Physical Chemistry

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1960

SovietRxiv

Abstract

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SENSITIZATION OF THE PHOTOEFFECT IN SEMICONDUCTORS BY ORGANIC DYES–ACIDITY INDICATORS

In a preceding series of studies in our laboratory, the phenomenon of optical sensitization of the internal photoeffect of a number of semiconductors—oxides and halides—by organic dyes of various classes was established and studied in detail (^1). In the present work, organic dyes were used as sensitizers whose molecules, by attaching or donating a proton, sharply change their color and the position of their absorption band in the spectrum.

The photoeffect was measured by the capacitor method (^2) in TlJ and ZnO layers dyed with acidity-indicator dyes, first, as usual, in air or in vacuum, and then after additional adsorption on them of HCl or NH_3 vapors. Vapors of concentrated hydrochloric acid and ammonia vapors were first carefully dried. For this purpose concentrated sulfuric acid was added to the hydrochloric acid. Further, the water vapors contained in the gases were frozen out by passing them through a trap cooled to −90°C. The vapor pressure of ammonia at −92° is 10 mm Hg, while vapors of pure HCl give the same pressure at −136° (^3). The experiments were carried out in air and in vacuum without substantial differences in the results.

According to Lutseyko (^4), the photo-e.m.f. of ZnO in the presence of ammonia vapors with an elasticity of 4 mm decreases by approximately a factor of two without a change in the spectral distribution. We found that the capacitor photo-e.m.f. of an undyed TlJ layer upon adsorption of HCl vapors increases by a factor of 2–3 without substantial change in the spectrum.

The results of experiments on the influence of gaseous HCl and NH_3 on the photoeffect of TlJ and ZnO dyed with various indicator dyes are given in Table 1 and in Fig. 1*. The total photoeffect in TlJ sensitized by indicators changed little in magnitude after adsorption of HCl, or even in some cases increased. But the spectral distribution of the sensitized photoeffect changed sharply, corresponding to the change in the absorption spectrum of the dye. After adsorption of gaseous NH_3, on the contrary, the sensitized photoeffect sharply decreased or disappeared completely in the case of TlJ. In contrast to TlJ, the sensitized photoeffect for ZnO disappears upon admission of HCl. Desorption of HCl leads to restoration of the former sensitized sensitivity of ZnO.

Thus, when in the neutral form, indicator dyes are optical sensitizers of the photoeffect both for the hole semiconductor TlJ and for the electron semiconductor ZnO. However, after the addition of HCl, i.e., in the protonated form, the same dyes sensitize the photoeffect in TlJ, but lose the ability to sensitize ZnO. In the anionic form, deprotonated under the influence of NH_3, the corresponding indicator dyes effectively sensitize the photoeffect in ZnO, but lose the ability to sensitize TlJ.

* In the figures, changes of the spectral curve in the region of the semiconductor' s intrinsic sensitivity are shown in a separate graph because of the difference in the scale of ordinates.

Table 1

Sensitization of the photoeffect in TlJ and ZnO by dyes–acidity indicators

Dyes	Color of aqueous solution and λ_{max} (mμ)*	Corresponding pH	Color of stained TlJ and ZnO	Sensitization of TlJ present	Sensitization of ZnO present
Aurin	Yellow. 540	6.9	Yellow.	+	+
Aurin	Red.	8.0	+ NH_3, red.	−	+
Aurin	Red.	8.0	+ HCl, yellow.	+	+
Safranin T	Red. 540	7.0	Red.	+	+
Safranin T	Red. 540	7.0	+ NH_3, red-brown. (540)	−	+
Safranin T	Red. 540	7.0	+ HCl, blue	+	−
Thymolphthalein	Colorless.	9.4	−		
Thymolphthalein	Blue	10.6	+ NH_3, blue	−	+
Thymolphthalein	Blue	10.6	+ HCl, colorless.		
Bromothymol blue	Brown. 580, 540	6.0	Brown.	+	+ (520)
Bromothymol blue	Blue 620, 540	7.6	+ NH_3, blue	−	+
Bromothymol blue	Blue 620, 540	7.6	+ HCl, yellow.	+(540)	−

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

Dyes	Color of aqueous solution and λ_{max} (mμ)*	Corresponding pH	Color of stained TlJ and ZnO	Sensitization of TlJ present	Sensitization of ZnO present
Nile blue	Blue 630	10	Blue	+	+
Nile blue	Pink	11	+ NH_3, pink.	−	+
Nile blue	Green 680	11	+ HCl, green	+	−
Congo red	Red. 520	5.2	Red.	−	+
Congo red	Red. 520	5.2	+ NH_3, violet.	−	+
Congo red	Blue 750, 540	3.0	+ HCl, blue	+	−

* The absorption maxima of the dyes in adsorbates of TlJ and ZnO are shifted somewhat toward longer wavelengths relative to the maxima in solutions.

The absence of sensitization of TlJ when it is colored with Congo red is explained by the fact that the dye gives up a proton when adsorbed on this semiconductor.

Fig. 1. Spectral distribution of the photo-e.m.f. in TlJ and ZnO stained with safranin T (**A**) and bromothymol blue (**B**): **1** –in air; **2** –after adsorption of HCl vapors; **3** –after adsorption of NH_3 vapors.

Fig. 2. Spectral distribution of the photo-e.m.f. in TlJ and ZnO stained with Congo red: **1** –in air; **2** –after adsorption of HCl vapors; **3** –after adsorption of NH_3 vapors; **4** –after very weak acidification with HCl vapors; **5** –after additional acidification of the dye with HCl vapors.

Indeed, when HCl vapor at a slight pressure is admitted onto a TlJ layer colored with Congo red, a sensitized photoeffect is immediately observed (Fig. 2), whose long-wavelength maximum belongs to the protonated form of the dye, while the maxima at 540 mμ belong to the neutral dye.

In addition, preliminary experiments were carried out on the influence of gaseous NH_3 and HCl on the photoeffect in TlJ colored with other dyes. Adsorption of HCl vapor by a TlJ layer colored with erythrosin, methylene blue, or malachite

Fig. 3. Spectral distribution of the photo-e.m.f. in TlJ colored with malachite green; 1 —in vacuum; 2 —in HCl vapor, at a pressure of 1-5 mm Hg.

Figure 3: Fig. 3. Spectral distribution of the photo-e.m.f. in TlJ colored with malachite green; 1 —in vacuum; 2 —in HCl vapor, at a pressure of 1-5 mm Hg.

green led to some increase in the intrinsic and sensitized sensitivity (Fig. 3). Adsorption of ammonia vapor somewhat decreased the intrinsic photoeffect and considerably suppressed sensitization.

Fig. 3. Spectral distribution of the photo-e.m.f. in TlJ colored with malachite green; **1** —in vacuum; **2** —in HCl vapor, at a pressure of 1-5 mm Hg.

The results obtained can be explained by the following effects on the surface levels of the semiconductor. Being adsorbed on the colored layers, HCl protonates the dye and at the same time creates acceptor levels on the surface of the semiconductor, depleting the surface electron levels formed on ZnO by adsorbed oxygen molecules, and on TlJ by adsorbed iodine molecules. But it is precisely from these surface levels, according to our concepts ([1]), that electron transfer to the conduction band takes place: in the case of ZnO, at the expense of an energy quantum absorbed by the dye. Therefore, upon adsorption of HCl, the dye-sensitized photoeffect decreases. In the case of TlJ, however, sensitization involves transfer of electrons from the filled band to surface levels, and therefore their depletion, caused by adsorption of protons, is favorable.

Adsorption of NH_3 produces the opposite effect, since it promotes the filling of the surface levels of oxygen and iodine with electrons, to which the excitation energy of the dye is transferred.

This explanation should be preferred to considerations concerning the height of the level reached upon excitation of the dye molecule. Indeed, from Table 1 and the figures we see that the shift of the absorption maximum toward longer wavelengths, observed upon protonation or deprotonation, does not affect the efficiency of sensitization.

Received
8 VII 1960

CITED LITERATURE

1. E. K. Putseiko, A. N. Terenin, ZhFKh, **23**, 676 (1949); DAN, **70**, 401 (1950); E. K. Putseiko, *Radiotekhnika i elektronika*, **1**, 1354 (1955); I. A. Akimov, E. K. Putseiko, DAN, **102**, 481 (1955); I. A. Akimov, ZhFKh, **30**, 1037 (1956); DAN, **121**, 311 (1958); A. Terenin, E. Putzeiko, I. Akimov, *J. Chim. Phys.*, **54**, 716 (1957).

2. E. K. Putseiko, DAN, **67**, 1009 (1949); *Izv. AN SSSR, Ser. fiz.*, **16**, 34 (1952).

3. *Handbook of Chemistry and Physics*, part 2, Cleveland, 1956, pp. 2151, 2157.

4. E. K. Putseiko, A. N. Terenin, in: *Problems of Kinetics and Catalysis*, **8**, Moscow, 1955, p. 53.

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