

PHOTOCONDUCTIVITY AND LUMINESCENCE OF $Zn_xCd_{1-x}S$ FILMS PREPARED BY SOLUTION SPRAY TECHNIQUE

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$Zn_xCd_{1-x}S$ thin films are prepared in the composition range $x = 0 \div 0.3$ from aqueous mixture of $CdCl_2$, $CS(NH_2)_2$ and $ZnCl_2$ using a chemical solution spray technique. Lattice constants and band gap of the films are measured. Dark electrical resistivity, photoconductivity, transmission and luminescence of $Zn_xCd_{1-x}S$ films are studied as a function of film composition. The obtained results may be explained by considering the fact that increasing the percentage of ZnS in the solid solution results in an increase of the $Zn_xCd_{1-x}S$ band gap.

1. INTRODUCTION

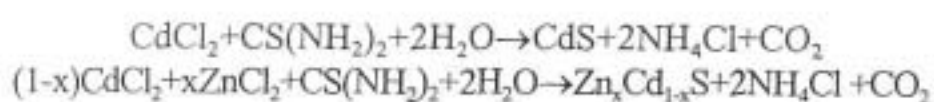
The search for low-cost, stable solar cells with high conversion efficiency has led to the development of several thin film semiconductor materials systems. Thin film solar cells, based on $Zn_xCd_{1-x}S$ and its alloys, are considered to be one of the most promising systems due to a number of favorable properties [1,2]. Solar cells based on $Zn_xCd_{1-x}S$ have been reached high efficiencies despite the fact that there is little knowledge of electrical and optical properties of this material [3,4].

One of the prospective procedures used to prepare $Zn_xCd_{1-x}S$ thin films is the method of chemical solution spray. This method gives the possibility to prepare sufficiently perfect films with large areas having strong adhesion and high mechanical strength in comparison with those prepared by the other methods.

In this work the photoconductivity and luminescence spectra of $Zn_xCd_{1-x}S$ ($x = 0 \div 0.30$) thin films prepared by the chemical solution spray technique is experimentally investigated.

2. EXPERIMENTAL METHODS

The $Zn_xCd_{1-x}S$ thin films were prepared by the solution spray technique, which basically involves the spraying of an aqueous mixture of $CdCl_2$, $ZnCl_2$ and thiourea $CS(NH_2)_2$. The concentration in the above aqueous mixture is varied depending on the $ZnCl_2$ concentration in the above aqueous mixture is varied depending in the $Zn_xCd_{1-x}S$ solid solution. The CdS and $Zn_xCd_{1-x}S$ films were formed by the pyrolytic decomposition of the spray particles on the surface of the substrate according to the following reaction:



The temperature of the substrate (a chemically cleaned glass slides) was kept at $400^\circ C$ and measured with the help of a chromel-alumel thermocouple fixed to the surface of the substrate.

The spray rate was about $5 \text{ ml} \cdot \text{min}^{-1}$, which provided a deposition rate of about $50 \text{ nm} \cdot \text{min}^{-1}$. The $Zn_xCd_{1-x}S$ films used in this investigation were 0.5 cm^2 in areas and had thickness $\sim 10 \mu\text{m}$.

The X-ray diffraction patterns of samples were taken, using the K_α line of Cu X-ray source.

The optical absorption edge was determined from transmission spectrum obtained using a SPM-2 monochromator and computerized complex KSVU-2 at room temperature.

Excitation of luminescence is realized by means of a pulsed nitrogen laser ($\lambda = 337 \text{ nm}$) with 1 ns pulse width, 2MW peak power and repetition frequency up to 20 Hz. The laser intensity absorbed by the films was varied by means of a set of calibrated neutral density filters. Luminescence was detected under a small angle with respect to the surfaces of films. Luminescence spectra were analyzed by means of a diffraction grating monochromator (JOBIN-YVON) with the reciprocal dispersion 2.4 nm/mm . The output signal was detected by a photomultiplier and then was sent to a recorder (HP-7475A) through a storage oscilloscope (Le Croy 9400).

Photocurrent measurement has been carried out a Rodhamine 6G-dye laser pumped by the above mentioned nitrogen laser (tenability range 473 to 547 nm).

The Ohmic contacts to the samples for electrical and photoelectrical measurement were made by vacuum evaporation in indium. The measurement methods were explained in previous works [5-7].

3. RESULTS AND DISCUSSION

The structural analysis obtained by the X-ray diffraction pattern of $Zn_xCd_{1-x}S$ thin film shows that, the increase of the Zn concentration ($x = 0 \div 0.30$) does not change the grain orientation, but essentially increase the angle of reflection from (101), (002) and (100). A variation less than 5 % was detected in the lattice constants (Tabl.1).

Table 1. Lattice parameters of $Zn_xCd_{1-x}S$ thin films

| x | 2θ [100] | 2θ [002] | 2θ [101] | a (Å) | c (Å) |
|------|--------------------|--------------------|--------------------|---------|---------|
| 0 | 23.89 | 26.51 | 28.15 | 4.297 | 6.718 |
| 0.05 | 23.98 | 26.60 | 28.20 | 4.142 | 6.696 |
| 0.10 | 24.86 | 26.69 | 28.23 | 4.133 | 6.676 |
| 0.15 | 24.89 | 26.70 | 28.35 | 4.127 | 6.668 |
| 0.20 | 24.95 | 26.76 | 28.42 | 4.116 | 6.656 |
| 0.30 | 25.18 | --- | 28.65 | 4.079 | 6.583 |

In Fig.1 the dark resistivity, ρ of $Zn_xCd_{1-x}S$ thin films is shown as a function of Zn concentration. As it is seen from

the figure, by varying the value of x from $x = 0$ to $x = 0.30$ ρ increases exponentially from $6 \cdot 10^1$ to $1 \cdot 10^4 \Omega \cdot \text{cm}$. The obtained results may be explained by considering the fact that the increase the percentage of ZnS in the solid solution results on increase of the $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ band gap. These results have in a good agreement with previous works [8,9]. According to them the $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ band gap is shifted with x between the band gap of CdS (2.5 eV) and ZnS (3.56 eV) [10] and depends on the concentration x .

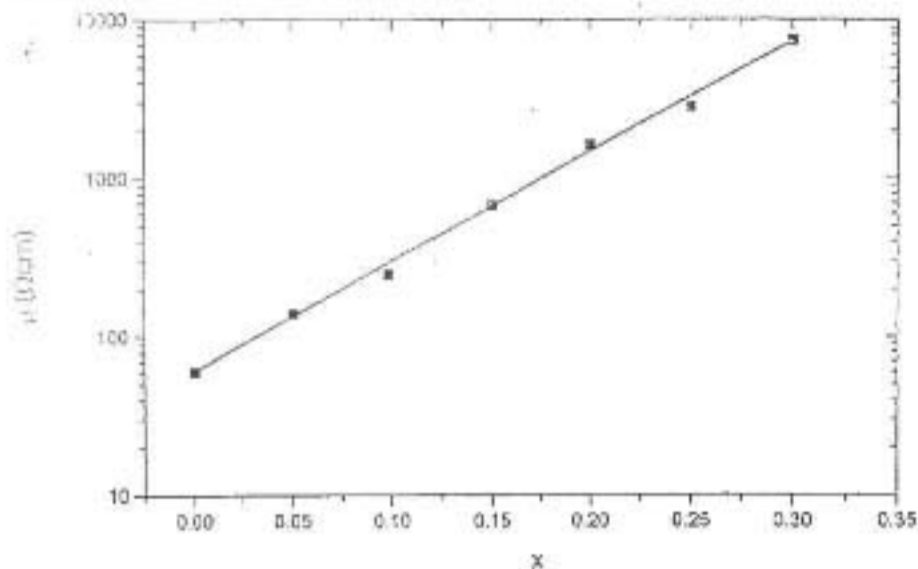


Fig. 1. Resistivity versus x values for $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ thin films.

The photoconductivity, $\Delta\sigma$ spectra of $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ thin films for different x are given in Fig. 2. As it is seen, the photosensitivity spectrum stretches in the wavelength from $\lambda = 40$ nm up to 520 nm. The maximum of photoconductivity is shifted towards short wavelength by the increase of the x value. The comparison of the photoconductivity spectra of these films with their corresponding measured transmission spectra (Fig. 3) shows that these photoconductivities are intrinsic (band-band transition). So, the maxima of photoconductivities let us to evaluate the band gap of each composition. A plot of the band gap, E_g , of the alloys films is shown as a function of composition in Fig. 4. As it is seen from this figure, the band gap increases linearly from 2.42 eV for CdS ($x = 0$) to 2.52 eV for $\text{Zn}_{0.3}\text{Cd}_{0.7}\text{S}$ ($x = 0.30$).

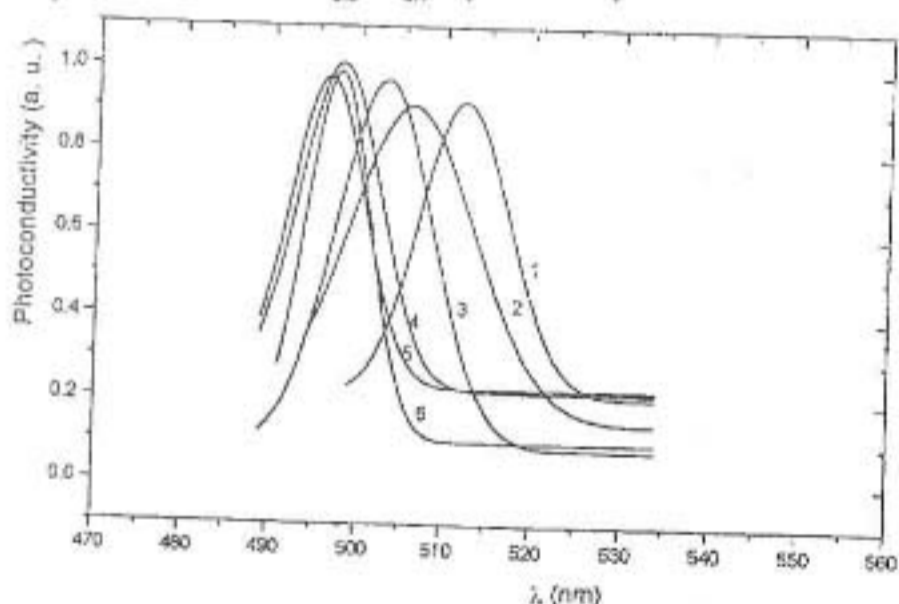


Fig. 2. Photoconductivity spectra of $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ thin films for different x values:
1 - 0, 2 - 0.05, 3 - 0.15, 4 - 0.20, 5 - 0.25, 6 - 0.30.

Dependence of the photoconductivity on excitation power is shown in Fig. 5. The curves of this figure show that for all

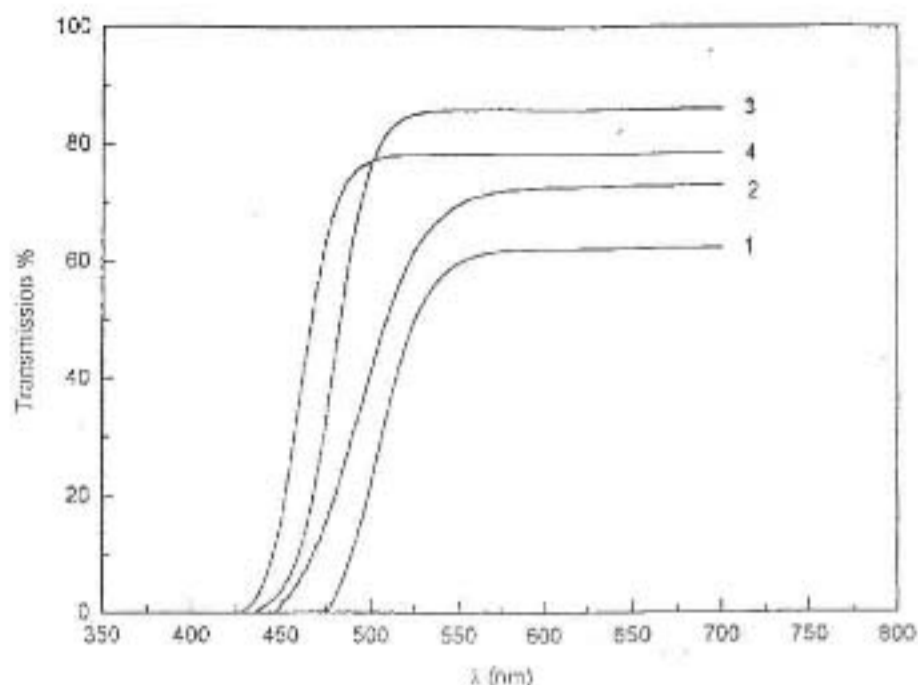


Fig. 3. Transmission spectra of $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ thin films for different x values:
1 - 0, 2 - 0.10, 3 - 0.15, 4 - 0.20.

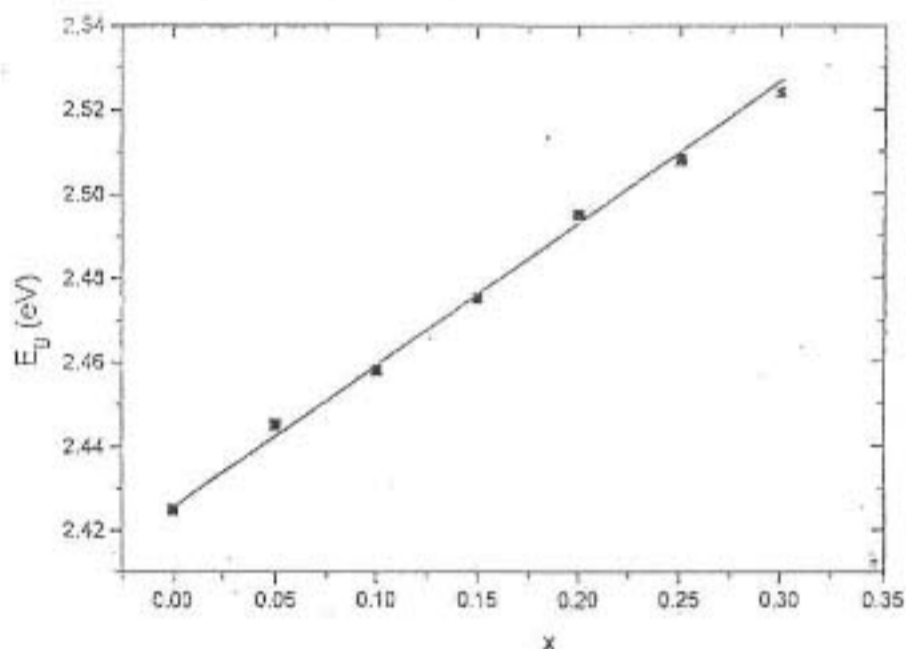


Fig. 4. Band gap of $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ thin films as a function of x .

composition, photoconductivity changes linearly with the excitation intensity. So, we can conclude that the recombination processes are linear [11]. Our experimental results show that the relaxation curve of photoconductivity for all composition is the same and independent of illumination intensity which correspond to a linear recombination. The

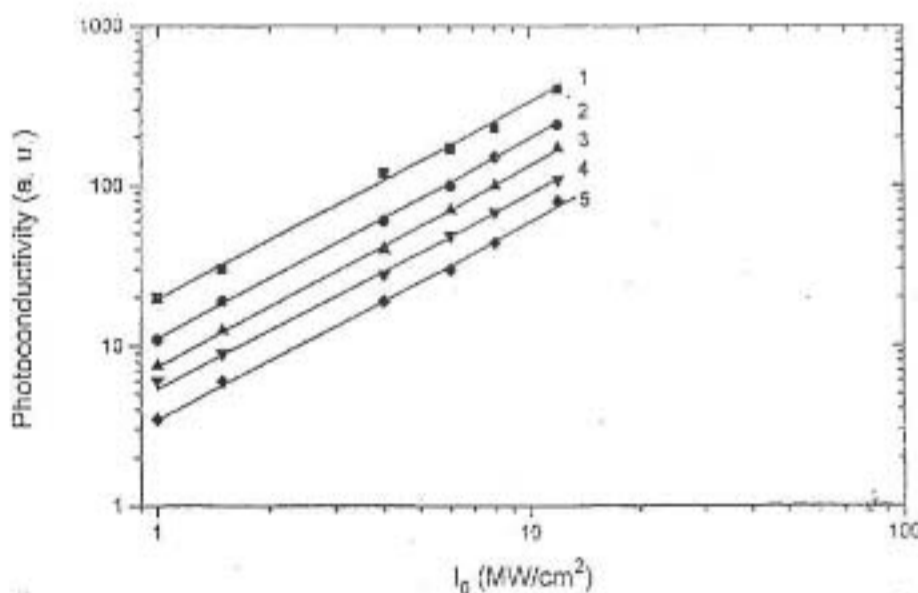


Fig. 5. Dependence of the photoconductivity on the excitation intensities in $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ thin films for different x values:
1 - 0, 2 - 0.05, 3 - 0.15, 4 - 0.25.

luminescence spectra $Zn_xCd_{1-x}S$ films for different composition are illustrated in Fig.6. As it is seen from the figure these spectra include two recombination lines which are shifted to the higher energies when x increase. The short-wavelength peak emission is present only at small zinc concentration ($x = 0+0.10$). For $x = 0$ (CdS) the shortwavelength line is due to the well-known zero-phonon recombination of the free excitons [12]. The ionization energy of the free exciton has been accurately determined from the hydrogenic absorption series of the excitonic states and it results in 10 meV [13].

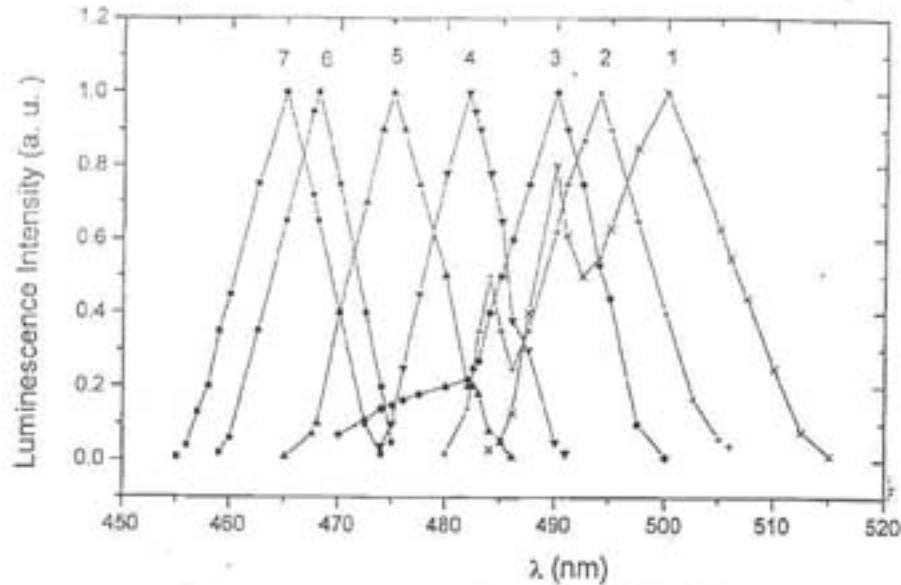


Fig.6. Luminescence spectra of $Zn_xCd_{1-x}S$ thin films at 80 K for different x values: 1- 0, 2- 0.05, 3 - 0.10, 4 - 0.15, 5 - 0.20, 6- 0.25, 7- 0.30.

Knowing the energy gap for different composition and their dependence on temperature ($dE_g/dT = -5 \cdot 10^{-4} eV/K$ [14]) we can conclude that the shortwavelength emission line for different composition correspond also to free exciton line. The disappearance of this line for $x > 0.1$ is probably due to the nonexistence exciton in ZnS compound. So, approaching this compound by increasing the Zn value in composition $Zn_xCd_{1-x}S$ the exciton emission line will be disappeared. The long-wavelength emission lines taking places at all composition being due to the structural defects existing in $Zn_xCd_{1-x}S$ films (Table 2) [15, 16].

Table 2. Features of the luminescence lines of $Zn_xCd_{1-x}S$ films at 80 K.

| x | Short-wavelengths (nm) | Long-wavelengths (nm) |
|------|------------------------|-----------------------|
| 0 | 490 | 500 |
| 0.05 | 484 | 494 |
| 0.10 | 480 | 490 |
| 0.15 | -- | 482 |
| 0.20 | -- | 475 |
| 0.25 | -- | 468 |
| 0.30 | -- | 465 |

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MƏHLULDAN TOZLANDIRMA ÜSULU İLƏ ALINMIŞ $Zn_xCd_{1-x}S$ İNCƏ TƏBƏQƏLƏRİNİN FOTOKEÇİRİCİLİYİ VƏ LÜMİNESSENSİYASI

$CdCl_2, CS(NH_2)_2$ və $ZnCl_2$ sulu məhlulunun tozlandırma üsulu ilə $Zn_xCd_{1-x}S$ ($x=0+0.3$) incə təbəqələri alınmışdır. Qəfəs sabiti və qadağan olunmuş zolağın eni ölçülmüşdür. Xüsusi müqavimətin, fotokeçiriciliyin, buraxmanın və lüminessensiyanın təbəqənin tərkibindən asılılığı öyrənilmişdir. Alınmış nəticələr bərk məhlulda ZnS -in artması ilə qadağan zonanın eninin artması faktı ilə izah olunur.

А.И. Байрамов

ФОТОПРОВОДИМОСТЬ И ЛЮМИНЕСЦЕНЦИЯ $Zn_xCd_{1-x}S$ ПЛЕНОК, ПОЛУЧЕННЫХ МЕТОДОМ РАСПЫЛЕНИЯ РАСТВОРА

Получены $Zn_xCd_{1-x}S$ тонкие пленки в интервале состава $0 \div 0.3$ и водных растворов $CdCl_2 \cdot CS(NH_2)_2$ и $ZnCl_2$ при использовании метода распыления раствора. Измерены константы решетки и ширина запрещенной зоны. Исследовались зависимости удельного сопротивления, фотопроводимости пропускания и люминесценции от состава пленок. Полученные результаты объяснены в основе того факта, что увеличение ZnS в твердом растворе приводит к увеличению ширины запрещенной зоны.

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