Photosensitivity Spectra of Thin Films from a CdSe$_x$S$_{1-x}$ Solid Solution

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Abstract

The results of a study of the energy spectra of the activation of intrinsic defects of a photosensitive film made from the CdSe$_x$S$_{1-x}$ solid solution depending on the conditions of preparation and heat treatment in various media are presented. It is shown that at $x = 0.8$ cadmium vacancies create a deep level with an activation energy $E_v + (0.63 \pm 0.02)$ eV, a complex of chlorine atom with a cadmium vacancy creates a level $E_v + (0.43 \pm 0.02)$ eV, as well as the fast recombination center $E_v + (0.92 \pm 0.02)$ eV. The formation of selenium vacancies due to the introduction of chlorine and its combination with cadmium leads to the appearance of a sticking level $E_c - (0.19 \pm 0.02)$ eV. CdSe$_{0.8}$S$_{0.2}$ films can be used to develop light emitting diodes, photo sensors, IR and visible lasers.

Keywords

Thin Polycrystalline Film, Solid Solution, Photoconductivity, Activation Energy Spectrum, Substrate Temperature, Deep Impurity Centers

1. Introduction

Thin films of CdSe and CdS are important photoconverting materials for optoelectronic devices in the visible region of electromagnetic radiation. The photoelectric properties of polycrystalline films from the CdSe$_x$S$_{1-x}$ solid solution are very sensitive to point defects in the crystal lattice, which create local deep levels in the band gap of the semiconductor, and to structural defects present at grain boundaries [1] [2] [3] [4]. Such inhomogeneities cause the manifestations of various anomalous physical processes occurring in the volume and at the film grain boundaries under the action of IR and visible light [4] [5] [6].

The aim of the work was to obtain and study some spectral characteristics of semiconductor films of the CdSe$_x$S$_{1-x}$ solid solution for the development of ul-

trasensitive photo resistors, photo sensors and other photo converters. The main attention is paid to a more detailed study of the energy spectra of activation of intrinsic defects of a photosensitive $CdSe_xS_{1-x}$ film obtained by thermal evaporation in vacuum, depending on the conditions of preparation and heat treatment (HT) in various media. This undoubtedly leads to a deeper understanding of the essence of physical processes in polycrystalline films. It was shown that small steps are observed in the photoconductivity spectra of as-prepared films obtained at different substrate temperatures. Graphical analysis determined local deep levels $E_v + 0.63 \pm 0.02$ eV and $E_c - 0.41 \pm 0.02$ eV. During heat treatment of the films for ~4 min in air in the presence of $CdCl_2$, an additional level $E_c - 0.24 \pm 0.02$ eV at the bottom of the conduction band is clearly manifested in the spectral distribution, and the level $E_v + 0.43 \pm 0.02$ eV at the top of the valence band. The investigated films can be used to develop new light emitting diodes, photo sensors, IR and green-red lasers.

2. Technological Method

To obtain $CdSe_xS_{1-x}$ films, we used method of thermal evaporation in vacuum [7] [8] [9], characterized in that to achieve the stability of operating parameters and increase the photosensitivity of the films, the method of additional cascade heat treatment in a quasi-closed volume in the presence of various vapors was used. The vacuum unit was assembled on the basis of a fore-vacuum pump and a steam-oil diffusion pump, which provided a pressure of residual gases of the order of ~10^{-2} Pa. Crucibles made of aluminum oxide or beryllium were used as the evaporator. The evaporation temperature of the semiconductor was achieved by the design of the crucible and current regulation. The substrates were heated using an oven, the design of which makes it possible to change the substrate temperature up to 873 K. The temperature of the substrates and the evaporator was controlled by chromel-alumel thermocouples fixed directly on them. Glass and mica with transparent contacts were used as substrates. The substrate was cleaned by treatment in a boiling 0.5% nitric acid solution, then degreased in acetone and repeatedly boiled in distilled water, wiped with medical alcohol, and placed in an evaporation chamber. After reaching a vacuum of ~10^{-2} Pa the substrates were degassed by heating at a temperature of 573 K for 30 min. Powdered CdSe and CdS grade "for semiconductors" were used as the starting material. $CdSe_xS_{1-x}$ films were obtained by evaporating a mixture of CdSe and CdS in various proportions. Prior to the establishment of a stationary mode of evaporation, the crucible was covered with a damper, which makes it possible to more accurately control the deposition time of the material. To preserve the composition of the charge and the initial flow of the evaporated material, before the evaporation of CdSe, the charge was annealed in the evaporation mode for 20 - 25 min. In order to obtain films with large thicknesses and to increase the deposition temperature, as well as to avoid direct contact of particles with the substrate, the surface of the crucible was covered with a quartz plate. With the use of appropriate technological devices, we managed to obtain layers in a wide range of thicknesses

(5 - 20 μm) and at high substrate temperatures (~673 K). The film thickness was determined using an interference microscope and, in some cases, by weighing. The photoelectric properties of $CdSe_xS_{1-x}$ films are easily controlled in a wide range depending on the condensation rate, substrate temperature, HT time, and relative content of chalcogens x. Here we confine ourselves to considering the spectral properties of films with $x = 0.8$.

3. Experimental Results and Their Discussion

Freshly prepared $CdSe_{0.8}S_{0.2}$ film samples with a thickness of $d \sim 10.0 - 15.0$ μm and an area of 5×20 mm^2 turned out to be low-resistance with electronic conductivity. The study of the spectral distribution of the specific photoconductivity σ_{ph} of $CdSe_{0.8}S_{0.2}$ films showed that the initial films obtained at different substrate temperatures T_s exhibit qualitatively similar spectra of local levels. Curves of spectral dependences $s_{ph}(h\nu)$ for freshly prepared films with substrate temperature T_s = 723 K and photosensitivity factor $S = \sigma_{ph}/\sigma_t \approx 10^2$, measured at a temperature of 300 K (crosses), are shown in **Figure 1**. The experimental results were compared with the theoretical curves (points) calculated using the Lukovsky formula [10]

$$\sigma_{ion} = \left(16\pi e^2 \hbar m^* / 3cn\right) \left(E_{eff}/E_0\right)^2 \left(E_{ion}\right)^{1/2} \left(h\nu - E_{ion}\right)^{3/2} \left(h\nu\right)^{-3}, \tag{1}$$

where e is the elementary charge, $h\nu$ is the energy of the incident photon, E_{eff}/E_0 is the coefficient of the crystal field, m^* is the effective mass of the electron bound
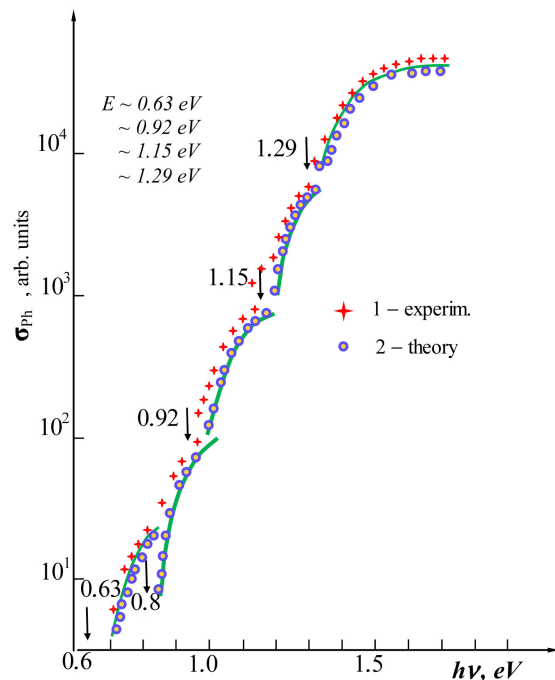

Figure 1. Spectral dependence of σ_{ph} of freshly prepared $CdSe_{0.8}S_{0.2}$ films. Points 2 are obtained by subtracting the theoretically calculated solid curves from the experimental data 1. The arrows in the figure indicate the optical ionization energy of the deep center used in calculating the theoretical curves.

at the center, c is the speed of light, n is the refractive index of the substance, σ_{ion} and E_{ion} are the cross section and energy of the optical center ionization. In this case, it is assumed that for a given frequency of light, the impurity specific photoconductivity σ_{ph} is proportional to the photoionization cross section of the impurity center under consideration [11] [12] [13].

By graphical analysis of the experimental and theoretical spectra, it was established that the films obtained at T_s = 723 K have deep levels with an activation energy: E_v + (0.63 ± 0.02), E_v + (0.8 ± 0.02), E_v + (0.92 ± 0.02), E_c − (0.55 ± 0.02) and E_c − (0.41 ± 0.02) эB.

In all photoconductivity spectra of freshly prepared films obtained with different substrate temperatures, when excited by light with photon energies of ~0.6 and 1.2 eV, local levels of E_v + (0.63 ± 0.02), E_c − (0.41 ± 0.02) эB.

To increase the photosensitivity, freshly prepared films were subjected to HT in various media. With short-term HT ~ 4 min in air in the presence of CdCl$_2$, the photosensitivity factor reaches values of $S \approx 10^4$ and an additional level E_c − (0.24 ± 0.02) eV or the same as E_v + (1.46 ± 0.02) eV at the bottom of the conduction band (**Figure 2**), and on the curves of optical photoconductivity quenching—the level E_v + (0.43 ± 0.02) eV at the top of the valence band (**Figure 3**).

As the HT time increases, the spectrum of local levels changes insignificantly. In the long wavelength region of the spectrum up to $h\nu < 1$ eV, the course of the curves of the spectral dependences of photoconductivity is determined by both local levels located in the upper half of the band gap (with increasing concentration of which the photosensitivity in this region of the spectrum increases), and
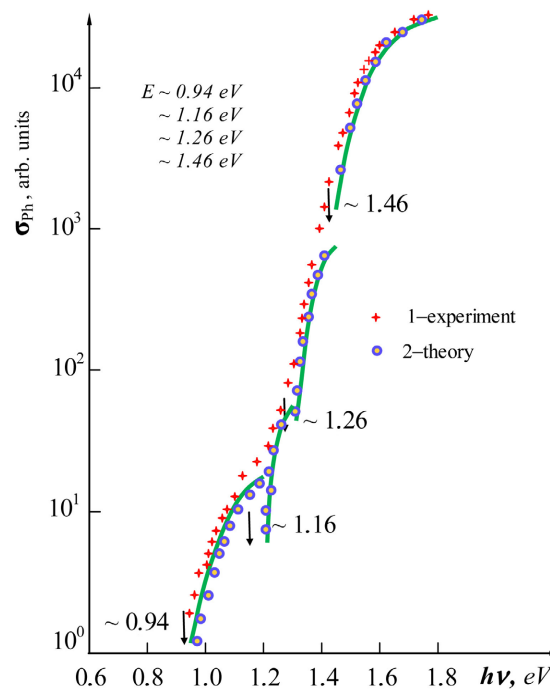

Figure 2. Spectral dependence σ_{ph} of CdSe$_{0.8}$S$_{0.2}$ films after heat treatment in air in the presence of CdCl$_2$ for 4 min.
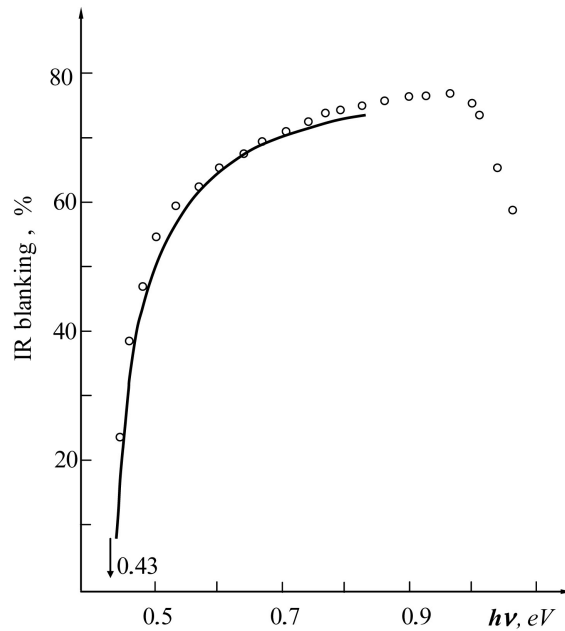
Figure 3. IR photoconductivity quenching curves for CdSe$_{0.8}$S$_{0.2}$ films heat-treated in air in the presence of CdCl$_2$. Points-experiment, solid line-theory [4].

local levels located in the lower half of the band gap. Most of the detected levels are the centers of photosensitivity, which is established by the bands of infrared quenching of photoconductivity (**Figure 3**). According to the curves of the spectral dependence of photoconductivity, the depths of the sticking levels for electrons $E_c - (0.19 \pm 0.02)$ eV and $E_c - (0.42 \pm 0.02)$ eV were also established.

On the basis of known materials (see, for example, [4] [7]), we will try to qualitatively explain the experimental results obtained above. Thermal treatment of films in various media leads to a change in the concentration of their own local levels, as well as to the appearance of new levels due to dopant impurities. An impurity atom can be introduced into the film, occupying either a site or an interstitial site in the crystallite, and can also be located in the intercrystalline region. The location of the introduced impurity atom is mainly determined by the value of its ionic radius. If the latter is smaller than the ionic radii of the film components, then such an atom has a high probability of being located at the site of the components, the radius of which is not less than the radius of the impurity. Whether an impurity, replacing an atom of the host substance, will act as a donor or acceptor depends on the number of valence electrons on the impurity and substituted atoms.

At the initial moments of thermal treatment in air in the presence of cadmium chloride, dislocated chlorine atoms embedded in the bulk of crystallites and replacing Se or their vacancies form a shallow donor level, and some of them react with cadmium atoms and their vacancies. A compensating acceptor level $E_v + (0.43 \pm 0.02)$ eV appears due to the complex of cadmium vacancy with chlorine ($V_{Cd}^- Cl_{Se}^+$). The appearance of sensing centers $E_v + (0.43 \pm 0.02)$ eV leads to an increase in photosensitivity. An increase in the HT time to 6 - 8 minutes leads to

an increase in the concentration of cadmium vacancies and complexes of cadmium vacancies with chlorine, *i.e.* to an increase in the concentration of sensing centers $E_v + (0.43 \pm 0.02)$ and $E_v + (0.63 \pm 0.2)$ eV, respectively, and photosensitivity.

In the case of heat treatment in air in the presence of $CuCl_2$, the dissociated copper and chlorine atoms diffuse into the bulk of the crystallites and the intercrystallite regions of the film. Since the covalent radius of copper is less than the radius of cadmium, the copper atom replaces the cadmium atom in the lattice site. Chlorine atoms accelerate this process, since, by reacting with cadmium, they lead to an increase in the concentration of cadmium vacancies, and copper atoms more easily occupy this vacancy. This leads to the formation of a compensating acceptor level $E_v + (0.66 \pm 0.02)$ eV and to an increase in its concentration, which determines the increase in photosensitivity.

We believe that in the future it is necessary to conduct a more thorough study of the parameters of the deep local centers found here by the method of low-temperature photoluminescence [14] [15] with the corresponding theoretical calculations [10] [16].

4. Conclusions

Thus, we can conclude that in the process of sensing by thermal treatment of $CdSe_{0.8}S_{0.2}$ films in air in the presence of $CdCl_2$ vapors, the main role is played by chlorine atoms, which lead to the formation and increase in the concentration of sensitized centers. In the case of the formation of a complex of a chlorine atom with a cadmium vacancy, a level with an activation energy of $E_v + (0.42 \pm 0.02)$ eV appears, and in the case of the formation of a cadmium vacancy, a level with an activation energy of $E_v + (0.63 \pm 0.02)$ eV, as well as the fast recombination center $E_v + (0.92 \pm 0.02)$ eV. The formation of selenium vacancies due to the introduction of chlorine and its combination with cadmium leads to the appearance of a sticking level $E_c - (0.19 \pm 0.02)$ eV. Thermal treatment in the presence of $CuCl_2$ stimulates the formation of compensating acceptor levels and an increase in the concentration of donor centers.

Note that the high photosensitivity and stability of the properties of the studied $CdSe_{0.8}S_{0.2}$ films make it possible to use them for the development of new light emitting diodes, photo sensors, IR and visible lasers.

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Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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