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Abstract

Full Text

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CHANGES IN THE SPECTRAL DISTRIBUTION OF THE INTRINSIC AND SENSITIZED PHOTOEFFECT IN SILVER HALIDES UNDER WEAK EXPOSURE

(Presented by Academician A. N. Terenin, 31 X 1960)

Photochemical transformations greatly complicate the study of the photoelectric properties of silver halides. Therefore most measurements of the photoconductivity of these substances have been carried out on single crystals, which possess weak photochemical sensitivity (^{1}). In a number of cases, however—for example, for the study of optical sensitization of the photoeffect—the use of dispersed layers is necessary. Meanwhile, the results of most photocurrent measurements made on powder layers of silver halides ($^{2-4}$) should apparently be attributed to exposed samples. In determining the spectral distribution of photoconductivity of silver-halide emulsions, this difficulty was avoided by using, for each subsequent measurement, a new, unexposed area of the film (^{5,6}). But such a procedure can be used only for sufficiently extended homogeneous layers.

In the present work an apparatus was developed for measuring the spectral distribution of the photoconductivity of semiconductors possessing photochemical sensitivity under weak exposure. On this apparatus, a study was carried out on powder layers of silver bromide and silver chloride.

Fig. 1. Schematic of the apparatus for measuring the spectral distribution of photoconductivity

Experimental Part

The principal scheme of the apparatus is shown in Fig. 1. Light from an incandescent lamp, modulated by a disk (D) at a frequency of 600 Hz, was focused on the entrance slit of the autocollimation monochromator of a rapid spectrometer (see Fig. 10 ([7])). After passing through a quartz prism, the light fell on a mirror (3), to which, by means of a cam mechanism (K), an oscillatory motion with a frequency of 1 Hz was imparted.* At each oscillation

* The relaxation time of the photocurrent in the silver-halide layers studied, measured by us on a taumeter, was of the order of 10^{-4} sec.; therefore the inertia of the receiver at the scanning rates used did not introduce distortions into the measurements.

the mirror in front of the exit slit of the monochromator ran through the entire spectrum in the region from 1000 mμ to 350 mμ and back. The light emerging from the monochromator fell on the photoresistor through a shutter, which opened once for 0.5 sec with the aid of a relay switched on synchronously with the beginning of the passage of the spectrum from 1000 mμ to 350 mμ.

The radiation receiver in the study of photoconductivity was a photoresistor with a layer of powdered silver halide on a glass plate with platinum electrodes, and in the study of photo-emf in a capacitor—a layer of silver-halide powder between the mica spacers of the capacitor. All preparatory operations with silver halides were carried out under inactive light. The measurements were made with the monochromator slits opened to 0.5 mm (dispersion at 400 mμ—80 Å/mm, at 700 mμ—240 Å/mm); during this time, in the measurement of one spectrum, energy of the order of 10^{-5} W/cm^2 fell on the layer. The photocurrent signal was fed to the input of a narrow-band amplifier (U)* with a pass band of 600±15 Hz and a gain of 70,000. At the amplifier output the signal was rectified and fed to the input of an ÉNO-1 oscilloscope; its beam sweep was effected by a triggered sweep, with a pulse synchronized with the beginning of the passage of the spectrum.

Thus, on the oscilloscope screen one observed the curve of the spectral distribution of the photocurrent (or photo-emf) of the layer under study, not recalculated per unit of incident energy. In measuring the photo-emf by the capacitor method, the apparatus, in combination with a synchronous detector ([8],[9]), also made it possible to determine the sign of the charge of the photocurrent carriers in different parts of the spectrum.

Discussion of the Results

The measurements were carried out on undyed silver halides, and also after the adsorption on them of organic sensitizing dyes. For each sample a series of spectra was measured. The difference of each subsequent spectrum from the preceding one was due to the photochemical change of the layer as a result of exposure to the radiation absorbed by the sample during the measurement of

Fig. 2 and Fig. 3

Figure 2: Fig. 2 and Fig. 3

the preceding spectrum (0.5 sec).

Figure 2 shows how, successively in the course of exposure, the spectra of the photo-emf (2a) and photoconductivity (2b) of silver bromide changed. Analogous changes were observed for silver chloride. The photo-emf of unexposed silver bromide had a red limit at 480 mμ and a maximum at 390 mμ, and for silver chloride—respectively 395 mμ and 365 mμ. In the course of exposure there arose a dip in the spectral curve of the photo-emf for AgBr at 415 mμ and for AgCl at 380 mμ, and at the long-wavelength edge of the spectrum there appeared a new maximum for silver bromide at about 450 mμ and for silver chloride at about 385 mμ; in addition, the photo-emf decreased throughout the entire short-wavelength region.

Measurements with the synchronous detector showed that, in the initial—unexposed—powders of AgBr and AgCl, the sign of the photo-emf corresponds to the diffusion of electrons into the depth of the layer from the illuminated surface. As the layer was exposed, the electronic diffusion current decreased, while the new maximum appearing at the long-wavelength edge was due to the diffusion of positive holes into the depth of the layer.

A different character of the changes upon exposure was observed in the photoconductivity spectra. The photoconductivity of unexposed powders of silver bromide had a red limit at 490 mμ and a maximum at 450 mμ, and for silver chloride—respectively at 400 mμ and 380 mμ. After the first illumination of the layer, as is seen in Fig. 2, the photoconductivity during the second illumination increased by 20-30% uniformly over the entire spectrum. With subsequent exposures the photoconductivity decreased. In this case the strongest changes in the photocurrent occurred in the short-wavelength region of the spectrum.

The indicated changes in the photo-e.m.f. and photoconductivity of AgBr and AgCl are irreversible and are apparently connected with a photochemical change in these substances.

The photoeffect band in the region of 580-620 mμ, caused by the appearance of colloidal silver particles, appeared in AgBr only after 10-15 exposures, and in AgCl after 20-30 exposures.

Fig. 2. Spectral distribution of the photo-e.m.f. (a) and photoconductivity (b) in polycrystalline layers of silver bromide. 1 —first spectrum measurement, 2 —

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* Since in the photoconductivity spectra under study the bands are sufficiently broad, it is possible to use here a narrow-band amplifier, in contrast to the wide-band amplifiers usually used in high-speed spectrometers (7). This allowed us to study photocurrents of the order of 10^{-13} A.

second measurement, etc.

Fig. 3. Spectral distribution of the photoconductivity of a silver bromide layer sensitized with the dye 1,1′-diethyl-3,3,3′,3′-tetramethylthiacarbocyanine iodide (conc. 10^{-4} mol/l). 1 –first spectrum measurement, 2 –second measurement, etc.

The observed phenomena can be explained only under the assumption that the photoconductivity is bipolar. This had previously been established for fused layers of silver bromide and chloride (10). In unexposed layers the electronic component predominates (in AgBr and AgCl single crystals (11) the mobility of holes is much less than the mobility of electrons). It is possible that, as a result of exposure, acceptor levels arise in the forbidden band of the crystal, on which electrons are trapped, and therefore the role of the hole component increases (9), while the centers formed create an additional absorption band at the edge of the crystal absorption (10). In addition, changes in the diffusion of the photocurrent carriers may in part result from a decrease, in the unexposed microcrystals, of the upward band bending caused by screening by surface electron levels arising upon exposure (12).

It was established earlier that in silver and thallium iodides there is a considerable sensitization of the internal photoeffect by dyes, whereas in bromides it is very small (13–16,4). A study of the influence of exposure on the photoconductivity spectra of powder layers of silver bromide and iodide colored with cyanine dyes—sensitizers—led to the following results.

In AgJ the sensitized photoeffect does not change at all under exposure. In AgBr, during exposure of the layer, the photoelectric sensitivity in the region of dye absorption rapidly decreases, becoming insignificant in comparison with the photoeffect in the absorption region of the semiconductor itself. Figure 3 shows how, under successive exposures, the spectral curve of the photoconductivity of silver bromide colored with a thiacarbocyanine dye changes.

The observed disappearance of the sensitized photoeffect in silver bromide is naturally explained by destruction of the dye by bromine liberated as a result of the photochemical decomposition of AgBr. It should be noted, however, that even in unexposed layers of silver bromide the efficiency of sensitization of the photoeffect is an order of magnitude lower than in silver iodide. The latter is apparently due to the possibility of transfer of energy from the sensitizing dye to local electronic levels on the surface of the semiconductor (4,9,13–16).

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