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THE EFFECT OF OXYGEN AND WATER ON THE ELECTRICAL CONDUCTIVITY OF ZINC OXIDE DYED WITH ERYTHROSIN

(Presented by Academician A. N. Terenin, 23 V 1960)

In previous communications ([1]) we considered a possible mechanism of electron exchange occurring on the surface of a number of oxide semiconductors with electronic conductivity when they are illuminated in the region of their intrinsic absorption in the presence of oxygen and water vapor. It was shown that the suppression of the electrical conductivity of these semiconductors by water vapor is due to the interaction of the latter with chemisorbed oxygen, as a result of which it is oxidized to hydroxide. The action of light evidently consists in the desorption of the radicals that are formed.

The works of E. K. Putseiko and A. N. Terenin ([2,3]) showed that the photoconductivity of zinc oxide can be sensitized to visible light by dyeing it with organic dyes. We undertook a comparative study of the change in the electrical conductivity of polycrystalline zinc oxide samples under the action of illumination in the region of the semiconductor' s intrinsic absorption and in the sensitization region, as well as of the influence of oxygen and water on these processes. Zinc oxide photoresistors were prepared by the method described earlier ([1]). To prepare sensitized samples, zinc oxide powder was mixed with an alcoholic solution of erythrosin of concentration $\sim 10^{-5}$ M/l.

The advantage of erythrosin in comparison with other sensitizing dyes consisted in its low absorption in the region of the photoelectric sensitivity of zinc oxide, owing to which one and the same dyed sample could be studied both in this region (mercury line 366 mμ) and in the sensitization region (mercury line 546 mμ).

Measurements of electrical conductivity were carried out with a direct-current amplifier that made it possible to measure currents from $3 \cdot 10^{-13}$ to $3 \cdot 10^{-5}$ a. The samples were illuminated by an SVDSh-250 mercury lamp through narrow-band light filters. The illumination of the sample was, for $\lambda 366$ mμ, 2.5–3 μW/cm^2, or 4.5–5.5 $\cdot 10^{12}$ quanta/cm$^2 \cdot$ sec, and for $\lambda 546$ mμ, 3–4 μW/cm^2, or 8–11 $\cdot 10^{12}$ quanta/cm$^2 \cdot$ sec. Taking into account that the dyed sample absorbs about 35–40% of the radiation with $\lambda 546$ mμ, which was verified by measuring

Fig. 1. Growth of the electrical conductivity of the specimen under illumination and decay in the dark in air at atmospheric pressure. 1 —undried air, λ546 mμ; 2 —the same at λ366 mμ; 3 —dry air, λ546 mμ; 4 —the same at λ366 mμ.

Figure 1: Fig. 1. Growth of the electrical conductivity of the specimen under illumination and decay in the dark in air at atmospheric pressure. 1 —undried air, λ546 mμ; 2 —the same at λ366 mμ; 3 —dry air, λ546 mμ; 4 —the same at λ366 mμ.

the diffuse-reflection spectrum of the samples, the number of absorbed quanta for this wavelength was 2.5—$4.5 \cdot 10^{12}$ per 1 cm^2 in 1 sec.

Figure 1 shows the change in the electrical conductivity of dyed zinc oxide upon illumination in atmospheric, undried air. In this case the magnitude of the stationary current upon illumination in the sensitization region (curve 1) is greater than upon illumination in the region of the intrinsic sensitivity of zinc oxide (curve 2), despite the fact that the number of absorbed quanta is smaller in the first case. The inertia of the process, especially of the decay, is considerably greater in the first case. Upon illumination in dry air (curves 3 and 4), the inertia of the processes is practically the same, while the stationary current is already greater for illumination in the region of the intrinsic sensitivity of ZnO.

Illumination in a high vacuum (Fig. 2, curves 1 and 2) is characterized by a considerable increase in electrical conductivity, somewhat greater for

illumination in the region of the intrinsic absorption of ZnO, and an extremely slow decay in the dark. This decay can be considerably accelerated if dry air or oxygen is admitted; moreover, the rate of decay from identical values of the electrical conductivity attained by illumination with radiation of λ546 or 366 mμ is also the same.

A substantial difference in the behavior of zinc oxide illuminated in the region of intrinsic absorption and in the sensitization region appears under the action of water vapor in the dark. Admitting water vapor at a pressure of 20 mm Hg to a specimen in vacuum, previously illuminated in the region of intrinsic absorption, causes a rapid and deep decrease of the electrical conductivity to the values that existed before illumination. The action of water vapor on the same specimen illuminated in the sensitization band proves to be considerably weaker (Fig. 3).

Fig. 1. Growth of the electrical conductivity of the specimen under illumination and decay in the dark in air at atmospheric pressure. 1 —undried air, λ546 mμ; 2 —the same at λ366 mμ; 3 —dry air, λ546 mμ; 4 —the same at λ366 mμ.

The observed features of the growth of electrical conductivity under illumination in the sensitization region and of its decay in the dark can be explained on the basis of the mechanism of sensitized photoconductivity (proposed by E. K.

Fig. 2. Growth of the electrical conductivity of the specimen under illumination in vacuum and decay in the dark upon admitting dry air. 1 —illumination with light of $\lambda 546$ mμ; 2 —the same at $\lambda 366$ mμ; 3 —decay upon admitting dry air after illumination with $\lambda 546$ mμ; 4 —the same at $\lambda 366$ mμ. The illuminances at $\lambda 546$ and 366 mμ were chosen so that the stationary current in both cases was the same.

Figure 2: Fig. 2. Growth of the electrical conductivity of the specimen under illumination in vacuum and decay in the dark upon admitting dry air. 1 —illumination with light of $\lambda 546$ mμ; 2 —the same at $\lambda 366$ mμ; 3 —decay upon admitting dry air after illumination with $\lambda 546$ mμ; 4 —the same at $\lambda 366$ mμ. The illuminances at $\lambda 546$ and 366 mμ were chosen so that the stationary current in both cases was the same.

Putsheiko and A. N. Terenin), which consists in the transfer of light energy to oxygen traps. Such traps may be surface compounds $Zn^+O_2^-$ (*), whose levels are located at a distance of ~ 1 eV from the bottom of the conduction band. Illumination with visible light with quantum energy > 1 eV (in our case 2.3 eV) causes decomposition of this compound and desorption of oxygen:

$$Zn^+O_2^- \underset{h\nu}{\rightleftharpoons} Zn^+ + e + O_2. \tag{1}$$

Fig. 2. Growth of the electrical conductivity of the specimen under illumination in vacuum and decay in the dark upon admitting dry air. 1 —illumination with light of $\lambda 546$ mμ; 2 —the same at $\lambda 366$ mμ; 3 —decay upon admitting dry air after illumination with $\lambda 546$ mμ; 4 —the same at $\lambda 366$ mμ. The illuminances at $\lambda 546$ and 366 mμ were chosen so that the stationary current in both cases was the same.

Under illumination in the region of intrinsic absorption, there is observed, in addition, desorption of hydroxyl radicals, occurring as a result of the decomposition of an exciton at the levels of their chemisorption, located, because of the greater electron affinity of hydroxyl, below the oxygen levels:

$$Zn^+OH^- \underset{h\nu'}{\rightleftharpoons} Zn^+ + e + :OH. \tag{2}$$

Under illumination in the sensitization region, desorption of hydroxyls does not occur, since the quantum energy of visible light proves already insufficient.

sufficient for the decomposition of the surface compound Zn^+OH^-. The hydroxyl chemisorption levels remain occupied, and therefore, upon subsequent admission of water vapor, decomposition of molecules of the latter and chemisorption of new hydroxyls do not occur. The slight decrease in electrical conductivity in this case, shown in Fig. 3 (curve 2), may be caused by chemisorption of water

Fig. 3

Figure 3: Fig. 3

molecules without their decomposition, but this assumption requires additional experimental confirmation.

Fig. 3. Decrease in the electrical conductivity of the specimen upon admission of water vapor in the dark after illumination in high vacuum with light of λ366 mμ (1) and λ546 mμ (2)

Admission of dry oxygen causes the same decrease in electrical conductivity (Fig. 2), regardless of the radiation with which the semiconductor had previously been illuminated, since in both cases the liberated oxygen levels are filled.

The absence of hydroxyl chemisorption after illumination in the sensitization region determines the characteristic features of the increase in electrical conductivity upon illumination in humid air and of the decrease in the dark. Upon illumination in the region of intrinsic absorption in the presence of water vapor, the reverse reaction according to equation (2) proceeds rapidly and the equilibrium proves to be shifted to the left; as a result, the value of the stationary (equilibrium) electrical conductivity is lower than upon illumination in the sensitization region, when reaction (2) does not take place, while the reverse reaction (1) proceeds slowly, as is evident from a comparison of the rates of decrease of electrical conductivity under the action of water and oxygen.

The considerations presented explain the absence of a photochemical reaction of photooxidation of water upon illumination of aqueous suspensions of colored zinc oxide with visible light (^5). Despite the formation of a large number of conduction electrons, decomposition of water molecules does not occur and the products of photooxidation—hydrogen peroxide and hydroxyl radicals—are not formed.

In conclusion, I express my gratitude to Academician A. N. Terenin, under whose guidance this work was carried out.

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