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Abstract

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SENSITIZED PHOTOLYSIS ON SEMICONDUCTORS AS A PRINCIPLE OF LONG-WAVELENGTH PHOTOGRAPHY

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It is known that the photolysis of silver halides, which underlies the formation of the latent photographic image, is an electron–ion process (the two-stage mechanism of Mott and Gurney). The electronic stage of this process consists in the formation of an electron–hole pair when a photon is absorbed by the crystal, and in the localization of the electron at a deep trapping level that plays the role of a sensitivity center. At the ionic stage, the trapped electron is neutralized by an interstitial silver ion, with the formation of a neutral silver atom. The latter also plays the role of a deep electron trap, which leads to the growth of latent-image centers. It is obvious that, in principle, the two-stage mechanism of latent-image formation can be realized for any semiconductor on whose surface metal ions are adsorbed. In this case, the role of interstitial silver ions in the silver halide lattice must be played by ions adsorbed on the surface of the semiconductor, while the electronic stage of the process is determined by the intrinsic or impurity photoconductivity of the semiconductor. As in the case of silver halides, the new photographic process will be effective only if the photolysis process predominates over recombination of photoexcited carriers. The latter presupposes efficient capture of holes by surface levels that play the role of a chemical sensitizer. It is essential that in this case the spectral sensitivity of the process should be determined by the width of the forbidden band of the semiconductor (in the case of an intrinsic semiconductor) and can vary over wide limits in going from wide-band-gap to narrow-band-gap semiconductors. Naturally, for narrow-band-gap semiconductors the photographic effect is limited by dark fog, caused by the reduction of metal ions by equilibrium carriers. For wide-band-gap semiconductors, the electronic and ionic stages may be separated in time. At the electronic stage, deep surface levels are filled. Dark regression of the latent image at this stage is the slower, the deeper the level and the lower the temperature. At the ionic stage, the latent image is formed in the form of neutral metal particles, which can subsequently be developed by methods of physical development. For narrow-band-gap semiconductors both stages must proceed simultaneously. A specific feature of the new process is also that the nonequilibrium electrons reducing the metal ions may be either majority or minority carriers.

Fig. 1

Figure 1: Fig. 1

The method indicated above has been realized in a number of independently performed studies (1–5). In (3,4) the same method was used for infrared photography on narrow-band-gap semiconductors.

We investigated the process of photoreduction of silver ions from aqueous solutions of silver nitrate on the surface of certain dielectrics and semiconductors (silicon, PbI_2, PbS, CdS, HgI_2, SbSI). For some of the listed dielectrics and semiconductors the spectral distribution of the photographic effect was recorded. In doing so, for semiconductors a sensitization phenomenon was found: reduction of silver

···occurred in the region of the semiconductor' s intrinsic photosensitivity. The experiment was carried out as follows. A plate of the semiconductor under study was immersed in a vessel containing a solution of silver nitrate. Through the bottom of the vessel, an image was projected onto the surface of the semiconductor in the required spectral region. After exposure, the sample was removed from the solution and developed with one of the physical developers. In some experiments the sample was exposed directly under a layer of the physical developer. In other experiments a layer of gelatin (or another binder) was applied to the surface of a dielectric or semiconductor; this layer was treated with an $AgNO_3$ solution and subsequently exposed and developed by the method described above. Negative images were obtained on the materials studied, indicating photostimulated reduction of silver. Here we present the spectral distribution of the photographic effect for polycrystalline HgI_2 layers and two different dielectrics (mica and polymethyl methacrylate).

Fig. 1. Relative spectral distribution of optical density, referred to unit incident energy, for mica (*a*), organic glass (*b*), and polycrystalline HgI_2 layers (*c*)

The corresponding curves are shown in Fig. 1, where the ordinate gives the difference between the optical densities of the print and the fog, referred to unit incident energy, and the abscissa gives the wavelength. The spectral distribution for HgI_2, shown in Fig. 1, *c*, reveals a sensitization band with a maximum near 520 mμ, characteristic of the spectral distribution of the photoconductivity of mercuric iodide. A distinct sensitization effect was also observed by us for polycrystalline CdS and PbI_2 layers. As for dielectrics, as is evident from Fig. 1, *a*, *b*, their spectral sensitivity lies in the blue region and does not depend on the nature of the dielectric. This indicates that the sensitivity of the dielectrics is not intrinsic and is possibly associated with surface films of silver chloride or silver oxides formed when the dielectric comes into contact with the solutions. This is also supported by the absence of a photographic effect on dielectrics when the electronic and ionic stages are separated in time.

Analogous results were obtained on PbS layers, which at room temperature exhibit a photoconductivity maximum at $\lambda \simeq 2.5\,\mu$. PbS layers of p-type, obtained by vacuum evaporation and also by chemical precipitation in the reduction reaction of lead complexes with thiourea, were studied. A photographic effect was obtained on PbS layers for wavelengths $\lambda > 1.8\,\mu$ (when the layer was illuminated through a germanium filter). To obtain dense images, an exposure of $\sim 10^2$ sec was required at an energy of $\sim 10^{-4}$ watt/cm^2. By measuring the spectral distribution of photoconductivity it was established that the photographic sensitivity of PbS correlates with the photoelectric sensitivity. The mechanism of latent-image formation in PbS does not in principle exclude the formation of Ag_2S. However, the photoconductivity of Ag_2S is limited to $\lambda \simeq 1.4\,\mu$, which was additionally confirmed by us by studying the spectral distribution of photoconductivity and of the photographic effect on Ag_2S layers.

The process of reduction of the dye methylene blue in contact with a PbS layer upon illumination of the latter through a germanium filter was also investigated. After exposure, the latent image in the dye layer was developed with a physical developer. The process studied is analogous to the reduction of methylene blue in silver-halide emulsions. In our case, reduction of the dye occurs under intrinsic excitation of a narrow-gap semiconductor.

Finally, it should be noted that for some semiconductors (for example, SbSI) we observed the phenomenon of reversal: upon illumination of the semiconductor in the region of its intrinsic photosensitivity, a positive image was obtained.

It has already been pointed out above that, as in the case of silver-halide emulsions, the efficiency of the photographic process on a semiconductor is the higher, the lower the probability of electron-hole recombination. This means that under conditions of effective photolysis the recombination mechanism at the semiconductor surface changes substantially. Adsorbed metal ions constitute a new effective channel for electron capture, while holes must be effectively captured by other levels. It is possible that these levels are hydroxyl groups adsorbed on the semiconductor surface or molecules of the reducing agent. In this latter case no space charge is formed, and the semiconductor layer remains neutral during photolysis, as in the case of photolysis in the bulk of silver-halide crystals. Thus, the problem of chemical sensitization of the layer for the process under consideration is formulated in the same way as for silver-halide photography, although the specific nature of the hole channel in the two cases may be different.

The phenomenon of sensitized photolysis on semiconductors can be considered within the framework of the electronic theory of catalysis on semiconductors ([6]), by analogy with photoadsorption and photodesorption phenomena. In this way one can explain the dependence of the fog density on the position of the Fermi level in the semiconductor, and the possible transition of a negative image into a positive one. However, the latter phenomenon may also be caused by chemical reactions at the surface. For example, the transition of a negative to a positive may be represented as the result of effective capture of holes by semiconductor anions (for example, halogen ions) and their subsequent interaction with silver.

The study of the new photographic process has not only independent significance but, apparently, is also of interest for studying the nature of latent-image centers in silver-halide emulsions. If in both cases the centers are one and the same (and there is no basis for supposing the opposite), then their investigation on the surface of a number of well-studied semiconductors (silicon, germanium) can be carried out with the aid of known techniques, for example, photoconductivity kinetics, the field effect, etc. In this way the parameters of silver centers and their evolution in the process of latent-image formation can be determined.

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