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PHOTOCONDUCTIVE PROPERTIES OF THIN ELECTROLYTICALLY DEPOSITED CdS LAYERS

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The surface and bulk photoconductivity of thin CdS layers — obtained by electrolytic deposition on the surface of a Cd-anode in a 0.1 molar aqueous solution of Na_2S has been studied. The photocurrent-illumination intensity characteristics, spectral distributions of photosensitivity and the dependence of the lifetime of photocurrent carriers on the illumination intensity, wavelength of the exciting light and temperature have been determined.

1. Introduction

Photoconductive cadmium sulphide is widely used in electronic devices, such as photoresistors, light amplifiers and image converters. Many methods for obtaining this material have been described [1–5]. Intensive studies have been carried out recently concerning thin CdS layers prepared by means of vacuum evaporation, sintering, chemical deposition, solution spraying and sputtering. All these methods have some advantages and disadvantages, and all are used for some special purposes. The main disadvantage of these traditional methods of preparing thin CdS layers lies in the necessity of using very complicated arrangements, such as, for example, high-vacuum chambers or high-temperature furnaces.

The photoconductive properties of CdS are dependent on the method of sample preparation. As it follows from the literature data [6–9], cadmium sulphide shows good photoconductivity when illuminated by visible light. According to Weith [9], the maximum

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photosensitivity of thin CdS layers obtained by vacuum evaporation technique occurs at a wavelength of about 500 nm. According to Jabłońska and coworkers [4] the position of the maximum of photosensitivity for these layers depends on the thickness of the sample and for layers 1—0.35 μm thick this maximum lies at a wavelength of about 470 nm. However, as is shown by Lashkarev [6], the maximum of photosensitivity of CdS single crystals is shifted toward the longer wavelengths in comparison to the thin CdS layers.

The present paper describes a new, very simple method of obtaining thin CdS layers with a large surface area by the electrolytic deposition technique. Some photoelectric properties are also demonstrated.

2. Preparation of thin CdS layers

Thin CdS layers were deposited electrolytically on a parent substrate of cadmium platellets (99.95% purity) containing admixtures of Zn (0.01%), Fe (0.03%), Cu (0.005%) and Tl (0.005%). Before the process of electrolysis, the cadmium platellets were cleaned

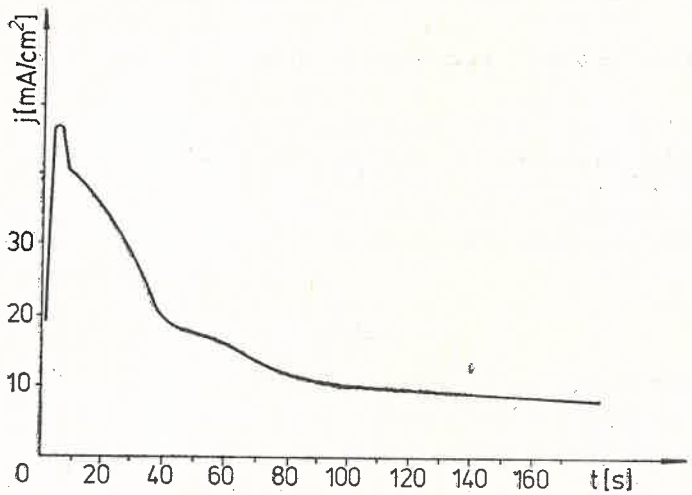

Fig. 1. Time dependence of the current density j during electrolytic deposition of CdS at a constant voltage (12 V)

and chemically polished in order to remove the surface impurities. Cadmium platellets prepared in such manner were used as anodes for the electrolytic formation of the CdS film in a 0.1 mol. aqueous solution of Na_2S. Platinum platellets served as the cathode.

Under these conditions a thin CdS layer is formed on the surface of the cadmium anode. The electrolytic deposition of CdS layers was carried out at a constant voltage (12 V). The changes in the current density during electrolytic deposition of CdS layers are shown in Fig. 1. As seen, the current density reaches its maximum in a short time and then slowly decreases. The process of electrolytic deposition of a CdS layer of the thickness of the order of 10^{-6} m persists merely a few minutes.

In order to check whether the layer formed on the surface of a Cd-anode was truly CdS, X-ray phase analysis was carried out using DRON-1.5 type diffractometer. The results of this analysis showed that the layer covering the Cd-anode is a mixture of crystalline (α and β) CdS, amorphic CdS and $Cd(OH)_2$.

3. Experimental conditions and methods

The surface photoconductivity of electrolytically deposited CdS layers was measured using gap type cells (Fig. 2), which were prepared as follows: a cadmium platellet coated with the CdS layer was glued to the slide of an organic glass. The CdS layer covering the opposite side of the cadmium platellet was removed mechanically and the cadmium substrate was dissolved in mercury by the method described by Huber [10]. Aluminium electrodes were evaporated onto the free surface of the CdS layer using a suitable mask. The effective length of the Al-electrodes and distance between them were 20 cm and 1 mm, respectively.

To study the photoconductivity through the layer thickness (bulk photoconductivity), sandwich type cells were used (Fig. 3). A glass slide coated with a conductive, transparent

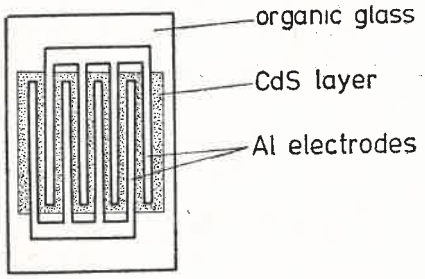

Fig. 2. The gap electrode type cell for the surface photoconductivity measurements

film of tin oxide was glued to the surface of the CdS layer with the aid of cyjanoacrylic paste. Under relatively small pressure the paste penetrates into the surface pores giving a good, direct contact between the transparent electrode and the examined CdS layer.

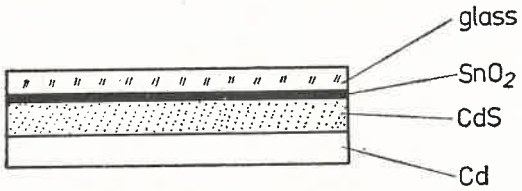

Fig. 3. Sandwich type cell for bulk photoconductivity measurements

As the second, nontransparent electrode the parent cadmium substrate was used. The surface area of sandwich type cells was about 4 cm^2.

Photocurrent as a function of the illumination intensity was measured using white as well as monochromatic light, obtained with the aid of interference filters. The intensity of

illumination of the cell's surface was controlled with the aid of a photomultiplier or luxmeter IO–16 with the Φ-102 type photoelement.

The spectral distribution of the photosensitivity of the investigated cells was measured using monochromatic light obtained with the aid of a ZMR-monochromator and a light source of known spectral energy distribution. The photocurrent was measured using a 219-type electrometer.

The time inertia of the photoconductivity was investigated by excitation of the photocurrent with the light beam modulated by means of a rotating shield modulator. The light beam modulated in the form of symmetrical or asymmetrical pulses was obtained by using the appropriate shields.

The measurements of the lifetime τ of the bulk photocurrent carriers were performed using the method described by Ryvkin [11]. The photocurrent was excited by an asymmetrically modulated light beam (Fig. 4). The lifetime τ of the photocurrent carriers was determined from the relation

$$\tau = \frac{\Delta\sigma_{st}}{\Delta\sigma_{\sim}} t_d. \tag{1}$$

The stationary value $\Delta\sigma_{st}$ of the photoconductivity increases and the value $\Delta\sigma_{\sim}$ of the increase of photoconductivity due to illumination by a modulated, rectangular light beam were recorded directly from the oscilloscope screen.

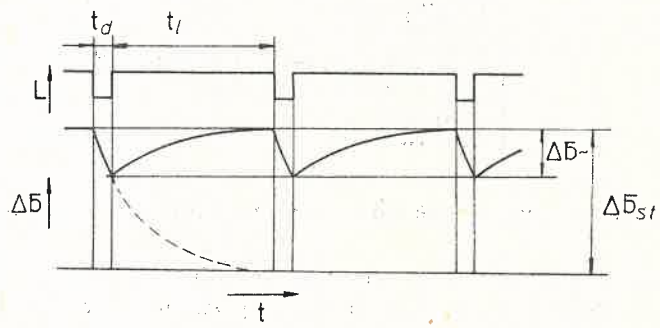

Fig. 4. Time dependence of the photoconductivity induced by asymmetrical rectangular light waves ($t_d \ll \tau \ll t_l$)

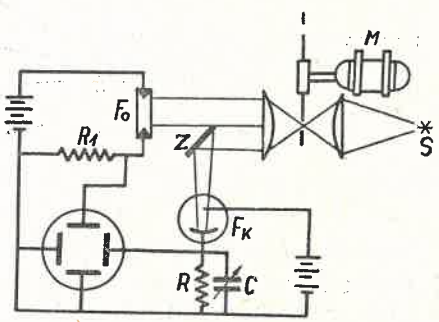

Fig. 5. Sketch of the apparatus for the lifetime measurements by the phase shift compensation method. M — modulator, S — light source, Z — mirror, F_k — photocell, F_o — investigated photoresistor

It must be noted, however, that relation (1) holds only for the case when $t_d \ll \tau \ll t_l$, where t_l — time of the sample's illumination and t_d — time interval during which the sample is kept in darkness. For the surface photoconductivity it is very difficult to satisfy this condition since, here, for the surface recombination the lifetime τ is much smaller than that for the bulk photocurrent carriers. Therefore, the lifetime of surface photocurrent carriers was measured using the so called phase shift compensation method, described in [11]. Fig. 5 shows a sketch of the arrangement used in these measurements. One part of the modulated light beam illuminates the investigated sample, the second — vacuum photocell. Photocurrent excited in the investigated sample is delayed as compared to the photocell's current. The voltage drop on the investigated sample circuit and in the photocell circuit are transmitted to the perpendicular and horizontal deflection systems of the oscilloscope and the hysteresis loop is observed on the screen. The phase shift can be compen-

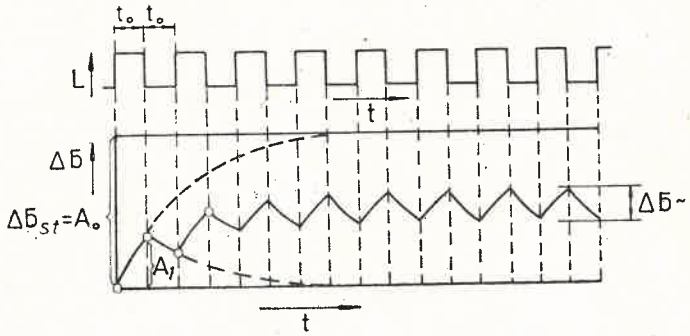

Fig. 6. Time dependence of the photoconductivity $\Delta\sigma$ of semiconductor illuminated with the symmetrical rectangular light waves

sated by adjusting the RC product in the photocell circuit (Fig. 5) and then a straight line on the oscilloscope screen is obtained. The value of the lifetime equals the RC product compensating the phase shift.

The frequency characteristics of the photoconductivity were determined by the method described by Ryvkin [11]. The photocurrent was excited using a modulated symmetrical rectangular light beam (Fig. 6). Under these conditions at $t = 0$, the hitherto nonilluminated sample starts to be illuminated by the rectangular light pulse. In the time interval from $t = 0$ to $t = t_0$ the photoconductivity increases according to the formula:

$$\Delta\sigma = A_0[1 - \exp(-\tau/t)], \tag{2}$$

up to the stationary value $\Delta\sigma_{st} = A_0$. At the moment $t = t_0$, however, the illumination is interrupted and the photoconductivity starts to decrease according to the formula:

$$\Delta\sigma = A_1 \exp(-\tau/t). \tag{3}$$

These grows and decays of the photoconductivity are lying on the curve increasing to the moment at which the lower and upper equilibrium position of the curve is reached

(Fig. 6). Values of $\Delta\sigma_{\sim}$ and $\Delta\sigma_{st}$ were recorded directly from the oscilloscope screen. The frequency of modulation of the light beam was measured with the use of stroboscope SB-05.

All the measurements were performed at room temperature.

4. Results of measurements

Thin, electrolytically deposited CdS layers show a good photoconductivity in the visible light range. Gap type cells show a dark resistivity of the order of $10^{13}\ \Omega$. Under illumination with an emittance efficiency of 1000 lx white light, the resistivity of these cells decreases by 4 orders of magnitude ($10^9\ \Omega$).

The dark resistivity of the sandwich type cells is of the order of $10^8\ \Omega$. Under illumination with an emittance efficiency of 1000 lx, the resistivity of sandwich type cells decreases by 2 orders of magnitude ($10^6\ \Omega$).

In order to determine some photoelectric properties of the investigated CdS layers, the dependence of the photocurrent I on the illumination intensity L must be previously determined. For a relatively narrow range of intensity of illumination L (in our case 0–10^4 lx) this dependence can be represented by the simplified formula:

$$I = CL^{\gamma}, \tag{4}$$

where: γ — constant for a given photoresistor, C — factor depending on the light wavelength. For the majority of photoresistors the value of γ is smaller than one ($\gamma < 1$) [12].

The measurements of the dependence of photocurrent I on the intensity of illumination L were carried under continuous illumination conditions. The cells were illuminated with a constant emittance efficiency L until the photocurrent reached its stationary value. Results of these investigations for the case where the cells were illuminated with white light are given in Fig. 7. In the case of illumination by monochromatic light (474 nm and 365 nm) the results are the same as those given in Fig. 7. The numerical values of γ were determined from the slope of straight lines representing the dependence $\ln I = f(\ln L)$. For gap type cells (surface photoconductivity) γ is approximately equal to 0.76. For the sandwich type cells (bulk photoconductivity) the value of γ is about 0.48.

The spectral distribution of photosensitivity of thin electrolytically deposited CdS layers was measured using monochromatic light (350 nm — 700 nm) with a constant emittance efficiency L. The results of these measurements are shown as curves denoted by $b-1$ and $s-1$ in Fig. 8. As it is seen, the maximum of the spectral sensitivity of bulk photocurrent lies at the wavelength $\lambda \simeq 500$ nm. This is in agreement with the literature data [8] on the spectral distribution of bulk sensitivity of thin CdS films obtained by the vacuum evaporation technique.

The maximum of the surface photosensitivity occurs at the wavelength $\lambda \simeq 460$ nm. The shift of the maximum of the surface photosensitivity toward the shorter wavelengths as compared to the bulk photoconductivity is probably due to the surface states, because, as it is known from literature [13], the stationary value of the photoconductivity and their spectral distribution may be affected by recombination at surface defects.

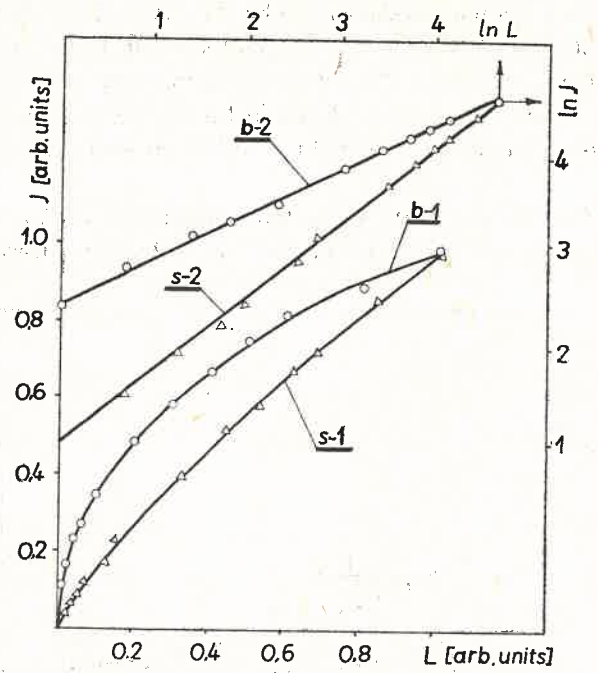

Fig. 7. Linear (*1*) and logarithmic (*2*) plots of the dependence of the photocurrent intensity I on the intensity of illumination L of the surface of the cells. *b* and *s* denotes a sandwich type and a gap type cell, respectively

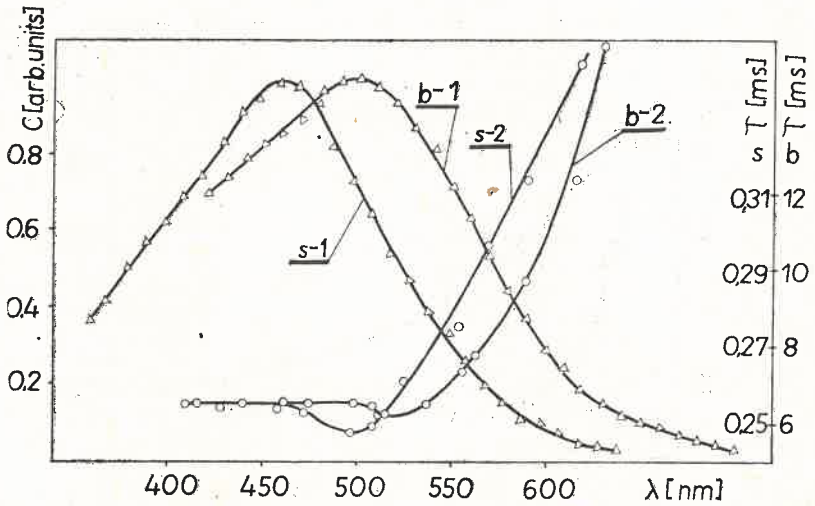

Fig. 8. Spectral distributions of the photosensitivity C (*1*) and lifetime τ of carriers (*2*) for sandwich type (*b*) and for gap type (*s*) cells

The time inertia of photoconductivity can be characterized by the so-called frequency characteristics, namely the dependence of the photocurrent on the frequency of modulation of a light beam. The frequency characteristics of the bulk- and surface photoconductivity of the investigated CdS layers are shown in Figs 9 and 10, respectively. The samples were illuminated using monochromatic light $\lambda = 474$ nm with a constant luminous efficiency.

As seen from Fig. 9 (curve *1*) the bulk photoconductivity of the CdS layers decreases to one-half of the stationary value at a frequency of 40 Hz. For surface photoconductivity

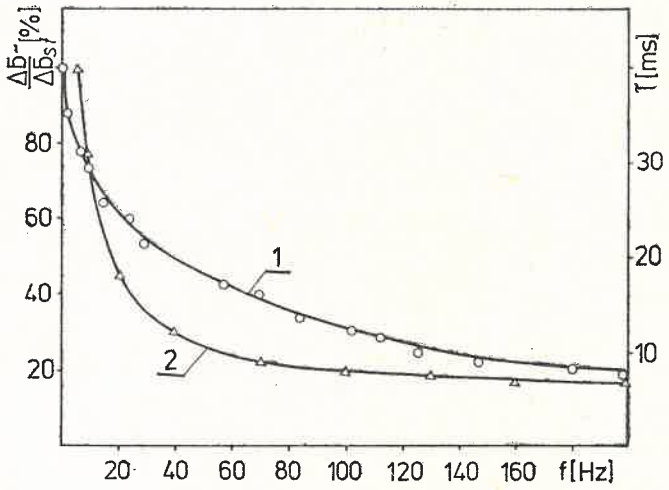

Fig. 9. Frequency characteristics of bulk photoconductivity (curve *1*) and the lifetime of photocurrent carriers (curve *2*) for electrolytically deposited CdS layers

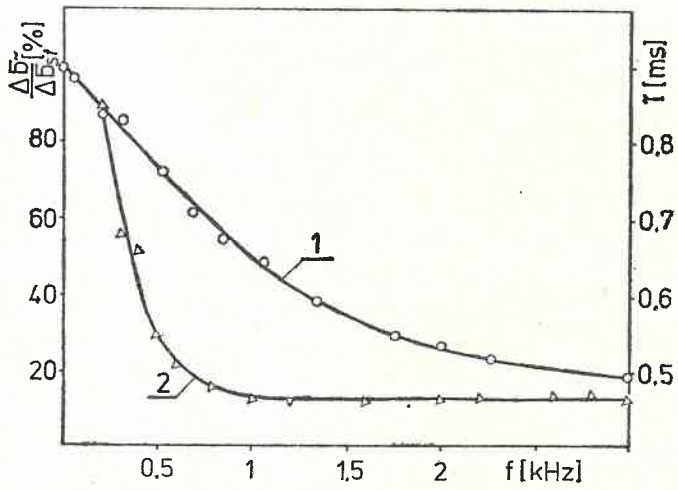

Fig. 10. Frequency characteristics of the surface photoconductivity (curve *1*) and the lifetime of photocurrent carriers (curve *2*) for electrolytically deposited CdS layers

(Fig. 10, curve *1*) its value decreases to one-half of the stationary value at a frequency of about 1 kHz.

From the frequency characteristics the lifetime τ of the photocurrent carriers can be determined, using the relation reported by Ryvkin [11]:

$$\Delta\sigma = \Delta\sigma_{st} \operatorname{th} \frac{1}{4\tau f}. \tag{5}$$

Frequency dependences of the lifetime for the bulk- and surface photoconductivity obtained in this way are shown as the curves *2* in Figs 9 and 10, respectively. As seen, the lifetime τ for the bulk photoconductivity reaches a constant value at frequencies higher than 80 Hz, whereas in case of the surface photoconductivity the lifetime τ is observed to have a constant value at frequencies higher than 1 kHz.

It must also be noted that the numerical value of this constant lifetime for surface conductivity (10^{-4} s) is one order of magnitude smaller than that for the bulk photoconductivity (10^{-3} s).

The dependence of the lifetime of photocurrent carriers on the intensity of illumination was also investigated. During these measurements the photocurrent was excited using

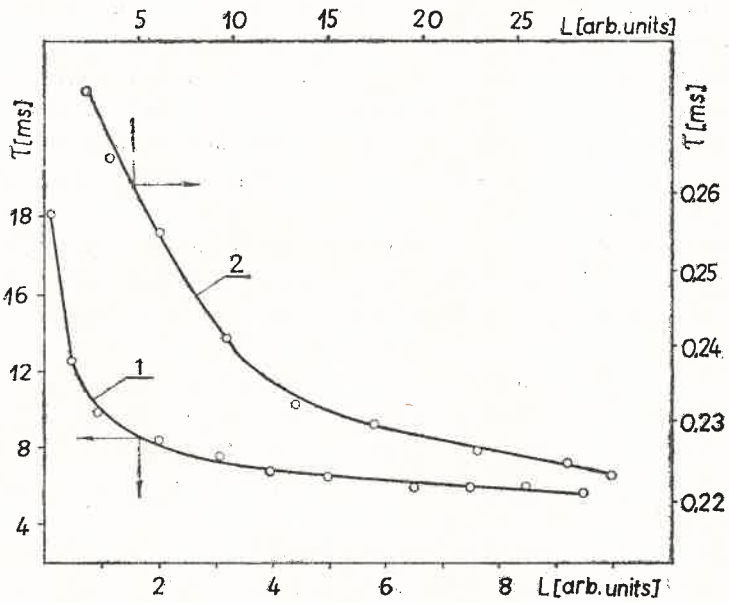

Fig. 11. Dependence of the lifetime τ of carriers on the intensity of illumination L of sandwich type (*1*) and gap type (*2*) CdS cells

monochromatic light of a wavelength corresponding to the maximum of photosensitivity. The bulk- and surface photoconductivity was excited using light of $\lambda = 510$ nm and 474 nm, respectively. The results of these measurements are shown in Fig. 11. It is seen that the lifetime is strongly dependent on the illumination intensity but only in the region of low intensities.

Curves *2* in Fig. 8 show the experimentally determined spectral distributions of the lifetime for the bulk- and surface photoconductivity. During these measurements the photocurrent was excited with monochromatic light obtained through interference filters. The shape of the spectral distribution of the lifetime for the investigated CdS layers (curves *2* on Fig. 8) is similar to the spectral distribution of the lifetime of photocurrent carriers in CdS single crystals reported by Lashkarev [6].

It must be noted that for the surface as well for bulk photoconductivity, the lifetime τ of photocurrent carriers does not depend on the wavelength for wavelengths shorter than λ_{max} at which the maximum of the photosensitivity occurs. In Fig. 8 it is also seen that on the spectral distribution of the lifetime a minimum occurs at the wavelength corresponding to the quantum energy equal to the width of the forbidden gap in the CdS (2.4 eV). In the wavelength range corresponding to the long wave decrease of the photosensitivity, the lifetime rapidly increases with increasing wavelength of the exciting light.

5. Conclusions

Thin CdS layers were prepared by electrolytic deposition on the Cd-anode from an aqueous solution of Na_2S. These layers show high dark resistivity.

The surface photosensitivity of thin electrolytically deposited CdS layers is greater than the bulk photosensitivity of the same layers ($\gamma_s = 0.76$; $\gamma_b = 0.48$).

The maximum of the spectral distribution of the surface photoconductivity of these layers is shifted toward shorter wavelengths (460 nm) as compared to the bulk photoconductivity (500 nm).

The positions of the maxima of spectral response of surface- and bulk photoconductivity of electrolytically deposited thin CdS layers are the same as in the case of surface- and bulk photoconductivity of the thin CdS layers obtained by the vacuum evaporation technique [4, 9].

The lifetime τ of the photocurrent carriers for bulk photoconductivity of electrolytically deposited CdS layers is of the same order of magnitude (10^{-3} s) as in case of CdS single crystals [6, 14]. In case of surface photoconductivity the measured value of the lifetime (10^{-4} s) is by one order of magnitude smaller than that for the bulk photoconductivity of the investigated CdS layers.

The shape of the spectral distribution of the lifetime of photocurrent carriers for surface- as well as for bulk photoconductivity of electrolytically deposited CdS layers is similar to that obtained by Lashkarev [6] for bulk photoconductivity of CdS single crystals.

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