

## Optical and photoelectrical properties of $\text{CdS}_x\text{Se}_{1-x}$ films produced by screen-printing technology

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In this paper the optical and photoelectrical properties of  $\text{CdS}_x\text{Se}_{1-x}$  films prepared using the screen-printing and sintering technique, were studied.  $\text{CdCl}_2$  was used both as a sintering flux and as a doping agent.  $\text{CuCl}$  was also used as a doping agent. The temperatures and times of preparation varied in the range of 500–600 °C and 5–60 min, respectively. The as-prepared films were characterized by the scanning electron microscopy, micro-probe X-Ray analysis, photoluminescence and photoconductance methods. Our investigations have shown that photoresponse of the  $\text{CdS}_x\text{Se}_{1-x}$  films prepared by a screen-printing method can be suitable for the production of large-area photosensitive devices.

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### 1 Introduction

The direct band gap semiconductors like CdS, CdSe and their solid solutions are excellent materials for the development of highly efficient and low-cost photovoltaic devices due to their high absorption coefficients and appropriate band gap [1, 2]. The band gap of  $\text{CdS}_x\text{Se}_{1-x}$  solid solution can be tuned over a wide range between 1.74 eV for pure CdSe and 2.44 eV for pure CdS [1].

$\text{CdS}_x\text{Se}_{1-x}$  films can be prepared by different techniques [3] such as screen-printing-sintering [4], chemical bath deposition [3, 5, 6], electrodeposition [7], laser ablation [8], sputtering [9], and vacuum evaporation [10]. Among these methods, which are claimed for the production of the low-cost large-area devices on the base of  $\text{CdS}_x\text{Se}_{1-x}$  films, the print-screen-sintering is a very attractive technique [11] due to simplicity of its realization.

The goal of this study was comparison of the optical and electrical properties revealed by  $\text{CdS}_x\text{Se}_{1-x}$  films prepared using the screen-printing and appropriate sintering techniques with the same characteristics of the films manufactured by some others methods.

### 2 Experimental

For preparation of the films we have used the screen-printing method. Some properties of the fabricated films were compared with those of the films produced by other methods (e.g. vacuum evaporation and sputtering). The screen-printing principle used in this study is shown schematically in Fig. 1. A paste of the powder material to be screen-printed was pressed through the screen by means of the squeegee. Im-

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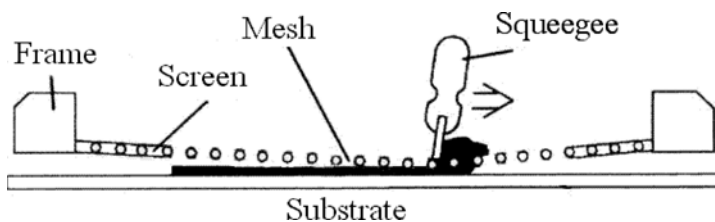


Fig. 1 Scheme of the used screen-printing process [11, 12].

important screen-printing parameters are [12] the paste viscosity, mesh number of the screen, distance between the screen and substrate, pressure and speed of the squeegee.

For the fabrication of the paste to be coated, crushed CdS and/or CdSe materials were mixed with a fixed amount of CdCl<sub>2</sub> (3–10 weight percent) and with a small amount of CuCl. Then the paste was sintered in a quartz chamber at a temperature of 500 °C for 1–1.5 h. A hard ingot formed as a result of this sintering procedure was then crushed to 2–3 μm powder in a rotor-planetary mill and mixed with an organic binder (propylene glycol) needed for the screen-printing process. The paste was screen-printed through a 120 mesh polyester screen onto the ceramic substrate and dried at 200 °C for 30 minutes to remove the binder. The screen-printed films were subjected to the sintering procedure at various temperatures from 500 to 600 °C from 5 min to 1 h in the regime of a quasi-closed air atmosphere. Quasi-closing was achieved by special locations of the sintered samples in relation to each other: the sintered samples were laid a stack with gaps about 0.5 mm between them. A sintering procedure was needed for the formation of a common conducting system due to the recrystallization process. Besides, diffusion of the dopant atoms (Cu, Cl) during heat treatment created donor and/or acceptor centers in the film bulk.

Loading of the samples in to the furnace area with the required temperature was carried out gradually in three stages with a 5-minute lag. A similar method was used for unloading of the samples. CdCl<sub>2</sub> was used in the sintering both as a sintering flux and as an n-type dopant [13]. CdCl<sub>2</sub> flux enables one to reduce the sintering temperature [12, 14]. As an n-type dopant, CdCl<sub>2</sub> was used to increase the light conductance of the synthesized material [15]. CuCl was used to increase the dark resistance of the synthesized material and to improve (increase) the light-to-dark conductivity ratio [15].

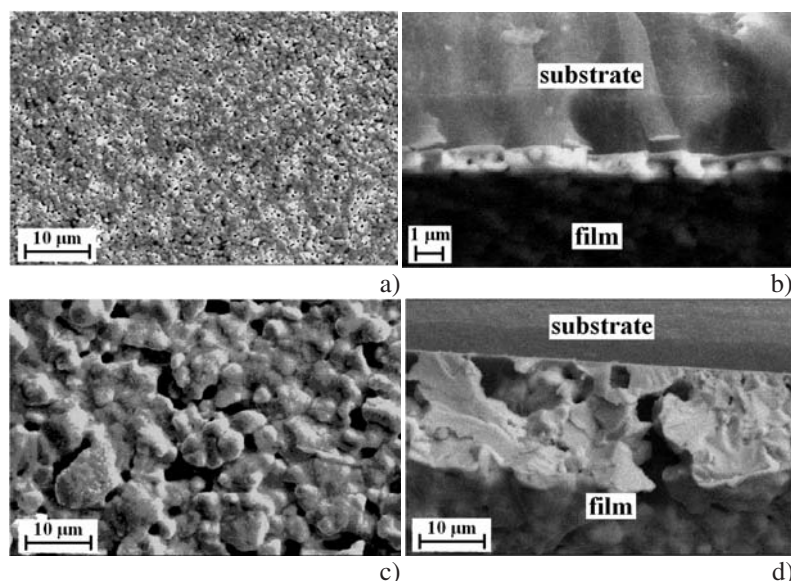
The surface morphology and cross view of the films were investigated by the scanning electron microscopy (SEM) technique using LEO1455VP. The chemical composition of the studied films was investigated using a special micro-probe X-Ray analyser in LEO1455VP.

The photoluminescence (PL) measurements were carried out using a scanning confocal Nanofinder-S microscope with a continuous wave He–Cd laser (441.6 nm). Diameter of the excitation spot was about 0.7 μm and excitation power was about 1 mW. All spectra described here were obtained at room temperature over the spectral range from 450 to 840 nm with a wavelength increment of 0.5 nm.

To study the film photoconductance, the samples were provided with indium contacts annealed at 180–200 °C. The photoconductance spectra were measured at room temperature, and the data were collected at a wavelength increment of 1 nm in the spectral range between 400 and 900 nm. The light from a tungsten halogen lamp was used for the photoconductance excitation. The photoconductance spectra were normalized to the light source spectrum.

### 3 Results and discussion

Figure 2 shows the scanning electron micrographs of CdS<sub>x</sub>Se<sub>1-x</sub> films which have been prepared using the screen-printing-sintering and vacuum evaporation procedures [16]. It is seen that (i) the films produced by the print-screen-sintering technique were thicker by an order of magnitude compared to the vacuum evaporated ones and (ii) had a strongly developed surface. Note that such a strongly developed surface is even more preferable for some purposes, for example for the production of photoresistors or solar cells.

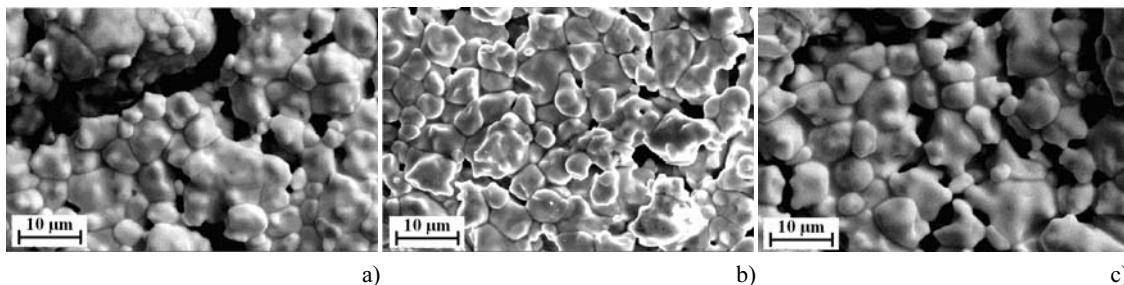


**Fig. 2** Surface morphology (a, c) and cross view (b, d) of the films prepared using vacuum evaporation (a, b) and screen-printing sintering (c, d).

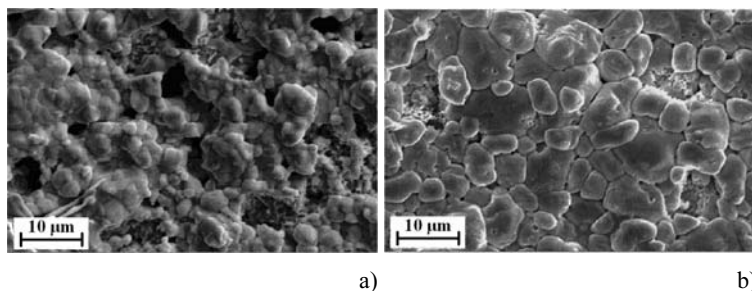
In Fig. 3 the surface of CdSe films subjected to different regimes of heat treatment is presented. Apparently, increase of the sintering time and temperature has resulted in the improvement of the film surface continuity. Similar results were observed for the films of other compositions. However, an increase of the synthesis temperature over 600 °C seems to be unacceptable due to the arising active evaporation of the synthesized material.

As it was noted above, the samples were unloaded from the sintering volume of the furnace during 15 min. To study the influence of the post-sintering cooling-off rate on the surface morphology of the samples studied, we have synthesized several sets of films with unloading time ranging from 15 to 120 min. Figure 4 illustrates the typical increase of the films surface continuity with a decrease in the post-sintering cooling-off rate.

Figure 5 represents the PL spectra of the sintered  $\text{CdS}_x\text{Se}_{1-x}$  films for different values of  $x$ . The photoluminescence spectra show a number of noteworthy features. One can see (i) the dominant near band-edge emission and (ii) low-energy region. A similar shape of the PL spectra taken at a room temperature was observed in [17] for the laser deposited CdS films. The dominant near band-edge emission shows the band gap variation with the composition of  $\text{CdS}_x\text{Se}_{1-x}$  films. Positions of near band-edge photoluminescence lines as function of  $\text{CdS}_x\text{Se}_{1-x}$  compositions correspond well to the values of band-gap energies



**Fig. 3** Surface of CdSe films after different regimes of heat treatment: a) 540 °C, 10 min; b) 540 °C, 30 min; c) 500 °C, 60 min.

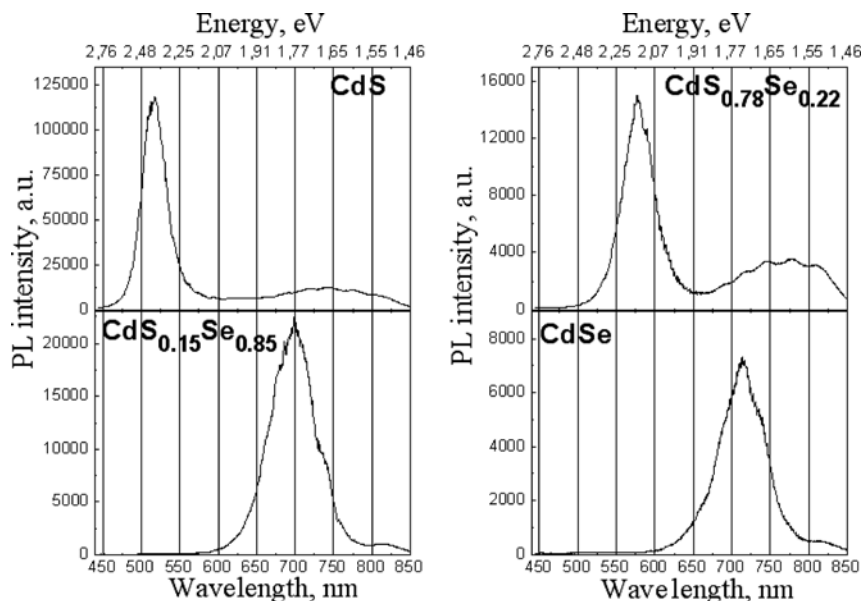


**Fig. 4** Surface view of the films synthesized at different unloading times from the sintering area: a) 15 min, b) 120 min.

obtained in paper [18] for the electrodeposited films. The deep level luminescence is found to have a lower integrated intensity than the near band-edge one. The observed deep levels in CdS–CdSe solid solutions are typically attributed to sulfur and selenium vacancies or extrinsic defects, their reduction being indicative of the good stoichiometry and high purity of the material [17, 19].

Figure 6 represents the photoconducance spectra for the sintered  $\text{CdS}_x\text{Se}_{1-x}$  films at different values of  $x$ . The results of the photoconducance research show the possibility to control the spectral selectivity of  $\text{CdS}_x\text{Se}_{1-x}$  films by means of  $x$  variation.

Comparison of Figs. 5 and 6 demonstrates the discrepancy between the maximum positions in PL and photoconducance spectra for each of the film compositions. As is seen, the maximum position in PL spectra for samples with different  $x$  values corresponds well to their band gap values. At the same time, the photoconducance maximum positions are shifted to long wavelength region as compared to PL maximum. Comparison of the photoconducance spectra for the screen-printed samples and vacuum deposited samples studied in [16] shows that the photosensitivity of screen-printed films is shifted to long wavelength spectral region. The observed shift of photoconducance spectra to the long wavelength region can be explained [20] by (i) high surface recombination due to the highly-developed sample surface (that suppress the short wavelength photoconducance) and (ii) imperfection of the studied films contributing to the sub-band gap photoconducance (probably due to the presence of the bandtail states).



**Fig. 5** Room temperature PL spectra of the screen-printed  $\text{CdS}_x\text{Se}_{1-x}$  films for different  $x$  values.

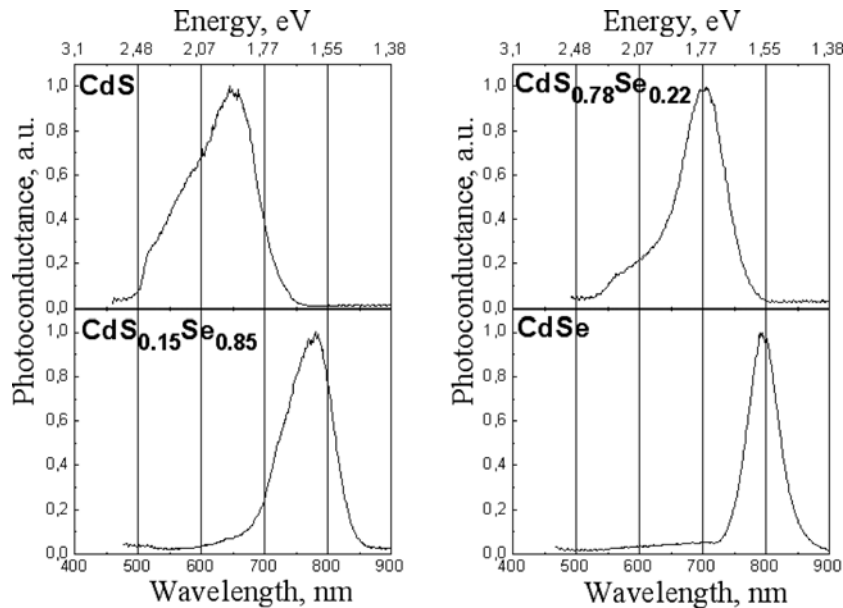


Fig. 6 Room photoconductivity spectra of the sintered  $\text{CdS}_x\text{Se}_{1-x}$  films for different  $x$  values.

#### 4 Conclusion

The conducted study has shown that the bulk and surface microstructure of the screen-printed  $\text{CdS}_x\text{Se}_{1-x}$  films and those sintered with the  $\text{CdCl}_2$  flux is determined by the sintering temperature and also by sintering and cooling-off times. The band gap decreases as the concentration of selenium in the sintered films is increased. As a whole, the study has shown that the photoresponse of the  $\text{CdS}_x\text{Se}_{1-x}$  films prepared by a screen-printing method can be suitable for the production of large-area photosensitive devices.

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