

Effect of Heat Treatment Conditions on Photo sensitivity of CdSe_xS_{1-x} Polycrystalline Films

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Abstract

The influence of thermal treatment on the lux-ampere characteristics of polycrystalline films from the $CdSe_{x}S_{1-x}$ solid solution obtained by the method of thermal evaporation in a vacuum has been investigated. It is shown that at low illumination intensities L < 2 lx, the mobility μ of electrons increases with a power law $\mu \sim L^{\gamma}$, first with the exponent $\gamma > 1$, then with $\gamma \approx 0.5$, and their concentration n almost does not change. Starting from the intensity L >12 - 15 lx, the electron concentration increases strongly $n \sim L^{\beta}$ from $\beta \approx 3.0$, and the parameters n and μ reach relatively high values ~(10¹⁵ - 10¹⁶) sm⁻³ and ~(150 - 200) sm²/V·s, however further, at L > 50 lx, a weak dependence of n(L) and $\mu(L)$ with β , $\gamma < 1.0$ is found. The obtained experimental results are interpreted on the basis of a model of a semiconductor film with intergranular potential barriers when the concentration and barrier mechanisms of photoconductivity operate simultaneously.

Keywords

Solid Solutions CdSe_xS_{1-x} Polycrystalline Thin Film, Photoconductivity, Thermal Treatment, Lux-Ampere Characteristic, Photocurrent, Light Intensity

1. Introduction

Polycrystalline CdSe and CdS films have high photoconductivity and photosensitivity, photoresistors based on which are widely used as photodetectors and optical converters in modern electronics and radio engineering [1] [2] [3] [4] [5]. Some photoelectric properties of such films, such as superlinearity, infrared and thermal quenching of photoconductivity can be explained on the basis of a model with two types of recombination centers in the band gap [4] [5]. However, the

question of the effect of graininess on various electrical characteristics of films is still open. Therefore, the electronic and photoelectric properties of granular semiconductors are currently attracting much attention. Of particular interest is the study of the photoconductivity of films from the $CdSe_xS_{1-x}$ solid solution for the creation of unique light-sensitive devices [6] [7] [8] [9] [10]. In this case, the main attention is paid to the development of a technology for obtaining films with specified characteristics determined by the heat treatment mode and optimization of the medium, as well as their influence on the formation of an oxide film on the surface of crystalline grains with the formation of an intergranular barrier layer. It is shown that the improvement of the microstructure and photoelectric properties ($K = R_D/R_L \ge 10^7$) of $CdSe_xS_{1-x}$ films can be achieved by activating photosensitivity (PS) during the heat treatment for 15 - 30 min in a quasi-closed air atmosphere at 550°C or for 5 - 15 min at 600°C with a low cooling rate (3°C/min) [9].

In the manufacture of photoresistive films, the main technological factor is the process of heat treatment (HT) in various media, which enables not only achieve the desired degree (K~10⁶ - 10⁹) of the PS [7]-[16] but also purposefully influence many electrophysical parameters and film structures. In works [1] [2] [3], with the participation of one of the authors, a special technology has been developed for obtaining photosensitive polycrystalline films of cadmium selenide, including HT processes in a vacuum. The lux-ampere characteristic (LAC) of such films at low light intensities L~10 lx, in contrast to typical bulk photoresistors made of cadmium chalcogenides with two deep levels [4] [5], contains two characteristic regions with different slopes instead of one, and the temperature dependence of the dark conductivity reveals an anomalous character [3]. Such features of these phenomena are naturally associated with the effect of the interface between crystal grains on photoelectric and kinetic processes in polycrystal-line semiconductor films.

The purpose of this work is to study the effect of HT on the LAC of films from the CdSe_xS_{1-x} solid solution obtained using the method of thermal evaporation in a vacuum and to interpret the experimental results based on the model of a semiconductor polycrystalline film with intergranular potential barriers. At the same time, we state with satisfaction that the photoelectric properties of CdSe_xS_{1-x} films are easily controlled in a wide range depending on the method, time, temperature, HT and relative content of chalcogens *x*. Below, we restrict ourselves to consideration of the properties of films with x = 0 and x = 0.8. It has been experimentally shown that at low illumination intensities L < 10 lx, the mobility μ of electrons changes with a power law $\mu \sim L^{\gamma}$, first with the exponent $\gamma > 1$, then with $\gamma \approx 0.5$, and their concentration *n* almost does not change. Starting from the intensity L > 12 - 15 lx, the electron concentration increases strongly as $n \sim L^{\beta}$ from $\beta \approx 3.0$, and the parameters *n* and μ reach relatively high values $\sim (10^{15} - 10^{16})$ sm⁻³ and $\sim (150 - 200)$ sm²/V·s. Further, at L > 50 lx, a weak dependence of n(L) and $\mu(L)$ with β , $\gamma < 1.0$ is found. These results confirm that in polycrystalline films of $CdSe_xS_{1-x}$ solid solutions at low intensities $L < 10^2$ lx, the concentration and barrier mechanisms of photoconductivity operate simultaneously.

2. Technological Method

According to the technology of obtaining thin films by thermal vacuum evaporation, we developed the methods used in [17] [18] [19], using the method of two crucible evaporation. Polycrystalline $CdSe_{0.8}S_{0.2}$ films with a thickness of 5 - 20 µm and an area of 5 × 20 mm² were fabricated by thermal evaporation of CdSe and CdS with a mass ratio of 4:1 from individual crucibles onto glass substrates in vacuum at a pressure of 10⁻⁴ mm·Hg. Art. residual gases. Powdered cadmium selenide and cadmium sulfide grade "for semiconductors" was used as the starting material. Evaporation was carried out from aluminum oxide crucibles. The temperature of the substrate and evaporator during deposition and condensation was controlled by chromel-alumel thermocouples attached directly to them.

Freshly prepared film samples of CdSe and CdSe_{0.8}S_{0.2} with a thickness of $d\sim 4.0$ - 5.0 µm and an area of 5 × 20 mm² on glass or quartz substrates ($T_s =$ 300° C - 350° C) turned out to be low-resistance with a more moderate PS (K~ 10^{2}) and were subjected to additional heat treatment: in the "vacuum + CdCl₂" medium (~10⁻⁴ mm Hg, 15 - 25 min) at the temperature range of 350°C - 500°C; in a quasi-closed volume "atmospheric air + CdCl₂" at 470°C for 8 min. After HT, photosensitivity is achieved up to $K \approx -10^4$ - 10^6 values. Electron microscopic and X-ray diffraction studies have shown that the grown layers have a polycrystalline columnar structure, predominantly with a hexagonal modification. The sizes of individual crystallites were 1 - 2.5 µm. Additional annealing of the films leads to a change in the structure of the surface and, especially, the intercrystalline regions. The correct faceting of the vertices disappears, which acquires a rounded shape, and the columnar structure extends over the entire thickness of the film, which makes it possible to manufacture large-area light-sensitive devices and switching elements. According to Hall measurements, the films before and after HT had n-type electrical conductivity.

3. Experimental Results and Discussion

Numerous experiments carried out on various photoresistors show that in most cases, the dependence of the photocurrent I_{ph} on the light intensity L can be approximated by the following expression (see, for example, [5]):

$$I_{ph} = AL^{\alpha} . (1)$$

The index α LAC can have different values not only in different samples but also for the same photoresistor, depending on the range of light intensities. There are three cases: $\alpha = 1$ (linear), $\alpha < 1$ (sub-linear) and $\alpha > 1$ (super-linear).

We studied the LAC of polycrystalline films CdSe, CdSe_{0.8}S_{0.2} depending on

the manufacturing technology and the HT method. In Figure 1, the LAC of a freshly prepared sample in the longitudinal mode of photoconductivity at various temperatures and voltages are given. It can be seen that at all temperatures the LAC measurements are sublinear ($\alpha \le 0.63$ curve (1), $\alpha = 0.12$ (2); $\alpha = 0.15$ (3); $\alpha = 0.6$ (5); $\alpha = 0.65$ (4)) in the entire range of intensities except the initial section.

In the initial region of the light intensity, quasi-saturation of the photoconductivity of the films is observed, and this region expands significantly with increasing temperature. In addition, with an increase in the voltage applied to the photoresistor, the slope of the sublinear section of the LAC increases. These two circumstances are a consequence of the influence of the levels of attachment for electrons and high-resistance regions (HR) of the film on the characteristics of the photoconductivity of the films. Indeed, it is known that a freshly prepared sample CdSe has donor centers corresponding to intrinsic defects, in particular, selenium vacancies. The levels of these centers in most cases are sticking centers.

It is known [4] that the presence of sticking levels under certain conditions causes the sublinearity of the LAC of semiconductors. On the other hand, the equivalent circuit of a polycrystalline sample can be roughly represented as series-connected HR and low-resistance regions (LR). The role of the HR can be played by a depleted near-contact layer, space charge regions at the boundaries of crystal grains, and also the region of the crystal where excitation does not fall due to the rapid decay of the light intensity as it penetrates into the deep layers of the photoresistor. The resistance of HR depends little on the intensity of light.



Figure 1. LAC of the untreated CdSe film at various temperatures and voltages: T = 200 (curve 1), 300 (3, 5), 323 (2, 4) °C; U = 5 (curve 2, 3), 10 (1, 4, 5) V.

Low-resistance layers correspond to quasi-neutral regions of crystallites and their resistivity strongly depends on the excitation intensity. The photocurrent density in a longitudinal photoresistor can be roughly represented as [5],

$$\dot{\boldsymbol{j}}_{ph} = \frac{V_{ph}}{\rho_h \boldsymbol{d}_h + \rho_l \boldsymbol{d}_l} \tag{2}$$

here ρ_h, ρ_l are the specific resistances of high-resistance and low-resistance regions; d_h, d_l the thicknesses of the corresponding areas. Of these quantities, only ρ_l depends significantly on the illumination. As follows from formula (2), in the case when the condition

L

$$\rho_h d_h \gg \rho_l d_l$$
 (3)

photocurrent very weakly depends on the intensity of illumination. Apparently, this circumstance takes place for our freshly prepared samples at high temperatures (see curves 2 and 3 in **Figure 1**), when the Fermi level is below the sticking level and the latter is depleted to some extent. If the condition opposite to condition (3) is satisfied for the sample, then the photocurrent through the longitudinal structure depends on the light intensity. This case is well implemented at low temperatures and at relatively high voltages V_p (curves 1, 4, 5), as well as at high light intensities (see the corresponding sections of curves 4, 5).

In contrast to freshly prepared samples, in the films sensitized with the help of additional HT, in addition to ionized donor centers, which play the role of sticking levels, that is, traps, there are also recombination levels of two types: r- and s-centers. This difference should be appropriately reflected in the LAC of these films. **Figure 2** shows the LAC curves of the sensitized samples annealed under the



Figure 2. LAC of films $CdSe_{0.8}S_{0.2}$, sensed by the methods "vacuum + $CdCl_2$ " (1 - 3) and "air + $CdCl_2$ " (4) at T = 300 (1, 4), 210 (2) and 350 (3) °C.

condition "vacuum + CdCl₂", measured at three temperatures (curves 1, 2, 3), and "air + $CdCl_{2}$ " (4), obtained at room temperature. As can be seen from curves 1 and 4 taken at room temperature, the LAC of optimally sensitized samples with HT in different media qualitatively coincide. The lux-ampere characteristics of these photosensitive films at temperatures at which thermal quenching of photoconductivity (TQP) is observed, similarly to semiconductor single crystals CdSe, consist of three regions. At low illumination $L \le 1.0$ lx, first a linear and then a sublinear LAH is observed with $\alpha \approx 0.5$, a region of low PS. Starting from a certain illumination intensity (for example, $L \approx 10$ lx for curves 1 and 4), the photocurrent increases sharply with a LAC index greater than unity (a superlinear section of the LAC with an average PS for curves 1 and 4 $\alpha \approx 3.5$). With a further increase in the light intensity, the LAC passes into linear dependence (linear section with a high PS). The region of change in the light intensity corresponding to the superlinear section is somewhat shifted, but for both curves 1, 4 it extends by no more than one order of magnitude ($10 \le L \le 10^2$ lux). According to [5], this makes it possible to conclude that for our sensitized films, the case is indeed realized when the concentration of vacancies at the recombination centers does not depend on the concentration of free electrons.

At lower temperatures, when the demarcation level for holes is located below the level of r-centers, there are no regions of low and high PF on the $L \approx 10^3$ lux LAC (curve 2); on the contrary, at high temperatures (corresponding to TQP), in a wide range of The PS of the film is low (curve 3).

Figure 3 shows the LAC of two samples thermally treated under the "vacuum + $CdCl_2$ " condition, for one of which the HT time is equal to the optimal one (curve 2), and for the second, it is longer than the optimal one (curve 1). When the HT time is $t > t_{opo}$ in accordance with the results of work [3] in **Figure 3** it can be seen that the PS of the film is greatly reduced and this is accompanied, firstly, by a shift of the superlinear section of the LAC to the region of high illumination intensities, secondly, by a significant increase in the length of this region, thirdly, by a sharp decrease in the LAC index for sections with an average and high frequency response. According to the results of work [5], LAC of type 2 in **Figure 3** is realized in the case when $m = const \cdot n^k$ where $k \le 1$, *n* and *m* are the concentrations of free electrons and those at the levels of attachment. In this case, LAC has a superlinear section with a small exponent *a* in the region of several orders of magnitude of light intensity change.

An analysis of the experimental results shows that pronounced drift barriers exist in the obtained $\text{CdSe}_{0.8}\text{S}_{0.2}$ films. Since in such cases, the mobility of charge carriers depends on the light intensity $\mu = \mu(L)$, then, based on the fact that the current strength is $I \sim n(L)\mu(L)$, the following expression can be written for the LAC index α :

$$\alpha = \beta + \gamma$$

where β is the index of the degree of dependence $n \sim L^{\beta}$, γ is the index of the degree of dependence $\mu \sim L^{\gamma}$. Therefore, for a more detailed analysis of the



Figure 3. *L*AC of films $CdSe_{0.8}S_{0.2}$ annealed under the condition "vacuum + $CdCl_2$ " at $t = t_{opt}(2)$ and $t > t_{opt}(1)$.

features of LAC, considered in **Figure 2** and **Figure 3**, we additionally measured the mobility and concentration of electrons in the corresponding films depending on the illumination intensity. To determine the mobility μ and the concentration *n* of electrons in the films $CdSe_{0.8}S_{0.2}$, the E.M.F was measured. Hall is based on magnetic and electric fields.

When measuring the Hall effect in samples with a longitudinal phase filter, difficulties arise due to the fundamental features of these films. Therefore, we measured the Hall effect mainly for samples with a transverse PS obtained in a single technological cycle with longitudinal samples. As the results of the experiments showed, the values of μ_H for longitudinal and transverse specimens are close to each other. This is established by comparing the values of μ_H for longitudinal samples, defined in the following form:

$$\mu_H = \sigma \cdot R_H$$

where R_H is the Hall constant measured in the experiment for a transverse sample made in a single technological cycle with a longitudinal sample; σ is the specific conductivity of the longitudinal sample.

In **Figure 4**, the dependences of the mobility (curves 1, 2) and concentration (1', 2') of electrons on the illumination intensity for samples prepared under different HT conditions are shown. As can be seen from the figure, the course of dependences $\mu(L)$ and n(L) for samples with different HT methods coincides qualitatively. At low illumination $L \leq 10$ lux, the electron mobility first strongly increases, first with the exponent $\gamma \geq 1$, then with $\gamma \approx 0.5$, and their concentration



Figure 4. Dependences of the mobility (1, 2) and concentration (1', 2') of electrons on the light intensity for films $CdSe_{0.8}S_{0.2}$ sensed by the methods "vacuum + $CdCl_2$ " (1, 1'), "air + $CdCl_2$ " (2, 2') and the dependence $\mu(L)$ on a double logarithmic scale (dotted curve) for films that were sensed by the "air + $CdCl_2$ " method.

almost does not change. Beginning with intensities of 12 - 15 lux, the electron concentration increases strongly ($a \approx 2.8$), and μ reaches high values but changes slightly with increasing illumination intensity.

Based on the analysis of the results of dependences $\mu(L)$, n(L) in Figure 4 and dependences $\mu(1/T)$ and n(1/T) from [1], we can conclude that in the dark and at low illumination, the photoconductivity of the CdSe, CdSe_xS_{1-x} films is due to the barrier mechanism, and with increasing photoexcitation intensity, the concentration mechanism of current transfer dominates.

4. Conclusion

The photoconductivity of polycrystalline film samples of CdSe and CdSe_{0.8}S_{0.2} with three levels in the bandgap was studied for intrinsic absorption of light. It is shown that the LAC of optimally sensitized polycrystalline films differs from similar characteristics of the corresponding single crystals in the complex course of the initial section: first, an almost linear, then a sublinear dependence with an exponent $\alpha \approx 0.5$ is observed. At relatively low natural light intensities $L \leq 10$ lux, photoconductivity is due to the presence of intercrystalline barriers (μ -mechanism), and at intensities $L \geq 10$ lux, the role of direct carrier generation (n-mechanism) prevails.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

- Ayibjanov, M., Karimov, M.A., Saidov, M.S. and Yuldashev, N.Kh. (1996) Anomalnaya temperaturnaya zavisimosti infrakrasnoye gasheniye ravnovesnoy provodimostiv polikristallicheskix plenkax CdSe. *Fizika Tverdogo Tela*, 9, 1578-1584.
- [2] Karimov, M.A. and Yuldashev, N.X. (2004) Infrakrasniy fotopriyemnik izlucheniya na osnove legirovannoy polikristallicheskoy plenki CdSe. *Uzbekskiy Fizicheskiy Jurnal*, 4, 270-275.
- [3] Yuldashev, N.Kh. and Karimov, M.A. (2005) Lyuks-ampernaya xarakteristika plenochnix polikristallicheskix fotorezistorov iz CdSe s prodolnoy fotoprovodimostyu. *Uzbekskiy Fizicheskiy Jurnal*, 4, 254-259.
- [4] Polvonov, B.Z. and Yuldashev, N.Kh. (2016) Spectra of Low-Temperature Photolumines-Cence in Thin Polycrystalline CdTe Films. *Semiconductors*, 50, 1001-1004.
- [5] Rivkin, S.M. (1963) Fotoelektricheskiye yavleniya v poluprovodnikax. Fizmatgiz, Moskva.
- [6] Karimov, M.A. and Yuldashev, N.Kh. (2007) Short-Circuit Current Spectra of Photovoltaic CdTe and CdTe: In Films. *Russian Physics Journal*, 50, 71-74. https://doi.org/10.1007/s11182-007-0008-5
- [7] Lashkarev, V.S., Lyubchenko, L.K. and Sheynkman, M.K. (1981) Neravnovesniye prosessi v poluprovodnikax. Naukova Dumka, Kiyev.
- [8] Akhmadaliev, B.Zh., Yuldashev, N.Kh. and Yulchiev, I.I. (2018) Surface-Radiative Modes and Longitudinal Excitons in the Spectra of Exciton-Polariton Luminescence. *Optics and Spectroscopy*, **125**, 343-352. https://doi.org/10.1134/S0030400X18090023
- [9] Tivanov, M., Ostretsov, E., Drozdov, N., Survilo, L., Fedotov, A., Trofimov, Yu. and Mazanik, A. (2007) Optical and Photoelectrical Properties of CdSe_xS_{1-x} Films Produced by Screen-Printing Technology. *Physica Status Solidi* (*b*), **244**, 1694-1699. <u>https://doi.org/10.1002/pssb.200675137</u>
- [10] Akhmadaliev, B.Zh., Polvonov, B.Z. and Yuldashev, N.Kh. (2014) Influence of Exciton Decay on the Polariton Luminescence Spectra of CdTe Crystal. *Optics and Spectroscopy*, **116**, 244-248. <u>https://doi.org/10.1134/S0030400X14020027</u>
- [11] Meshkov, A.S., Ostretsov, E.F., Pogosov, W.V., Ryzhikov, I.A. and Trofimov. Yu.V. (2008) Photoconductivity of CdS-CdSe Granular Films: Influence of Microstructure. *Semiconductor Science and Technology*, 25, Article ID: 065013. https://doi.org/10.1088/0268-1242/25/6/065013
- [12] Karimov, M.A. and Yuldashev, N.Kh. (2007) Obliquely Deposited CdTe: In Films with Anomalous Photovoltaic Properties. *Bulletin of the Russian Academy of Sciences*. *Physics*, **71**, 1151-1153. <u>https://doi.org/10.3103/S1062873807080291</u>
- [13] Abbas, N.K., Naji, I.S. and Abdulmajeed, A.A. (2013) Electrical Properties of Thermally Evaporated CdSe_xS_{1-x} Thin Films. *International Review of Physics (IREPHY)*, 7, 70-75.
- [14] Trofimov, Y.V., *et al.* (2012) Physicochemical Features of Dielectrical Nano-Barrier Layers in CdSe_xS_{1-x} Films Formed by Screen Printing Method. *Lithuanian Journal of Physics*, **52**, 219-223. <u>https://doi.org/10.3952/physics.v52i3.2473</u>

- [15] Abdinov, A.Sh., Djafarov, M.A. and Mamedova, S.A. (2006) Relaksasiya fotoprovodimosti ximicheski osajdennix plenok CdSe_{1-x}Te_x. Bakinskiy Gosudarstvenniy Universitet. *Fizika i Astronomiya*, 2, 95-98.
- [16] Akhmadaliev, B.J., Polvonov, B.Z. and Yuldashev, N.Kh. (2016) On the Low-Temperature Photoluminescence and Photovoltaic Properties of Fine-Grained CdTe Films. *Journal of Surface Investigation. X-ray, Synchrotron and Neutron Techniques*, 10, 1173-1178. https://doi.org/10.1134/S1027451016050244
- [17] Imomalievich, R.T., Tolibjonovna, M.D. and Khaydarovich, Y.N. (2021) Photoelectric Phenomena in Thin Polycrystalline CdTe, CdSe, CdS Films under Mechanical Deformation. *European Science Review*, **11-12**, 40-49. https://doi.org/10.29013/ESR-21-11.12-40-49
- [18] Mamatov, O.M. (2020) Preparation by Thermovacuum Evaporation of Film Heterostructure n-CdS/p-CdTe with Anomalous Photoelectric Properties. *Scientific Technical Journal*, 3, 6-10.
- [19] Movlonov, P.I., Yunusov, N., Otazhonov, S.M. and Rakhmonkulov, M.Kh. (2021) Effect of Heat Treatment on the Photovoltaic Properties of the SiO₂-Te-CdTe Heterostructure. *Science and World International Scientific Journal*, **89**, 22-27.