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Fig. 1

Figure 1: Fig. 1

Abstract

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Photoconductivity of Photographic Layers at a Frequency of 10^{10} Hz

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The study of the photoeffect in silver halides makes it possible to investigate the primary stage in the formation of the latent photographic image. Among the numerous investigations, of special interest is a small group of works ($^{1-9}$) carried out not on model systems in the form of mono- and polycrystalline layers of silver halide, but on real photographic emulsions. However, measurement of photoconductivity in emulsion layers is associated with great difficulties, since the gelatin in which the photoconducting microcrystals of silver halide are suspended is a very capricious high-ohmic ballast resistance which, when an external electric field is applied, undergoes complex changes. This makes the measurements very laborious and limits the conditions under which they can be carried out: a reduced gelatin content in the emulsion, a strictly defined humidity, and relatively high temperatures, when the resistance of the gelatin interlayers is comparable with the resistance of the silver halide.

Fig. 1. Schematic diagram of the setup for measuring photoconductivity at microwave frequencies.
1 –klystron (microwave generator), 2 –magnetic decoupling (gyrator), 3, 6 –attenuators, 4 –resonator, 5 –sample, 7 –AFC detector, 8 –bolometric detector, 9 –narrow-band amplifier, 10 –synchronous detector, 11 –galvanometer, 12 –AFC unit (automatic frequency tuning unit), 13 –monochromator, 14 –modulator, 15, 16 –light sources, 17 –photoconductivity of the synchronous detector.

In the present work these difficulties were largely overcome because, for investigating the photoconductivity of emulsions, we used not the commonly adopted method with a constant electric field, but a contactless method for measuring conductivity at microwave frequencies ($^{10-13}$).

Method. To measure photoconductivity at microwave frequencies, an EPR radiospectrograph with a bolometric detector of the type described in (^{14}) was used, without employing a magnetic field*. The sample (a photographic film

Fig. 2. Spectral distribution of microwave photoconductivity of silver-halide emulsions at −196°C: 1 —cine negative film A, 2 —isopanchrome film, 3 —X-ray film, 4 —Unibrom No. 4 photographic paper

Figure 2: Fig. 2. Spectral distribution of microwave photoconductivity of silver-halide emulsions at −196°C: 1 —cine negative film A, 2 —isopanchrome film, 3 —X-ray film, 4 —Unibrom No. 4 photographic paper

measuring 4×10 mm^2, or a 0.5 g powder charge) in an ampoule 4 mm in diameter of a quartz Dewar vessel was placed at the maximum of the electric field of a cylindrical resonator operating on a wave of the H_{011} type, and was illuminated through an aperture in the resonator. A block diagram of the setup is shown in Fig. 1. The microwave power generated by the klystron ($\gamma = 9660$ MHz, $p = 50$ mW) passes through the resonator with the sample and is recorded by the bolometer. When the sample, located in the microwave field of the resonator, is illuminated, a microwave photocurrent arises in the sample, which leads to an increase in the losses in the resonator, a decrease in its quality factor, and a corresponding decrease in the microwave power passing through it. When the sample is illuminated with light modulated at a frequency of 600 Hz, the bolometric detector separates out a signal of the same frequency, proportional to the photoconductivity at microwave frequencies. The signal is amplified by a narrow-band amplifier and, after rectification by a photoelectric synchronous detector, is measured by a galvanometer. The circuit uses automatic frequency tuning (AFC), which makes it possible to eliminate frequency noise of the generator.

* The authors express their sincere gratitude to V. E. Kholmogorov and L. N. Ionov for providing the radiospectrograph for these measurements.

The light source was a tungsten incandescent lamp. The spectral distribution of the photoeffect in the region from 390 to 1200 nm was measured with an ISP-17A glass monochromator. The spectral photocurrent curves were referred to equal values of the incident monochromatic energy. In the experiments the spectral slit width at 400 nm was 1.5 nm, at 700 nm it was 10 nm, and the incident energy was, respectively, $1.5 \cdot 10^{-5}$ and $1.4 \cdot 10^{-3}$ W/cm^2.

Fig. 2. Spectral distribution of microwave photoconductivity of silver-halide emulsions at −196°C: 1 —cine negative film A, 2 —isopanchrome film, 3 —X-ray film, 4 —Unibrom No. 4 photographic paper

Results of measurements. Microwave photoconductivity was readily observed in various motion-picture and photographic films, photographic papers, and also in powders of silver halides. In the very first experiments it was found that microwave photoconductivity, when the temperature was lowered from +20 to −196°, increased by two orders of magnitude*. It is interesting to note that the direct-current photoconductivity of polycrystalline layers of silver and thallium halides decreases with decreasing temperature (^{15}), whereas in perfect single crystals it increases ([16], [17]). The latter is evidently the result of an increase in the mobility of photocurrent carriers in the bulk of the crystal with decreasing temperature ([18]). The increase of photocurrent with temperature in polycrystalline layers is explained by an increase in surface conductivity. From the data obtained it may be concluded that at microwave frequencies it is apparently mainly the volume conductivity of the microcrystals of silver halide that is measured. Such a dependence of the photocurrent on temperature makes it advantageous to carry out measurements at low temperatures, at which photochemical changes of the layer are absent at the moment of exposure. Therefore subsequent measurements were made at $-196°$.

A comparison of the relative photoelectric sensitivity at microwave frequencies of various photographic materials showed that the photoconductivity of cine negative films of different types was of the same order, while the sensitivity of photographic papers was an order of magnitude lower. It is curious that among samples prepared from one batch of emulsion, ortho- and panchromatic films had photoconductivities, respectively, 2 and 2.5 times smaller than nonsensitized ones. This result does not agree with the observation ([9]).

It is important to note that at microwave frequencies the photoelectric sensitivity of silver-halide powders without binder and of emulsion layers prepared from these powders was of the same order, whereas the direct-current photoconductivity of the emulsion layers was three orders of magnitude smaller than that of powdered layers of silver halide.

Next, the microwave photoconductivity of four emulsions (AgBr with an AgJ additive), differing only in the sizes of their microcrystals (0.16; 0.31; 0.61 and 0.81 μ^2)**, was compared. The ratio of the photocurrents in them was, respectively, 0.2; 0.4; 0.7; 1.0, i.e., a proportional increase of the photoconductivity of the emulsions with increasing microcrystal size was observed. This result can be explained by the fact that larger crystals have less— still more internal defects that hinder the motion of photoelectrons.

The photoconductivity of emulsion layers varied with illumination according to the law: $\sigma_\phi = kL^\alpha$. The exponent α was close to 1 at illuminations L of the order of 10^{-5} W/cm^2, and with increasing illumination it decreased, reaching a value of 0.5 at L of the order of 10^{-3}-10^{-2} W/cm^2. These data agree with measurements on direct current ([2]), but differ from observations ([9]). The photoconductivity of emulsions irradiated for a long time at $-196°$ changed noticeably. Exposure at room temperature led to a rapid decrease, and then to the disappearance, of photoconductivity at microwave frequencies, just as in measurements on direct current ([2,9]).

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* All photoconductivity studies, except spectral ones, for nonsensitized and sensitized materials were carried out with blue-violet light.

** The emulsions were kindly supplied to us by I. R. Protas.

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

Fig. 3. Spectral distribution of photoconductivity at microwave frequencies of silver bromide powders at −196°: 1 —not dyed; 2 —the same after exposure at +20°C; 3 —dyed with 3,3′-diethyl-4′,5′-diphenyl-4-keto-5(3″-ethyl-4″,5″-diphenylthiazolinidene-2″-ethylidene)-thiazolinothiazolo-cyanine ethyl sulfate (10^{-4} M); 4 —dyed with 3,3-diethyl-4-methyl-5-carbethoxy-4-keto-5-(3″-ethyl-6″,7″-tetramethylbenzthiazolinidene-2″-isopropylidene)-thiazolinothiazolocyanine iodide (10^{-4} M)

Further, the spectral distribution of photoconductivity at microwave frequencies was studied. Fig. 2 gives the spectral curves of the photocurrent for four different silver-halide emulsions. These curves are similar to the spectral curves of photographic sensitivity and photoconductivity on direct current. In the blue-violet region, on curves rising toward shorter wavelengths, there is a small maximum at about 430–450 nm. The red limit of the photoeffect for nonsensitized layers was at 480–500 nm, while in sensitized emulsions additional bands in the absorption region of the dyes—sensitizers—were very clearly manifested, despite the fact that the measurements were carried out at −196°. The positions of the maxima of the sensitized photoeffect coincide with the positions of the maxima of the sensitized photographic sensitivity of these films (^{19}).

Fig. 4. Spectral distribution of photoconductivity at microwave frequencies of sensitized zinc-oxide layers: 1 —electrophotographic paper EFO-1 at −196°C; 2 —EFO-1 at +20°C; 3 —ZnO powder dyed with xenocyanine (10^{-4} M) at +20°

The next figure gives analogous photoconductivity spectra for silver bromide powders (crystallite size 3-5 μ). Unexposed AgBr powder (curve 1, Fig. 3) was sensitive only to light with $\lambda < 470$ nm. After slight exposure at +20°, the photoconductivity in the short-wavelength region (especially near the maximum at 430 nm) decreased somewhat, and at the same time, in the longer-wavelength part of the spectrum, a photoeffect band appeared with a red limit at 1200 nm.

In powders with dyes adsorbed on them, a sensitized photoeffect was observed (3 and 4, Fig. 3). The curves of spectral sensitization of the photocurrent coincide with the absorption spectra of the adsorbed dyes and are similar to the photoconductivity curves for direct current (^{20}).

It should be noted that the efficiency of the sensitized photoeffect in silver halides at −196° was rather low and was approximately an order of magnitude lower than at +20°. A similar temperature dependence exists for the photographic sensitivity of sensitized emulsions ($^{22-24}$) and for the photoconductivity of dyed thallium iodide (^{21,15}). This is apparently explained by the fact that the filling of adhesion levels, from which photoelectrons are released by the energy of photons absorbed by the sensitizer, is accomplished thermally (^{15}).

Finally, SHF photoconductivity of electrophotographic layers was observed. Figure 4 shows the spectral distribution of the photoconductivity of EFO-1 electrophotographic paper at −196° (curve 1), whose photosensitive layer consists of zinc-oxide powder sensitized with eosin and suspended in polyvinyl butyral. Since in the case of such layers there is no danger of their photochemical fogging, measurements were also carried out at +20° (curve 2). The experiments showed that, in the case of zinc oxide, the dependence of the sensitized photoeffect on temperature is less sharp than for silver and thallium halides. The photocurrent curves presented completely reproduce the curve of the spectral photographic sensitivity of EFO-1 paper (^{25}).

For zinc-oxide powders without binder, sensitized with dyes, the same results are obtained as for electrophotographic layers. As an example, Fig. 4 (curve 3) shows the spectral distribution of SHF photoconductivity for ZnO powder dyed with the infrared sensitizer xenocyanine. Here, just as in the spectra of capacitor photo-emf and direct-current photoconductivity, maxima are observed near 930 and 840 nm, and the red limit of the sensitized photoeffect lies beyond 1000 nm.

The results presented show the broad possibilities for applying SHF techniques to the study of the photoelectric properties of photographic materials.

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