XIII_636

PREPARATION OF $CdS_{1-x}Se_x$ SOLID SOLUTION THIN FILMS WITH A DOMINATING SFALERITE STRUCTURE

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ABSTRACT

The method of chemical deposition of $CdS_{1-x}Se_x$ solid solution thin films is based on a chemical reaction of cadmium ions, with the selenium and sulphur ions, obtained by a thermal decomposition of the reactive compounds, thioacetamide and selenourea, in a neutral environment.

The composition vas verified by ionometric analyses and the structure of the thin films was studied by the X-ray diffraction analyses.

From the transmission optical spectra, and the spectral sensitivity of the photoconductivity, the value of the optical band gap E_g(opt) was evaluated for the whole set of thin $CdS_{1-x}Se_x$ for which x varies from 0 to 1.

It was found that E_g decreases with the increase of the molar fraction of the selenium in the solid solution (x).

INTRODUCTION

There are variety of methods for semiconducting thin films preparation, such as evaporation, spray-pyrolysis, electrolyses, molecular beam epitaxy, chemical deposition (electroless method)[1], etc.
The chemical deposition method is also utilized for preparation of thin semiconducting films of solid solutions, and ternary alloys,such as $CdS_{1-x}Se_x$ [2-4], $CdInSe_2$ [5], $Cd_{1-x}Pb_xSe$ [6], etc, which have a wide applicability for photovoltaic cell preparation, in the laser technology [7], LED, light sensors for VIS and NIR [8-9], photochemical cells [10], etc.

A new chemical method of deposition in one reaction bath, for thin $CdS_{1-x}Se_x$ film preparation, will be presented in this work. Some optical and photoelectrical properties will be examined and discussed below.

EXPERIMENTAL PART

The natrium-silicate glass substrates were initially degreased in chromsulphuric acid, and after rinsed with a distilled water, were vertically deepen in a beaker containing 100 ml of the reaction solution which consists of

0.08 mol/dm^3 $CdCl_2$,

CH_3CSNH_2 (thioacetamide) and NH_2CSeNH_2 (selenourea).

The sum of the molar fractions of the deposition reagencies, regardless to their mutual ratio, is always equal to 0,1. The alcality of the media was set to 6.7, at a temperature of

approximately 60°C. At those conditions, the thioacetamide and the selenourea decompose to H_2S and H_2Se which results into generation of sulphide and selenide ions in the reaction media. The deposition process was completed in about 50 min, and the films obtained are with a thickness of approximately 0,4 micrometers. After rinsed and soaked in a distilled water for several hours, and dried naturally, the samples were thermally treated at a temperature of 300°C in air, for three hours.

The composition and the crystal structure of the thin films were verified by X-ray diffraction analyses on a diffractometer type: JEOL MODEL DX-GO-F, Ni-filtered, Cu-anticathode. Quantitative analyses were undertaken by using conventional methods of ionometric analyses and polarography.

The optical spectra were recorded on Hewlett Packard 8452A spectrophotometer, and the spectral sensitivity of the photoconductivity was measured by the method of constant field [11]. A monochrometer XM-2 was used as a light source.

RESULTS AND DISCUSSION

From the X-ray patterns analyses on the pure samples (CdS and CdSe, Fig.1 (a) and (c)), it could be found that the d-values correspond to cubic and hexagonal crystal forms.
The analyses of the relative intensities I/Io [12] shows dominance of the cubic structure.From the X-ray diffraction

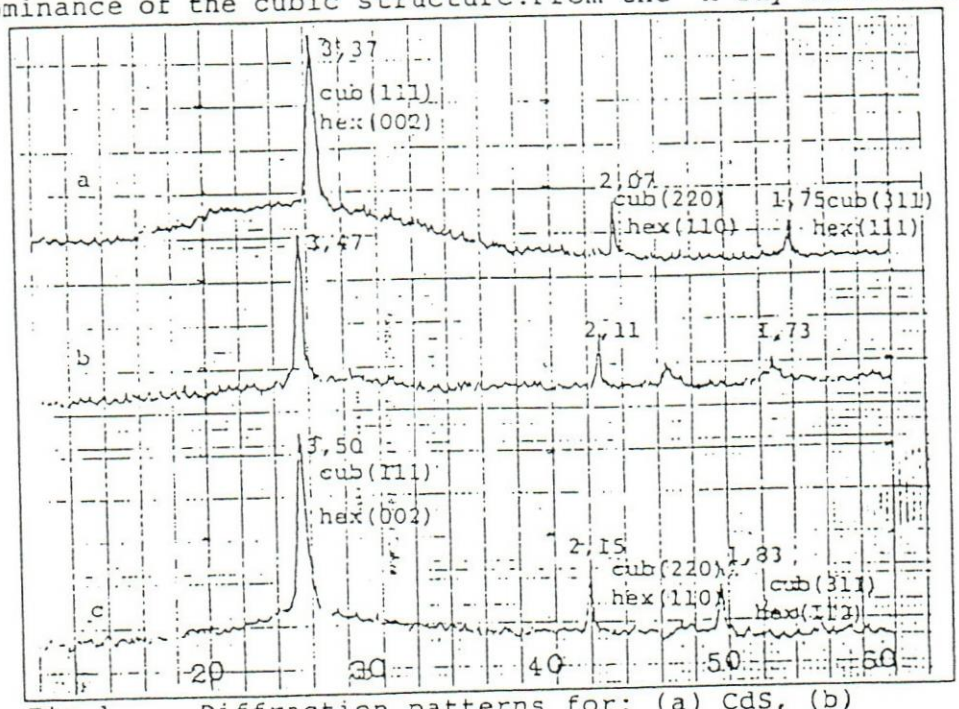

Fig.1 Diffraction patterns for: (a) CdS, (b) $CdS_{0.7}Se_{0.11}$, and (c) CdSe thin films

pattern of the thin $CdS_{0.7}Se_{0.21}$, presented on Fig.1 (b) it could be seen that none of the d-values corresponds to the d-values of the pure samples, CdS and CdSe, which proves that the abovementioned ternary compound thin film is actually a solid solution. The parallel shift of the diffraction maxima observed in all other mixed samples, proves the formation of solid solution between CdS and CdSe, $CdS_{1-x}Se_x$ for every $0<x<1$ [13].

The optical spectra of the examined set of thin $CdS_{1-x}Se_x$ films give a qualitative picture of the shift of the absorption edge towards a longer wavelength with the increase of the x (the molar fraction of the selenium in the compound). Other information obtained from the transmission spectra analyses are the values of the optical band bap $E_{g(tr)}$, Fig.3, Table I, with consideration that the solid solution $CdS_{1-x}Se_x$ films are direct type of semiconductors [14]. The values of the optical band gap were also evaluated from the spectral sensitivity of the photoconductivity, $E_{g(ph)}$. On Fig.3, only the peak values of the photoconductivity spectra are marked with up-pointed arrows to signify the corresponding values of the $E_{g(ph)}$ for all the studied samples [15]. It is obvious that the values for E_g obtained by two different methods show a good agreement,(see Table I)

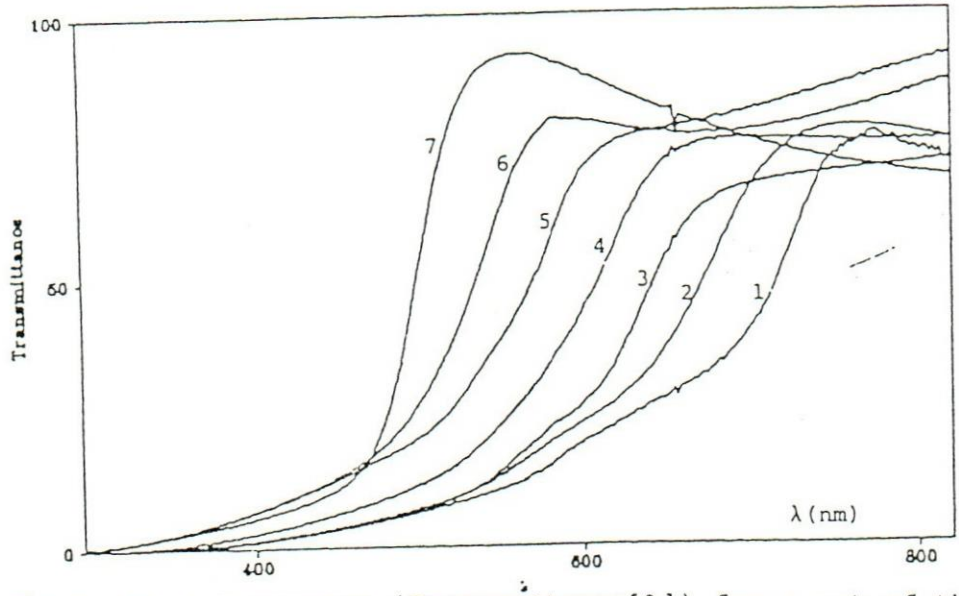

Fig.2 Optical spectra (Transmittance[%]),for a set of thin $CdS_{1-x}Se_x$, where x varies from 0 to 1 (use Table I as a legend).

Table I. *Calculated values for Eg(tr) and Eg(ph) for a set of seven thin films, where x varies from 0 to 1.*

film No.	$CdS_{1-x}Se_x$		$E_{g(tr)}$ [eV]	$E_{g(ph)}$ [eV]
	x	solid solution		
1	1.00	CdSe	1.70	1.80
2	0.87	$CdS_{0.13}Se_{0.87}$	1.79	1.88
3	0.77	$CdS_{0.23}Se_{0.77}$	1.89	2.05
4	0.65	$CdS_{0.35}Se_{0.65}$	1.97	2.06
5	0.43	$CdS_{0.57}Se_{0.43}$	2.20	2.16
6	0.21	$CdS_{0.79}Se_{0.21}$	2.35	2.41
7	0.00	CdS	2.50	2.53

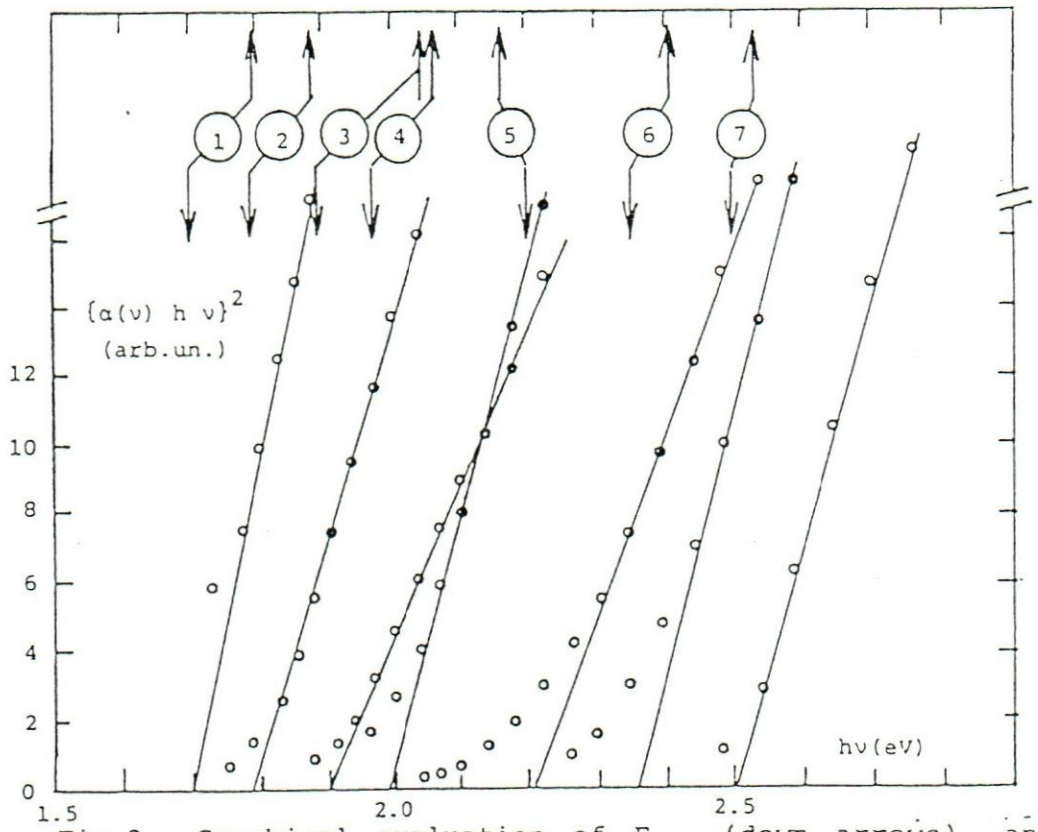

Fig.3 Graphical evaluation of $E_{g(tr)}$,(down arrows), and presentation of $E_{g(ph)}$,(up arrows), for seven $CdS_{1-x}Se_x$ samples. Use Table I, as a legend.

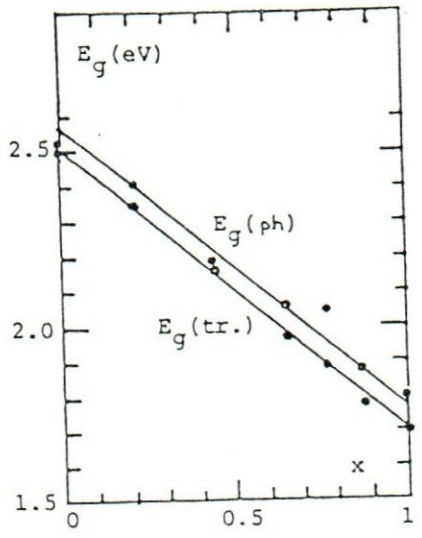

Fig.4 Dependence of the band gap (E_g) on the molar fraction of the selenium (x) in the compound.

The presentation of E_g as a function of x, Fig.4, shows linear dependence.

CONCLUSION

The samples obtained by the described method are a solid solution type $CdS_{1-x}Se_x$ thin films with a dominance of a cubic crystal lattice forms. The E_g decreases linearly with the increase of the molar fraction of the selenium (x) in the samples. The films show a good relative photoconductivity. The ratio between the conductivity of the thin films, when illuminated with white light (60mW/cm²), and their dark conductivity is of the order of magnitude od 10^3, which gives an opportunity, those materials to be used as photosensors in the optoelectrical device design and construction.

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