to the same incident energy. The sign of the photo-emf in the figures corresponds to the sign of the front illuminated side of the semiconductor layer.

Results and discussion. 1. The photo-emf of the initial TlJ layer over the entire spectral region had a negative sign, corresponding to diffusion of holes into the depth of the layer (Fig. 1, 1). When an external field was applied to the capacitor, a considerable change in the photo-emf of TlJ occurred immediately. The field effect reached a stationary value within 1-2 min and then remained stable during measurements in vacuum of 10^{-4} torr and higher. However, the

Fig. 1

Figure 1: Fig. 1

influence of the field disappeared completely within 1-2 min when the layer was in air, evidently as a result of shielding of the field by adsorbed molecules.

When a positive or negative potential was applied to the front plate of the capacitor, the photo-emf spectrum changed from curve 1 (Fig. 1) into curves 2 or 3, respectively. In the first case the drift hole current, whose spectral distribution is determined by curve 4 (photoconductivity), is added to the diffusion hole current; in the second case it is subtracted from it. In agreement with theory ([4]), the photo-emf in the region of strong absorption may be increased up to a certain limit or decreased, in the limiting case to zero, while in the region of weak absorption ($\lambda > 440$ mμ) the changes in the photo-emf are more significant. In particular, with a negative potential on the front electrode the photo-emf changed sign ("polarity reversal"). The phenomenon disappears completely reversibly when the voltage is removed from the capacitor.

Analogous results were obtained for AgBr, in which the photocurrent carriers are electrons. The photo-emf of the unilluminated layer over the entire spectral region had a positive sign with a maximum at 390 mμ.

An external voltage of negative polarity caused the appearance of an additional maximum of the photo-emf near 450 mμ, of the same sign; with a positive potential on the front electrode, "polarity reversal"of the photo-emf was observed in the region $\lambda > 420$ mμ.

Fig. 1. Spectra of the capacitor photo-emf $(1, 2, 3)$ and photoconductivity (4) of TlJ

2. Frontal short-wavelength steady illumination (420-430 mμ), similarly to a field of negative polarity, changed the spectral distribution of the photo-emf of TlJ from curve 1 to curve 3 (Fig. 1)*. With the same illumination from the rear side, the photo-emf spectrum changed from curve 1 to curve 2. These changes in the photo-emf spectrum are explained by the fact that the strongly absorbed illumination creates, respectively at the front or rear surface of the sample, a negative charge as a result of diffusion of holes into the depth of the layer ([6]).

Experiments on the simultaneous action of the field and illumination on the capacitor photoeffect showed that their influence is not only similar, but also strictly additive. This is quite natural, since the influence of both on the photoresponse consists mainly in the creation or change of a near-surface charge.

Long-wavelength (whether frontal or rear) illumination ($\lambda \geq 460$ mμ) somewhat decreased the photo-emf in the region of the TlJ absorption band and led to the absence of photo-emf in the region $\lambda > 470$ mμ. Such illumination could neutralize the effect of the external field. Numerous experiments showed

that long-wavelength illumination promotes the dissipation of the existing near-surface charge, and the photo-emf spectrum measured under such illumination is apparently close to the spectrum of the true diffusion photo-emf. It was further established that the effect of illumination (long-wavelength or short-wavelength) on the photo-emf in any region of the spectrum is proportional to the logarithm of the illumination intensity. The dependence found is explained by the fact that the surface potential of a semiconductor changes with illumination according to the same law ([7]) (i.e., the magnitude of the near-surface charge changes).

3. Analogous measurements were made on layers of TlJ, AgBr, and ZnO colored with dyes. The latter, as is known, sensitize the photoeffect in these semiconductors to the region of their absorption ([3,8–10]). In Fig. 2, for a powder-like layer of TlJ sensitized with methylene blue, the change in the photo-emf spectra under the influence of illumination by strongly absorbed light is shown. As can be seen, the photo-emf in the sensitization region changes similarly to the photo-emf in the region of weak absorption of the semiconductor. However, the possibility of obtaining the spectrum represented by curve 3 in Fig. 2 proves that the photo-emf in the sensitization region is created not only by the drift current of photocarriers in the field of the near-surface charge, but also by diffusion of carriers of the same sign as in the absorption band of the semiconductor itself. It follows from this that, in the sensitization region of TlJ, the photocurrent carriers are holes.

Similar changes in the photo-emf spectra of dye-sensitized layers of TlJ and AgBr occurred under the action of an external voltage–

* The influence of illumination on the spectrum of the intrinsic and sensitized photo-emf of TlJ was previously found in Ref. ([3]).

···measurements. These measurements showed that in AgBr the sensitized current is carried by electrons.

4. A surface charge in the investigated layers of TlJ and AgBr could also be produced by photochemical exposure of the specimen from the side of one of the electrodes (an excess of metal appeared at this surface), or, conversely, by adsorption of halide molecules from the side of only one surface. In the first case, a positive near-surface charge arose at the given surface of the specimen, and in the second, a negative one. Corresponding changes in the photo-e.m.f. then occurred. A reversal of sign in the photo-e.m.f. spectrum of hole-type TlJ was observed from the side of the specimen on which iodine molecules were adsorbed, and in electron-type AgBr–from the previously exposed side. This explains the results of works ([11,12]).

Fig. 2. Effect of bias illumination ($\lambda = 425$ mμ) on the photo-e.m.f. spectrum of TlJ sensitized with methylene blue: 1–without bias illumination, 2–back bias illumination, 3–front bias illumination of low intensity, 4–front bias illumination of high intensity.

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Figure 2: Fig. 2. Effect of bias illumination ($\lambda = 425$ mμ) on the photo-e.m.f. spectrum of TlJ sensitized with methylene blue: 1—without bias illumination, 2 —back bias illumination, 3—front bias illumination of low intensity, 4—front bias illumination of high intensity

Fig. 3. Spectra of the photo-e.m.f. of a ZnO layer (sublimate on mica), sensitized with brilliant green: 1 —illumination from the outer side, 2 —from the side of the mica substrate

Figure 3: Fig. 3. Spectra of the photo-e.m.f. of a ZnO layer (sublimate on mica), sensitized with brilliant green: 1 —illumination from the outer side, 2 — from the side of the mica substrate

5. The possibility of detecting near-surface charges in a semiconductor by their influence on the capacitor photo-e.m.f. made it possible to obtain additional data on the properties of typical photographic desensitizers. These dyes, like typical photographic sensitizers, sensitize the photoeffect in semiconductors ([3,8–10]). In addition, desensitizer molecules are traps for free electrons in the semiconductor. The latter was manifested in the fact that, after staining in a desensitizer solution (phenosafranine, pinacryptol yellow, pinacryptol green, methylene blue, naphthol green, brilliant green were used) of a TlJ or ZnO layer prepared by sublimation on a mica substrate, the outer side of the specimen usually proved to be negatively charged relative to the inner side (adjacent to the mica). This evidently occurs as a result of the capture of semiconductor electrons by desensitizer molecules, the concentration of which in the part of the layer adjacent to the mica is lower than at the outer, open side. The field that arose was detected from the change in the photo-e.m.f. spectra. For example, the spectral distribution of the photo-e.m.f. of a sublimed TlJ layer sensitized with methylene blue···

any; when measured from the side of the mica substrate it was represented by a curve analogous to curve 2 in Fig. 2, and when measured from the opposite, outer side, by curve 4. It is curious that both of these spectra could be transformed into curve 1 by illumination with $\lambda = 470$ mμ.

Unlike p-type TlJ, in electronic ZnO the "reversal" in the photo-e.m.f. spectrum was observed under illumination from the side of the mica substrate.

Fig. 3. Spectra of the photo-e.m.f. of a ZnO layer (sublimate on mica), sensitized with brilliant green: 1 —illumination from the outer side, 2 —from the side of the mica substrate

In this case, as is seen from Fig. 3, the sign of the photo-e.m.f. changes to the opposite both in the region of the absorption bands of the sensitizer (620 and 440 mμ) and at the edge of the ZnO absorption band (390 mμ), but remains positive in the region of strong absorption of the semiconductor. An analogous ability of electron capture by the semiconductor by molecules of an adsorbed dye was also observed for photographic sensitizers of various classes, when they were adsorbed on the semiconductor in an amount considerably exceeding the optimum for sensitization.

It should be noted that the ability of a molecule of a photographic desensitizer to sensitize the photoeffect and at the same time to act as an electron trap, demonstrated above by direct experiments, cannot be explained within the framework of the sensitization mechanism as electron transfer, but presents no difficulty from the standpoint of energy transfer from the dye to the semiconductor.

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