STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, LIV, 3, 2009

GROWTH AND CHARACTERISATION OF ZINC-CADMIUM SULPHIDE THIN FILMS WITH SPECIAL OPTICAL PROPERTIES

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ABSTRACT. Nanostructured ZnCdS thin films with variable thickness and high transparency were deposited under variable growth parameters on optical glass platelets, using chemical bath deposition. UV-VIS absorption/reflection spectroscopy, X-ray diffraction, fluorescence spectroscopy, electron microscopy investigations (SEM, EDX) were used to investigate the effect of growth and annealing regime on the films morphology and optical properties. The luminescence properties of copper activated ZnCdS thin films were also investigated. The deposition conditions (medium pH, reagent molar ratio, deposition time) and the presence of the doping ions (copper) influence the morpho-structural properties and optical characteristics of the nanocrystalline zinc-cadmium sulfide thin films.

Keywords: *thin films; chemical synthesis; optical properties; luminescence*

INTRODUCTION

Zinc sulfide (ZnS), cadmium sulfide (CdS) and their solid solution zinc-cadmium sulfide ($Zn_{1-x}Cd_xS$ or ZnCdS) are interesting wide band gap semiconductors, which attract much attention because of their interesting optoelectronic properties [1-4].

Due to their special optical and electrical properties, metal chalcogenide thin films have been used in various optoelectronic devices, such as solar energy absorbers, photodetectors and electroluminescent displays [5-7]. Different methods could be used for metal chalcogenide thin films preparation including sputtering [8], MOCVD (metal organic chemical vapor deposition) [9], SILAR (successive ionic layer adsorbtion and reaction) [10], pulsed laser deposition [11], chemical bath deposition (CBD) [12] or electrodeposition [13]. Among them,

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CBD is a simple and inexpensive method to produce uniform and adherent films onto a variety of substrates. There are few literature data referring to the chemical bath deposition of ZnCdS thin films with optical properties illustrating that the characteristic films properties strongly depend on chemical bath deposition conditions [14,15]. In order to control the quality of ZnCdS thin films, supplementary studies aiming at the optimization of CBD parameters are needed.

The paper presents our results on the growth and characterization of some reproducible ZnCdS thin films prepared by chemical bath deposition. The effect of cadmium ions addition into the chemical deposition bath on the quality of metal chalcogenide thin films is investigated. Moreover, attempts were made to prepare ZnCdS thin films with luminescent properties using a special doping procedure, not mentioned in the literature.

RESULTS AND DISCUSSION

The preparation of ZnCdS thin films by CBD was based on the reaction, in alkaline medium (NH_3), between zinc acetate, $Zn(CH_3COO)_2$ and cadmium acetate, $Cd(CH_3COO)_2$ as metal sources and thiourea $(NH_2)_2CS$, as chalcogen source. The main chemical process for zinc-cadmium sulphide thin films formation is described by the following equation:

$$M(CH_3COO)_2 + (NH_2)_2CS + 2OH^- \rightarrow MS + H_2CN_2 + 2H_2O + 2CH_3COO^-$$

where M=Zn and Cd

The formation of thin films takes place either in the bulk of the solution due to the spontaneous precipitation of ZnS and CdS (homogeneous reaction) or at the surfaces of the substrate leading to the film formation (by heterogeneous reaction).

Our previously studies on chemical bath deposited ZnS thin films [16] pointed out the importance of sodium citrate [Cyt] as complexing agent. Based on our results, the standard chemical deposition bath corresponds to the following reagent ratio: $[Zn^{2+}]$: $[Cyt^{3-}]$: $[NH_3]$: [thiourea] =1:3:20:10. Starting from this bath, ZnCdS /glass/ ZnCdS hetero-structures were prepared by replacing 5 ÷100 mol % of zinc acetate with cadmium acetate.

Zinc-cadmium sulfide thin films were grown by multilayer technique. Four consecutive layers were deposited on glass platelets to give ZnCdS /glass/ ZnCdS heterostructures. For the same deposition time, addition of cadmium acetate into the standard chemical bath used for ZnS-film deposition does not deteriorate the film quality. The as obtained ZnCdS thin films possess good adherence to the substrate, are transparent and show colors varying from white-yellowish to orange-yellowish, depending on the Cd^{2+} - amount from the chemical deposition bath.

According to the literature data [17], the deposition of ternary materials by chemical bath methods is a problem due to the different hydrolytic stabilities of the two metals. This is illustrated with the fact that, ZnCdS films obtained by CBD show properties that vary non-linearly with the bath composition.

The packing density of ZnCdS thin films varies non-monotonically with Cd^{2+} - concentration, thus suggesting the existence of more different competitive deposition processes with consequences on the film homogeneity (Fig. 1).

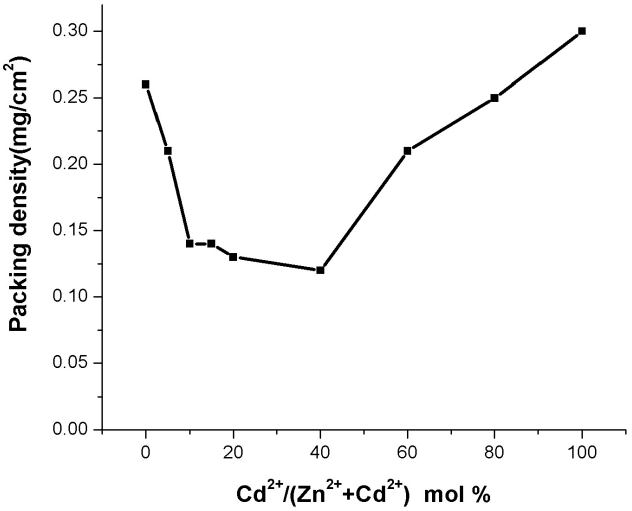

Figure 1. Packing density of ZnCdS *versus* Cd^{2+}-concentration from the chemical deposition bath

The optical properties of ZnCdS thin films are strongly influenced by the deposition technique and CBD bath composition. The transmittance spectra of ZnCdS thin films obtained from chemical bath with different Cd^{2+} amounts are depicted in figure 2.

UV-Vis transmittance spectra illustrate the non-monotonous variation of film transparency with Cd^{2+} content. Films obtained from bath containing 5-10 mol% Cd^{2+} are the most transparent and optical homogeneous. The absorption edge (Fig. 3) shifts non-linearly from UV domain (~ 300 nm for 0 mol% Cd^{2+}) to blue domain (~455 nm for 100 mol% Cd^{2+}). Evaluation is based on the wavelength corresponding to 0.1 % transmittance values.

UV-Vis reflectance spectra (Fig. 4) illustrate that the behavior of ZnCdS films is very different in respect with their specular reflectivity. The reflection peak shifts non-monotonically from ultraviolet (0 mol% Cd^{2+}) to red domain (100 mol% Cd^{2+}). The most light reflecting films are obtained in bath containing 5 ÷ 20 mol % Cd^{2+}.

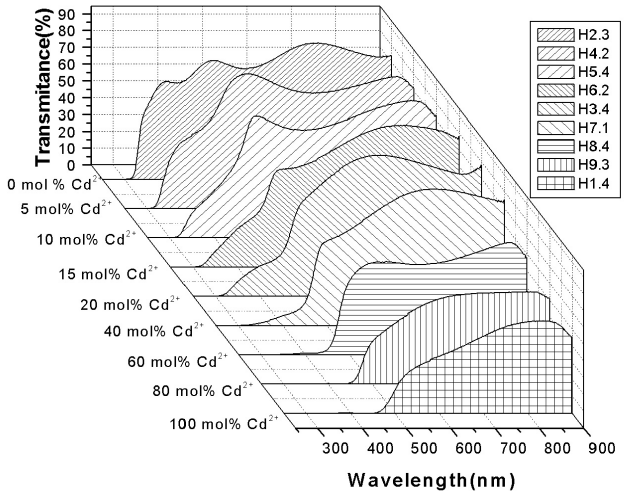

Figure 2. Transmittance spectra of ZnCdS thin films obtained from chemical bath with different Cd^{2+} amounts

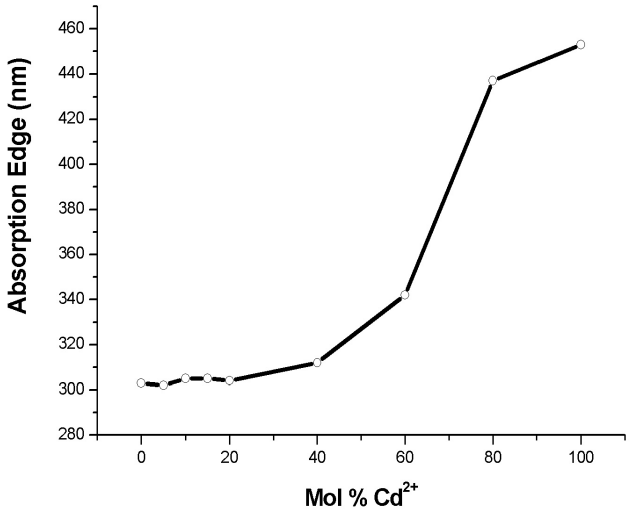

Figure 3. Variation of absorption edge position of ZnCdS thin films with Cd^{2+}-amount from chemical bath

The specular reflectance was evaluated as difference between total reflectance (measured at 8° incidence) and diffuse reflectance (measured at 0° incidence).

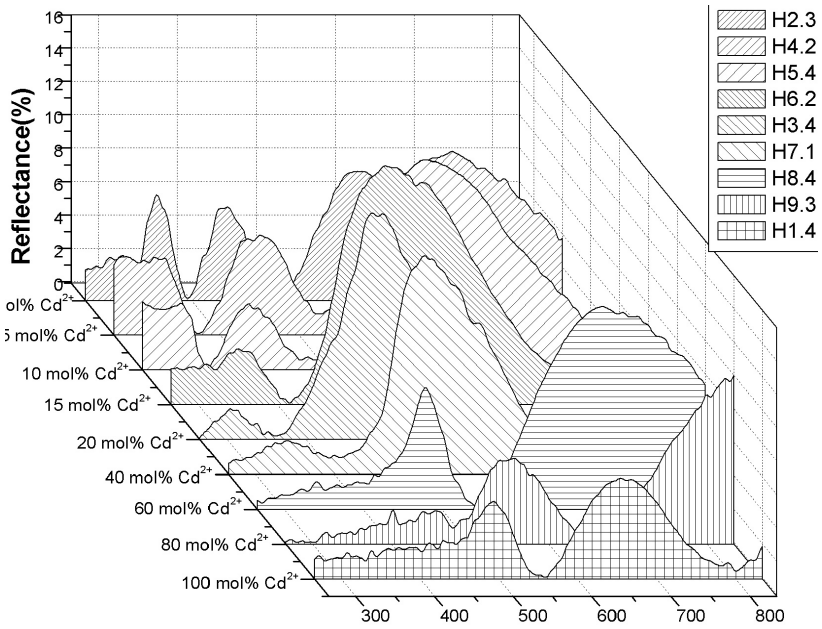

Figure 4. Specular reflectance spectra of ZnCdS thin films obtained from chemical bath with different Cd^{2+} amounts

Morphology of ZnCdS films was investigated by scanning electronic microscopy (Fig. 5). SEM images put in evidence that the surface of films deposited from bath with different Cd^{2+} amounts, is variable. The most structured/particulate film is obtained from bath containing only cadmium acetate.

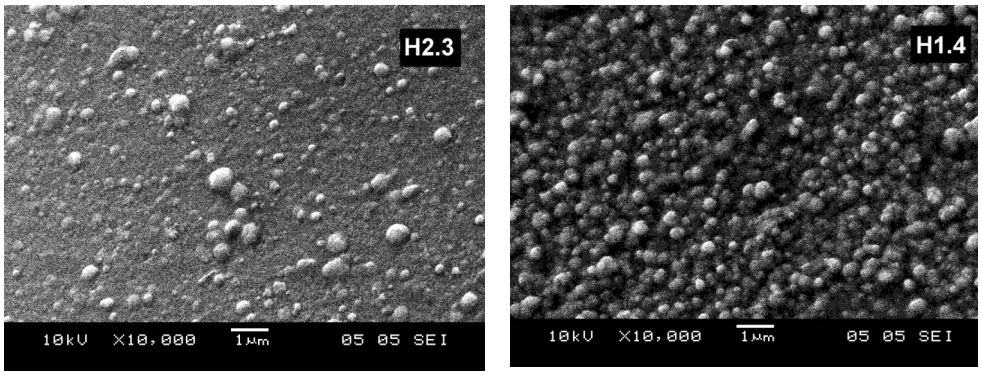

Figure 5. SEM images of ZnS film (H2.3) and CdS film (H 1.4)

EDX investigations proved that film composition is different of that one of the chemical bath, as already suggested by the UV-Vis spectroscopic investigations (Table 1). For instance, the composition of film H7.2 obtained from bath with 40 mol% Cd^{2+} contains about 75 mol% Cd^{2+}. One notes also that the ZnCdS are usually thinner than the pure ZnS or CdS films). As expected, the preferential precipitation of cadmium sulfide is observed and Cd-rich ZnCdS films are usually growth in our CBD conditions.

One can also note that, according to the EDX data, the heterostructure contains Zn, Cd and S from the chalcogenide films and Si, O, Ca, Na, Mg and Al from the glass substrate (the electron beam penetrates the thin ZnCdS film and enters into the glass substrate, see table 1).

Table 1. Composition of the ZnCdS/glass/ZnCdS films heterostructures obtained from chemical bath with different compositions (where others = Na, Mg, Al, K, Ca, O)

Code	Zn/Cd in bath	Heterostructure composition (mol %)					Zn/Cd in film	Packing density (mg/cm^2)
		Si	Others	Zn	Cd	S		
H2.1	1:0	10.70	72.51	11.25	0	5.54	1:0	0.26
H3.2	1:0.25	62.89	29.79	1.23	1.56	4.53	1:1.27	0.13
H7.2	1:0.66	29.89	67.03	0.29	1.05	1.74	1:3.62	0.12
H9.2	1:4.00	29.76	62.54	0.19	3.27	4.24	1:17.21	0.25
H1.5	0:1	29.65	56.00	0	6.53	7.82	0:1	0.30

The crystalline structure of ZnCdS thin films has been investigated by the X-ray diffraction technique (Fig. 6). All films deposited on glass substrate are amorphous, as illustrated by the X-ray scattering curves; an organization tendency of CdS containing layers in comparison with ZnS films can be observed.

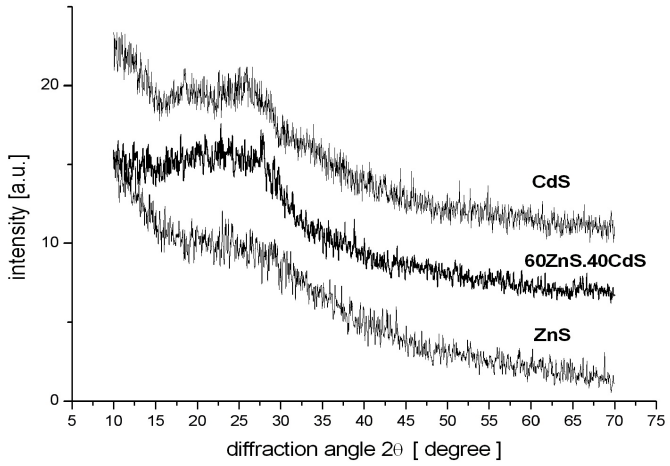

Figure 6. X-ray scattering curves of some ZnCdS films (MoK_α)

The light emitting properties of metal chalcogenide thin films are highly sensitive to the annealing regime as well as to the doping conditions [16]. In order to develop photoluminescent properties, ZnCdS /glass/ ZnCdS heterostructures were activated with copper ions, using indirect doping technique [16]. Emission spectra of Cu doped heterostructures obtained from chemical bath with different Cd^{2+} amounts are presented in figure 7.

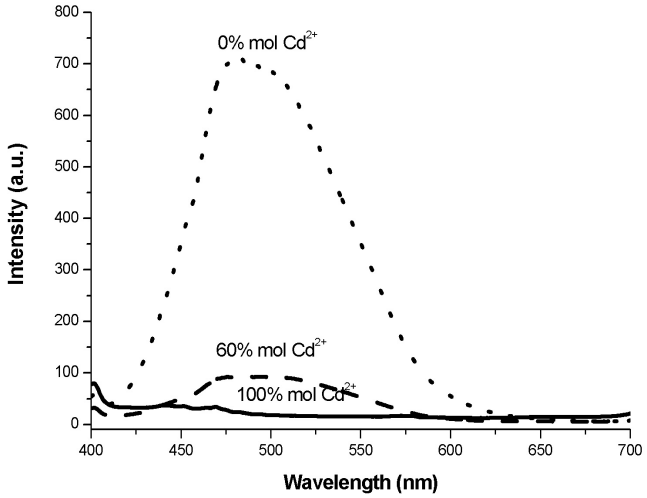

Figure 7. Emission spectra of ZnCdS: Cu films obtained from chemical bath with different Cd^{2+} amounts

ZnS:Cu film show intense green luminescence, with maxima at 483 nm and 500-510 nm. The addition of cadmium into the bath produces a dramatic decrease of the photoluminescent emission and a small shift of the emission peak toward higher wavelengths.

CONCLUSIONS

High quality zinc-cadmium sulfide thin films with special optical properties were prepared by chemical bath deposition onto optical glass platelets using zinc acetate- cadmium acetate– sodium citrate - ammonia – thiourea system. The deposition from chemical bath with variable cadmium amounts leads to ZnCdS /glass/ ZnCdS heterostructures with very different morpho-structural and optical (transmittance/reflectance) characteristics.

Photoluminescence measurements performed on some Cu-doped ZnCdS films illustrate that CBD grown metal chalcogenide films can be activated with different cations, using the indirect doping technique. Further investigations are needed in order to obtain more performing luminescent ZnCdS layers.

EXPERIMENTAL SECTION

ZnCdS thin films have been grown on 3 x 4.5 x 1 cm^3 optical glass substrates by CBD using the multilayer technique already employed. The deposition of ZnCdS thin films was carried out using the method employed for the chemical bath deposition of ZnS and CdS, respectively. The starting point was the chemical bath used for ZnS film deposition, as follows: [zinc acetate] = 0.015 M; [sodium citrate] = 0.045 M; [ammonia] = 0.3 M; [thiourea] = 0.15 M. ZnCdS thin films were deposited from chemical bath obtained by replacing 5 ÷100 mol % of the zinc acetate from the standard chemical bath with cadmium acetate. The glass substrates have been previously ultrasonically cleaned in acetone-ethanol mixture. During the deposition, the bath temperature was maintained at 82-86°C and the solution pH at 9.5-10.5. Luminescent ZnCdS thin films were prepared using indirect doping technique. In this purpose, ZnCdS /glass/ ZnCdS heterostructures were introduced into a Cu-containing doping mixture based on high-purity ZnS powder and annealed at 550°C. The details of the experimental technique and conditions have been described in our previous works [16, 18-20]

Chemical bath deposited ZnCdS /glass/ ZnCdS structures have been analysed as grown or after annealing. Packing density was determined by the micro-weighing method. An UNICAM Spectrometer UV4 has been used for optical investigations of ZnCdS thin films and a Perkin Elmer 204 Fluorescence Spectrophotometer was used to investigate photoluminescence characteristics. The structural properties of the films were studied with a standard DRON-3M Diffractometer using the filtered Kα emission of molybdenum (λ=0.70932 Å). Morphology of the films was studied with a JEOL-JSM 5510LV Electron Microscop. Chemical composition of the films was detected by Energy Dispersive X-ray Analysis (EDX) in a JSM 5510LV Scanning Electron Microscop atached with an Oxford Instruments, Inca 200 analytical system.

ACKNOWLEDGEMENTS

The work was financially supported by the Romanian Ministry of Education and Research MEC-CNCSIS Grant Td 8/52- 2007.

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