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Abstract

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PHYSICS

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TEMPERATURE DEPENDENCE OF THE PHOTOCONDUCTIVITY OF THALLIUM IODIDE SENSITIZED WITH DYES

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Some semiconductors possessing their own photoelectric sensitivity in the blue and ultraviolet regions of the spectrum can be sensitized, by dyes adsorbed on them, to longer-wavelength light up to 1.0–1.2 μ ($^{1-16}$). According to one theory, the energy deficit for the occurrence of this process, amounting to about 1.0–1.5 eV, is made up from the energy reserve of the sensitizer-dye molecules (^{17}), while according to the ideas of other authors ($^{18-21,\ 5-14}$), it is made up from the lattice energy of the semiconductor. In both cases, thermal activation of the process must exist. Indeed, in the work of E. K. Pushcheiko and A. N. Terenin (^{5}), in studying the capacitor photo-emf of TlJ colored with methylene blue, it was established that, with an increase in temperature from +20 to +70°, the sensitized sensitivity increased by approximately a factor of 3, while when the temperature was lowered to −50° it decreased by a factor of 2, whereas the photoeffect in the absorption region of the semiconductor itself changed only insignificantly. These observations coincide with the results of studies of the temperature dependence of the photographic sensitivity of silver-halide emulsions sensitized with dyes. When the temperature is lowered, in the region of spectral sensitization there occurs a sharper drop in sensitivity than in the blue part of the spectrum ($^{22-26}$). However, from the available data it is difficult to draw conclusions about the magnitude of the thermal activation energy of the process of spectral sensitization, both because the data are insufficient and because, in the author’ s opinion, one should compare not only the temperature dependences of the intrinsic and sensitized photoeffect of colored semiconductors, but also study the temperature dependence of the photoeffect in the long-wavelength part of the spectrum before and after sensitization of the semiconductor.

In the present work, the temperature dependence of the dark conductivity and photoconductivity in the blue and red parts of the spectrum of thallium iodide

Fig. 1. Temperature dependence of the dark conductivity and
photoconductivity of TlJ layers

Figure 1: Fig. 1. Temperature dependence of the dark conductivity and photoconductivity of TlJ layers

layers before and after their sensitization with dyes was studied.

Method. TlJ layers were deposited by sublimation in a vacuum of the order of 10^{-5} mm Hg on quartz plates with platinum electrodes, applied by cathodic sputtering, of the usual type with one gap (distance between electrodes 3 mm, length 10 mm) or in the form of a "raster" (distance between electrodes 0.1 mm, total length 80 mm). The layers had a thickness of 5-8 μ, which was measured with an MII-4 microinterferometer or with an MIS-11 double microscope. Investigations were also carried out on powder-like layers with a thickness of about 0.1 mm. Adsorption of organic dyes on TlJ was carried out from alcoholic solutions with a concentration of 10^{-4} mol/l, followed by washing of the colored layer with ethanol. The dyes used were: rhodamine B (I), erythrosin (II), 1,1-diethyl-3,3,3′,3′-tetramethylcarbocyanine iodide (III), and 3,3′-diethyl-5,5′-dinitrothiacarbocyanine-*p*-toluenesulfonate (IV). Conductivity was measured in the temperature interval $+20 \div -170^\circ$ in air in a Dewar of special construction or in a vacuum vessel at a pressure of 10^{-5} mm Hg. A copper-constantan thermocouple was soldered to one of the electrodes of the photoresistor. Dark conductivity and photoconductivity under constant illumination were measured with an E6-3 teraohmmeter. In addition, with the aid of a resonant alternating-current amplifier, photoconductivity under intermittent illumination (600 Hz) was studied. The intrinsic photoeffect of TlJ was measured at 436 mμ, and the sensitized one at 578 mμ for

dyes with a sensitization maximum around 580 mμ and at 546 mμ for erythrosine, which has a sensitization maximum around 545-550 mμ. Monochromatic light of the required regions was isolated from the radiation of an SVD-120 mercury lamp by means of light filters for isolating the lines of the mercury spectrum. The illuminance of the light incident on the layer was measured with a calibrated

Fig. 1. Temperature dependence of the dark conductivity (σ_t) and photoconductivity (σ_ϕ) of TlJ layers in air before staining with dyes (σ^{n}) and after staining (σ^{ok})

thermopile and was, at wavelengths of 436 mμ, $0.8 \cdot 10^{15}$ quanta $\cdot$ cm^{-2}; at 546 mμ, $1.5 \cdot 10^{15}$; and at 578 mμ, $1.8 \cdot 10^{15}$ quanta $\cdot$ cm^{-2}.

Results and discussion

The results of measurements of the temperature dependence of the dark conductivity and photoconductivity under constant illumination in air, illustrated by the data of Fig. 1 for four thallium iodide layers before and after staining them with dyes, reduce to the following:

1. The dark and light conductivities of sublimed and powder-like TlJ layers decrease as the temperature is lowered. In the temperature dependences of the current for each specimen one can distinguish two regions with different activation energies; the transition point between them lies, for the dark current, at about -50°, and for the photocurrent at about $-80 \div -100^{\circ}$.
2. The increase of the dark electrical conductivity with temperature follows the law $\sigma_{\mathrm{t}} = \sigma_0 e^{-E_{\mathrm{t}}/2kT}$, with activation energies at temperatures below -50° of about 0.15-0.25 eV, and at higher temperatures of the order of 1.0-1.2 eV. As a result of adsorption of dyes, the conductivity of the layers may change somewhat.
3. The activation energies of the photocurrent in the blue region of the spectrum, determined from the formula $\sigma_{\phi} = Ae^{-E_{\phi}/kT}$, are 0.02-0.03 eV and 0.12-0.14 eV in the temperature ranges respectively below and above -80°. Adsorption of the dye practically does not change the temperature dependence of the photoconductivity in the absorption region of the semiconductor itself.
4. The weak photoconductivity of unstained layers in the yellow-green part of the spectrum falls more strongly with decreasing temperature than the photoconductivity in the blue region: in the interval from +20 to -160° the former decreases by 3, and the latter by 2 orders of magnitude. The thermal activation energies of the photocurrent in the long-wavelength region are 0.15-0.18 and 0.05-0.08 eV.
5. After adsorption of dyes on TlJ, the long-wavelength sensitivity of the layers increases. However, the temperature dependence of the photocurrent in this spectral region remains approximately the same as before sensitization. This latter result is of undoubted interest for elucidating the mechanism of spectral sensitization. The stronger temperature dependence of the sensitized effect, compared with the sensitivity in the blue region, noted earlier by many authors, is perhaps a consequence of the sharp temperature dependence of the weak long-wavelength sensitivity of unsensitized layers. The impurity centers determining the weak long-wavelength sensitivity of the semiconductor before sensitization by the dye may, in our layers, be excess metal and metalloid formed as a result of partial photochemical decomposition of TlJ. To clarify the influence of excess thallium and iodine on the temperature course of the photocurrent in TlJ, measurements were carried out for layers in a vacuum of 10^{-5} mm Hg and for layers with adsorbed iodine.

It was established that, for unstained TlJ, the dependence of the photocurrent in the red region on temperature in vacuum is considerably weaker than in air. But for stained thallium iodide these dependences are the same in air and in vacuum.

Moreover, there is no difference in air and in vacuum for the photoconductivity in the blue part of the spectrum.

From the results of measurements of photoresistance in air before and after adsorption of iodine molecules, we note two basic facts: TlJ layers with excess iodine possess increased dark and light conductivity, and at the same time the photocurrent in them depends more strongly on temperature. The results did not depend on whether the photocurrent was measured under constant or intermittent (600 Hz) illumination. In analyzing the results it should be borne in mind that the layers studied possess a strongly developed surface, and therefore the fraction of surface conductivity in them may be significant. In addition, these specimens evidently always contain an impurity in the form of excess thallium and iodine because of partial photolysis of TlJ.

The conductivity of TlJ is mixed, with a predominance of the hole component ([8]). The latter is also confirmed in the present work by the observed increase in dark and light conductivity upon adsorption of iodine vapor.

The width of the forbidden band of TlJ, determined from absorption and photoeffect spectra, is about 2.5 eV ([7],[8] ,[27]). Therefore, the values we determined

thermal activation energies of the dark conductivity (0.15–0.25 and 1.0–1.2 eV) evidently refer to impurity conduction. The nonmonotonic decrease of conductivity with increasing temperature observed in a number of cases in the temperature interval $-70 \div -40^{\circ}$ (Fig. 1) may be the result either of depletion of shallow impurity levels or of polarization of the specimens, in which the fraction of ionic conductivity at these temperatures becomes appreciable. The increase of photocurrent with temperature is naturally explained by thermal liberation of electrons from shallow traps. In our case such traps are apparently created by excess thallium on the surfaces of the TlJ microcrystals. The more shallow traps there are, the less steeply the photocurrent decreases as the temperature is lowered. The number of such traps increases when the specimen is placed in vacuum and decreases after it is treated in iodine vapor. The layer of adsorbed dye partially protects the TlJ surface from iodine evaporation. The role of iodine molecules is not confined merely to oxidation of excess thallium; in addition, having a high electron affinity (2.3 eV) (28), they themselves create deep sticking levels, with which the long-wavelength photoelectric sensitivity of TlJ and the sensitization process are to a considerable extent connected (8–13).

The fact of an identical temperature dependence of the photocurrent in the long-wavelength region on the falling edge of the intrinsic sensitivity before and after staining thallium iodide with sensitizing dyes serves as confirmation of our explanation of the mechanism of spectral sensitization of the photoeffect as the transfer of the energy of absorption of a light quantum from the dye to the semiconductor, with liberation of electrons from local levels of the semiconductors (6–14). Thermal activation of the process consists in the filling by electrons of sticking levels created by iodine molecules, from which the latter can be transferred into the conduction band of TlJ. If, for the process of energy transfer from the dye to the semiconductor to occur, an additional thermal activation energy is required, then its value is apparently no more than a few hundredths of an electron-volt.

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