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I. A. AKIMOV

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## Abstract

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**I. A. AKIMOV**

# OPTICAL SENSITIZATION OF THE PHOTOEFFECT IN SILVER AND THALLIUM BROMIDES BY ORGANIC DYES

*(Presented by Academician A. N. Terenin, 24 III 1958)*

A number of works have been devoted to the study of optical sensitization of the internal photoeffect in inorganic semiconductors by organic dyes. However, the results of various authors who studied sensitization of the photoeffect in AgBr are contradictory, and the question of the possibility of sensitizing the photoeffect in impurity-free silver bromide has not been clarified. As early as 1940, on AgBr electrodes obtained by electrolytic bromination of silver plates and then stained with a thiacarbocyanine dye, Sheppard et al. ([1]) observed sensitization of the photovoltaic effect. However, Nodda k et al. ([2]), who recently studied the photovoltaic effect on the same electrodes, did not detect sensitization. In a brief communication, Kameyama et al. ([3]) did not describe the conditions under which they observed sensitization by dyes of the photoconductivity of fused silver bromide layers. Later, West and Carroll ([4]) established and investigated the phenomenon of optical sensitization of the photoconductivity of bromo-iodide gelatin emulsions. In the works of Terenin, Putseiko, and Akimov ([5–7]), which investigated the photoeffect in powdered, sublimed, and fused layers of silver and thallium halide salts by capacitor and photoconductivity methods, it was shown that, whereas significant sensitization is observed for iodides, it is practically absent in silver and thallium bromides. Amsler ([8]) found that silver bromide barrier-layer photocells prepared by electrolytic bromination of silver plates can be sensitized by dyes.

The present work was devoted to clarifying the conditions under which sensitization of the internal photoeffect in silver and thallium bromides by dyes can be observed. The photoeffect was studied by the capacitor method described in works ([9], [10]). By this method the photo-emf induced in a capacitor under modulated illumination is measured. The use of this method allowed us to conduct the investigation on powdered layers, which had a composition close to stoichiometric and possessed a large specific surface area. In addition, this method makes it possible to carry out measurements on layers with different dark conductivities, which was essential for our experiments with adsorption of bromine vapors, since the conductivity of AgBr changes strongly under the action of bromine ($^{11}$). The dyes were adsorbed onto powders from alcoholic solutions with a concentration of $10^{-4}$ mol/l. The spectral distribution of the photoeffect was measured in the region from 390 to 1000 m$\mu$ using a UM-2 glass monochromator. The spectral curves of the photoeffect shown below represent the value of the photo-emf measured at the amplifier output, reduced to equal values of the incident monochromatic energy.

In the spectral distribution of the photoeffect, measured both by the photoconductivity method and by the capacitor method, in the visible region AgBr usually exhibits a maximum near 430 m$\mu$ ($^{12}$, $^{13}$), while TlBr exhibits a maxi-

maxima near 410 and 430–440 m$\mu$ (^14). The position of the photoelectric-effect maxima of the powders we studied coincided with those indicated above. The long-wavelength boundary of the photoelectric effect in both bromides was at about 500 m$\mu$.

Numerous experiments established that powder-like layers of AgBr and TlBr, in contrast to AgI and TlI, after being stained with various dyes do not exhibit sensitization of the photoelectric effect. The striking influence of adsorbed vapors and gases on the sensitization effect, discovered earlier in our laboratory (^15, ^6, ^7), showed that surface electronic levels, created upon adsorption of molecules possessing electron-acceptor properties, play an essential role in the phenomenon of sensitization. The aim of the present work was to investigate the influence of adsorption of bromine molecules on the photoelectric sensitivity of unstained and stained layers of AgBr and TlBr. In these experiments, only dyes stable to the action of bromine vapors could be used as sensitizers, such as, for example, malachite green, crystal violet, methylene blue, and thionine.

The experiments showed that admission of bromine vapor at a pressure of about 0.1 mm Hg to unstained AgBr and TlBr layers exerts a substantial influence on the magnitude and spectral distribution of the photoelectric effect. After adsorption of bromine, the photoelectric sensitivity in the region 400–450 m$\mu$ increased in AgBr, while in TlBr it decreased somewhat. At the same time, in the visible and near-infrared region there appeared a slight sensitivity with weakly expressed maxima near 500 and 900 m$\mu$. Removal of the adsorbed bromine by freezing out or by heating the layer in air restored the initial sensitivity.

Especially strong changes in the spectral distribution of the photoelectric effect were found upon adsorption of bromine vapors on stained AgBr and TlBr layers. Fig. 1 gives curves of the spectral distribution of the photoelectric effect in TlBr powder stained with malachite green. Whereas before adsorption of bromine vapors (curve 1) no photoelectric sensitivity was observed in the absorption region of the dye (600–700 m$\mu$), after adsorption of bromine on this layer a distinct maximum of the sensitized photoelectric effect appeared near 680 m$\mu$ (curve 2).

The position of this maximum of the photoelectric effect coincides with the absorption maximum of the dye adsorbed on TlBr powder and is shifted toward longer wavelengths relative to the solution of the dye in ethanol. Upon partial

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

desorption of bromine molecules, the sensitized photoelectric effect decreased noticeably (curve 3), and after complete removal of the adsorbed bromine the layer again lost its photoelectric sensitivity to long-wavelength light. It should be noted that adsorbed bromine molecules were held more firmly on stained layers than on unstained ones. Adsorption of bromine vapors on stained silver bromide also led to the appearance of a sensitized photoelectric effect (Fig. 2), which after desorption of bromine molecules decreased reversibly. A similar picture was observed upon adsorption and desorption of bromine on silver and thallium bromides stained with other dyes (thionine, crystal violet). The positions of the maxima of the photoelectric effect sensitized by one and the same dye in AgBr and TlBr differed somewhat.

In the case of layers stained with methylene blue, adsorption of bromine vapors not only changed the sensitized photoelectric effect in magnitude, but also led to a considerable change in the spectral distribution of the photoelectric effect in the absorption region of the dye. Upon adsorption of bromine at low vapor pressures (about 0.01 mm), the photoelectric effect sensitized by methylene blue had a maximum near 680-700 m$\mu$ (Fig. 3, curve 1). After additional adsorption of bromine vapor, the indicated photoelectric-effect band decreased noticeably and, at the same time, another distinct band arose with a maximum at 780-800 m$\mu$ (Fig. 3, curve 2). Fig. 4 shows

spectral distribution of the photo-emf for an AgBr layer dyed with the same dye after the action of bromine vapor on it. Desorption of bromine from these layers

Fig. 1. Spectral distribution of the photo-emf in a TlBr layer dyed with malachite green: 1 –before adsorption; 2 –after adsorption of bromine vapor, $P \sim 0.1$ mm Hg; 3 –after partial desorption of bromine

Fig. 2. Spectral distribution of the photo-emf in an AgBr layer dyed with malachite green: 1 –after adsorption of bromine vapor, $P \sim 0.1$ mm Hg; 2 –after partial desorption of bromine

was accompanied first by the disappearance of the maximum of the photoeffect at 800 m$\mu$, and then at 700 m$\mu$. In the case of other dyes, bromine vapors affected only the magnitude of the sensitized photoeffect. It should be noted that the efficiency of sensitization, estimated as the ratio of the magnitude of the photoeffect in the absorption region of the adsorbed dye to the photoeffect in the absorption region of the semiconductor itself, achieved in these experiments

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

for AgBr and TlBr, even in the presence of bromine vapor, was much smaller than in the case of ZnO, TlJ, and AgJ (5–7).

Fig. 3. Spectral distribution of the photo-emf in a TlBr layer dyed with methylene blue: 1 –after adsorption of bromine vapor, $P \sim 0.01$ mm Hg; 2 –after additional adsorption of bromine, $P \sim 0.1$ mm Hg.

Fig. 4. Spectral distribution of the photo-emf in an AgBr layer dyed with methylene blue, after adsorption of bromine vapor, $P \sim 0.1$ mm Hg.

By the capacitor method, using a synchronous detector at the amplifier output [15], the sign of the photocurrent carriers in the layers under study was determined. The photocurrent carriers, both in the absorption region of the semiconductor itself and in the absorption region of the dye, were holes.

The results of the present work are in complete agreement with earlier studies [15,6,7] on the effect of gases and vapors on the sensitization of the photoeffect in semiconductors by dyes. The increase in the sensitized photoeffect in AgBr and TlBr upon adsorption of bromine vapors is analogous to the previously observed [6] effect of iodine vapors on the photoeffect in colored silver and thallium iodides. The mechanism of sensitization by dyes of the photoeffect in silver and thallium bromides, as in the iodides [7], apparently consists in the transfer to the semiconductor of the photon energy absorbed by the dye and, under the action of this energy, the transfer of an electron in the semiconductor to a local level formed by an adsorbed bromine molecule. The hole thereby liberated in the valence band is the photocurrent carrier. According to this conception of the mechanism of the phenomenon, a necessary condition for the possibility of sensitization of the photoeffect by dyes is the existence of acceptors that create local electronic levels on the surface of the semiconductor. In our case such levels were created by adsorbed bromine molecules. The energy of the photon absorbed by the dye molecule is apparently sufficient to transfer an electron in the semiconductor to this acceptor level.

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