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PHOTOSORPTION OF OXYGEN ON CADMIUM SULFIDE

(Presented by Academician A. N. Terenin, 9 XII 1963)

Until now, photosorption and photodesorption of gases and vapors have been found for a very small number of semiconductor adsorbents. Photosorption has been observed for J_2 on TlJ ([1]), O_2 on ZnO ([2]), TiO_2 ([3]), ZnS ([4]), H_2 on TiO_2 ([5]), and photodesorption of O_2 from ZnO ([6]).

We have discovered and investigated photosorption of O_2 on CdS. In the work, polycrystalline CdS samples were used, both industrial ("pure," "for semiconductors") and laboratory-prepared ones (the surface area of the adsorbents was not measured). With respect to photosorption of O_2, all of them behaved qualitatively alike. The experiments were carried out mainly on "pure" CdS samples and on laboratory-prepared samples. CdS powder was placed in a flat glass cuvette measuring $10 \times 10 \times 1$ mm. The working vessel, with a volume of about 35 cm^3, which included, in addition to the cuvette, the sensor of a Pirani manometer and a branch tube for gas analysis by condensability, was separated from the rest of the vacuum apparatus by a greaseless brass valve with a fluoroplastic seal. A vacuum of 5×10^{-7}–1×10^{-6} torr was produced by two mercury diffusion pumps connected in series. The manometer sensor was a tungsten filament of diameter 11 μ placed in a thin-walled glass tube (diameter 8 mm). At an operating temperature of 100° the resistance of the sensor was about 50 ohms. The sensor was connected into one arm of a Wheatstone bridge. The bridge was adjusted by changing the bridge supply current. The bridge unbalance signal was first amplified by one stage of an FEOU-15 photoelectric amplifier and recorded by an EPP-09 automatic potentiometer. The sensitivity of the manometer to oxygen was 1×10^{-6} torr per 1 mm of scale. Incandescent lamps of 30 or 300 W power were used to illuminate the adsorbent. In most experiments, illumination of the CdS layer was carried out with a 30-watt lamp without a condenser. Infrared radiation was filtered out with a water filter. Spectral measurements were carried out with a homemade high-aperture (1 : 3) mirror monochromator with a replica diffraction grating. Conditioning of the

Fig. 1

Figure 1: Fig. 1

adsorbent consisted in heating in vacuum at 300° for 6–8 hours and for about an hour at 400°. This was sufficient to stop gas evolution from the sample both in the dark and under illumination. Oxygen, obtained by decomposition in vacuum of $KMnO_4$ ("chemically pure"), was admitted into the working vessel to a pressure of $5 \cdot 10^{-3}$–$2 \cdot 10^{-2}$ torr. Illumination of the adsorbent was carried out after saturation of dark adsorption.

Below are described the results of an investigation of the reproducibility and of the dependence of photosorption of O_2 on CdS on the temperature, intensity, and wavelength of the light.

Figure 1 presents the experimental curve of the irreversible decrease in the pressure of O_2 in the working vessel upon illumination of CdS. A control experiment with illumination, under the same conditions, of a cuvette without adsorbent showed no change in the pressure in the working vessel. Photosorption curves recorded successively

on the same CdS sample showed that from illumination to illumination the magnitude of photosorption decreases. It was found that, in order to restore the photosorption activity, after each illumination the sample had to be heated in vacuum at 200° for 10 min. Such treatment ensured reproducibility of the initial photosorption rate within 10% and of the subsequent course of the photosorption curve within 5% in experiments lasting 1–2 days (10–15 illuminations). Preliminary illumination of CdS powder in vacuum had no noticeable effect on the photosorption activity.

Usually the experiments on photosorption of O_2 were carried out at room temperature. Raising the temperature of the sample above room temperature led to a rapid decrease in photosorption. Conversely, when the temperature of the adsorbent was lowered from 20° to −60°, an increase in photosorption and an exponential growth of the initial photosorption rate V_0 were observed. The "activation energy" of photosorption, determined from the slope of a straight line in coordinates $\ln V_0$, $1/T$, proved to be equal to −4.5 kcal/mol.

Fig. 1. Photosorption of O_2 on CdS. Initial pressure of O_2 $2 \cdot 10^{-2}$ torr. The arrows indicate the beginning and end of illumination.

Measurement of the dependence of the initial photosorption rate on the intensity I of the light incident on the adsorbent was carried out with a 30-watt lamp. A 100-fold change in the light intensity was achieved by moving the light source relative to the cuvette (the minimum distance between them was 5 cm, the maximum 50 cm). The experiment consisted in obtaining a series of photosorption curves corresponding to different light intensities. To eliminate possible systematic error, illumination in the experiments was carried out both

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

while moving from low intensities to high ones and from high to low ones, and with alternation of low and high intensities. The results of the measurements, presented graphically in coordinates $\log V_0$, $\log I$, fell, within the limits of error, on a straight line (Fig. 2). On the basis of this, the relationship between the initial photosorption rate and the light intensity can be described by the equation

Fig. 2. Dependence of the initial rate of photosorption of O_2 on CdS on light intensity. The values of a are equal to 0.7 (1) and 0.8 (2).

$$\log V_0 = \log k + a \log I, \quad \text{or} \quad V_0 = kI^a,$$

where k and a are constants. The values obtained for a lay between 0.5 and 1. A value of a close to 0.5 was observed on fresh samples, while a value of a close to 1 was observed on samples after repeated experiments with photosorption of O_2. In

in multi-day experiments with a single specimen, a gradual increase in a from 0.5 to 1 could be observed.

In view of the uncertainty in the exact value of a, the study of the spectral dependence of the photosorption of O_2 on CdS was carried out with monochromatic radiation reduced to the same intensity. When an incandescent lamp and a monochromator were used, this was achieved by changing the filament heating of the lamp; the intensity of the monochromatic radiation was monitored with a thermopile. The investigation was carried out in the region 400–900 m . The spectral width of the monochromator slit was 10 m . Figure 3 gives the curve of the spectral dependence of the initial rate of photosorption of O_2 (curve 1) and the spectrum of diffuse reflection of CdS powder measured in air with a recording spectrophotometer SF-2m (curve 3). As can be seen from Fig. 3, the action spectrum of photosorption is characterized by a maximum near 540 m , located at the edge of the intrinsic absorption band of CdS powder, and may be associated with absorption of light by the adsorbent surface.

Fig. 3. Spectral dependence of the initial rate of photosorption of O_2 on CdS (1) and of the photoconductivity (2), diffuse reflection (3), and compensatory photo-e.m.f. (4) of CdS powder

The fact that the increase in adsorption of O_2 upon illumination of CdS is a phenomenon of nonthermal origin, caused by heating of the adsorbent by the

radiation it absorbs, is evident, first, from the experiments on the temperature dependence and, second, from the selectivity of the action of light. This, as well as the fact that enhancement of adsorption of O_2 upon illumination was observed on all CdS specimens of different origin investigated in the experiments, made it possible to regard this phenomenon as photosorption of O_2 on CdS.

Comparison of the data obtained for photosorption of O_2 on CdS with the information available in the literature on the photoelectric properties of CdS ([7]) makes it possible to assume the existence of a connection between photosorption of O_2 and photoelectric processes in CdS. In order to clarify the actual existence of such a connection, a series of experiments was carried out in which the photoconductivity of CdS powder was measured simultaneously with photosorption of O_2.

To measure the conductivity, two electrodes of gilded molybdenum wire were sealed into a cuvette of the same type as in the experiments described above; the gap between them, which was about 8 mm, was filled with CdS powder. The measurement was made with direct current (voltage on the specimen 5–20 V) using an EMU-3 amplifier, with the results recorded on an automatic EPP-09 potentiometer. The measure of photoconductivity ($\Delta\sigma_\phi$) was the difference between the stationary electrical conductivity under illumination ($1/R_\phi$) and in the dark ($1/R_t$). After training, the specimens had a resistance of 10^8–10^{12} Ω; upon illumination with a 30-watt lamp placed 5 cm from the powder layer, the resistance decreased by 1–2 orders of magnitude.

As the experiments showed, all CdS specimens on which photosorption of O_2 was studied possessed photoconductivity, and when the conditions of thermal treatment of the adsorbent were changed, the photosorption of O_2 and the photoconductivity of CdS changed in concert. The decrease in the initial rate of photosorption observed in the course of the experiments was accompanied by a decrease in photoconductivity as well; moreover, the conditions for reproducibility of photosorption of O_2 (10-minute heating

at 200° in vacuum proved suitable also for reproducing the magnitude of the photoconductivity of CdS.

When the intensity of the incident light was varied, both the photoconductivity of CdS and the initial rate of photosorption of O_2 changed in qualitatively the same way, obeying the power law found for photosorption (see above). The difference appeared in the value of the exponent a: the numerical value of a for the photoconductivity was smaller than the value of a for the initial rate of photosorption; in other words, when the intensity of the incident light was changed, the initial rate of photosorption changed more strongly than the photoconductivity.

Figure 3 presents curves recorded simultaneously for the spectral dependence of the initial rate of photosorption of O_2 (curve 1) and of the photoconductivity of CdS (curve 2). The spectral-dependence curves, similar in shape, proved to

be shifted relative to one another: the maximum of the photosorption spectrum is located near 540 mμ, and that of the photoconductivity near 600 mμ. For the same CdS sample with which curves 1, 2, and 3 in Fig. 3 were obtained, the spectrum of the capacitor photo-emf was measured in air (Fig. 3, curve 4). As can be seen from Fig. 3, the spectra of all the measured photoresponses (photosorption, photoconductivity, capacitor photo-emf) do not coincide with one another. In work [8] it was shown that, in measurements on thick samples, the spectra of the photoelectric sensitivity of semiconductors determined by different methods (photoconductivity, capacitor photo-emf, contact potential, dielectric losses) may fail to coincide with one another and with the absorption spectrum of the semiconductor. The powdered CdS samples investigated by us were thick layers, and it is possible that the discrepancy between the spectra of the various photoresponses is connected precisely with this circumstance. In any case, from consideration of the results presented in Fig. 3 it is evident that the spectrum of photosorption of O_2 lies in the region of the photoelectric sensitivity of CdS.

Thus, the results of the simultaneous study of photosorption of O_2 and photoconductivity of CdS showed that photosorption and photoconductivity change in parallel, that their dependence on the intensity of the incident light is qualitatively the same, and that photosorption of O_2 is caused by light falling in the region of the photoelectric sensitivity of CdS. Although the mechanism of photosorption of O_2 on CdS remains unclear, the investigation nevertheless shows a close connection between photosorption and photoelectric processes in the adsorbent.

In conclusion, I take this opportunity to express my gratitude to Academician A. N. Terenin for supervising the work.

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REFERENCES

[1] A. N. Terenin, *Problems of Kinetics and Catalysis*, **8**, 17 (1955); ZhFKh, **6**, 189 (1935); L. N. Kurbatov, ZhFKh, **14**, 1049 (1940).
[2] A. Terenin, Yu. Solonitzin, *Disc. Farad. Soc.*, **28**, 28 (1959).
[3] D. R. Kennedy, M. Ritchey, J. Mackenzie, *Trans. Farad. Soc.*, **54**, 119 (1958).
[4] A. Kobajashi, S. Kawayi, *J. Phys. Soc. Japan*, **10**, 270 (1955); **11**, 369 (1956).
[5] V. L. Rapoport, Yu. P. Solonitsyn, DAN, **143**, 1149 (1962).
[6] Yu. P. Solonitsyn, ZhFKh, **32**, 2142 (1958); I. A. Myasnikov, S. Ya. Pshezhetskii, DAN, **99**, 125 (1954).
[7] R. Bube, *Photoconductivity of Solids*, IL, 1962; L. Lambe, C. C. Klick, *Progress in Semiconductors*, **3**, London, 1958; E. K. Putseiko, Izv. AN SSSR, ser. fiz., **15**, 707 (1951); B. T. Kolomiets, DAN, **83**, 561 (1952); J. Woods, *J. Electronics*

and Control, **5**, 417 (1958).
[8] I. A. Akimov, E. K. Putseiko, *Fiz. tverd. tela*, **4**, 1542 (1962).

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