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SPECTROSCOPIC CHARACTERIZATION OF CHEMICAL BATH DEPOSITED CADMIUM SULPHIDE LAYERS

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Thin films of cadmium sulphide have been prepared by chemical bath deposition in alkaline ammonia solutions from cadmium acetate and thiourea, using sodium citrate and/or ammonium chloride as chelating agent. The films grown from the bath without citrate are uniform and adherent, have a high transmittance and good reflectance in the visible region, and are about 2 times thicker than the films deposited from the „standard" bath. The evolution of optical characteristics of CdS films after annealing process was influenced by the deposition conditions.

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1. Introduction

At present, the importance of cadmium sulphide thin films as wide energy gap semiconductors has experienced a fast rising, mainly due to its applications in piezoelectric transducers, laser materials and photovoltaic cells. The commonly used methods for depositing CdS thin films [1] are vacuum evaporation, sputtering, spray pyrolisis, molecular beam epitaxy and electrodeposition. The electron-beam obtain in a new method recently developed [2]. The chemical bath deposition (CBD) is an „electroless" technique that is attractive as a simple and low cost method [3-6]. Unfortunately, the deposition conditions (bath composition, reagent concentrations, temperature, pH etc.) strongly influence the film stoichiometry, microstructure and cristallinity. It is well known that these characteristics determine the optical and electrical properties of CdS films.

The aim of this paper is to study the optical properties of some mono- and multilayer CdS films prepared by CBD method. The effect of bath composition (the partial or total replacing with ammonium chloride of sodium citrate used as chelating agent) on the optical absorption coefficient and the band gap energy E_g of as-grown and annealed films is reported.

2. Experimental part

Cadmium sulphide films were prepared from cadmium acetate and thiourea by chemical bath deposition in alkaline solution:

$$Cd(CH_3COO)_2 + (NH_2)_2CS + 2HO^- \longrightarrow CdS + H_2CN_2 + 2H_2O + 2\ CH3\ COO^-$$

There were used three different bath compositions characterised by the following reagent molar ratios [cadmium acetate] : [sodium citrate] : [ammonium chloride] : [ammonia] : [thiourea]:

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Bath # 1: 1 : 40 : 0 : 100 : 10
Bath # 2: 1 : 40 : 0.2 : 100 : 10
Bath #3: 1 : 0 : 8 : 100 : 10

Films were grown on optical glass slides (30 × 45 × 1 mm), cleaned by special procedures, using an optimised solution temperature of 70 °C, a pH of 10 – 11 and a deposition time of 1 hour for one layer. Thick samples were produced by successive depositions. In the multi-step procedure, after each deposition stage, samples were carefully washed in distilled water to remove the porous cadmium sulphide overlayer and then immersed into renewed chemical bath.

Film thickness was determined by microweighing method.

The post–growth treatment of the samples consisted in 1hour air annealing at 350° and 500 °C, in an electrical furnace.

The transmission and reflection data were obtained by means of a UNICAM UV4 double beam spectrophotometer. The optical tramsmission of CdS films on glass support was measured at near normal incidence in the 300-900 nm wavelength range. Reflectance spectra at 8° (specular reflectance included) and 0° (diffuse reflectance) incidence angle were obtained using the integrating sphere RSA-UC-40 accessory and Spectralon reflectance standard.

Optical band gap energy (E_g) was determined graphically, after extrapolation of the plot at $\alpha = 0$, using the standard expression for direct transitions between two parabolic bands: $(\alpha h\nu)^2 = A (h\nu - E_g)$

To calculate the absorption coefficient values, the transmission was measured, after the removal of the film from one side of the substrate. Such structures are noted as CdS/glass.

3. Results and discussion

Cadmium sulphide films can be prepared by decomposition of thiourea in an alkaline solution containing cadmium salt. The deposition of CdS films is achieved from very dilute solutions. Sulphide ions are released in the bath by the hydrolysis of thiourea, in the presence of OH^- ions. Cd^{2+} ions are complexed with one or more of the chelating agents like NH_3 [directly added as NH_3(aq.) or evolved from NH_4Cl in the presence of NaOH or KOH, triethanolamine, $(CN)^-$, citrate, etc. This ensures slow release of Cd^{2+} ions in the solution.

The change of the bath composition influences the formation and the dissociation of cadmium ammonia and/or cadmium citrate complexes and finally the deposition rate of the CdS films and their characteristics.

Table 1. Thickness and growth conditions of CdS/glass samples.

Sample code	Chemical bath type	Deposition time	Film thickness (nm)
A16.2	1	1 × 1h	75
C1.1	2	1 × 1h	86
N2.1	3	1 × 1h	169
A16.3	1	2 × 1h	135
C2.1a	2	2 × 1h	125
N2.3	3	2 × 1h	403
A16.6	1	4 × 1h	261
C2.2	2	4 × 1h	275
C1.3	2	4 × 1h	298
N2.5	3	4 × 1h	807

Data from Table 1 show that CdS films prepared from the bath # 3 are about twice thicker than the other films obtained at equal deposition time. The rising of deposition rate does not alter the optical characteristics of these films.

Cadmium sulphide films characterisation

The optical homogeneity of all films was checked by measuring the transmittance spectra of different part of the samples. The optical transmittance of CdS/glass structures deposited from the „standard" chemical bath #1 is presented in Fig. 1. As expected, the film transmission decreases as the thickness increases. The pattern of interference fringes suggests that films are adherent and have enough uniform thickness.

XRD spectra showed that the as-grown cadmium sulphide films possess a hexagonal structure (reflexion lines at 3.5674; 3.3583; 3.1641 Å), with (002) preferential orientation.

The transmittance spectra of samples prepared from different baths are presented in Fig. 2. Although the film N2.1 deposited from chemical bath # 3 is thicker (169 nm), it has a higher transmission. This fact suggests a minimisation of the adsorbed colloids (the powdery layer) which increase the diffuse scattering of the film.

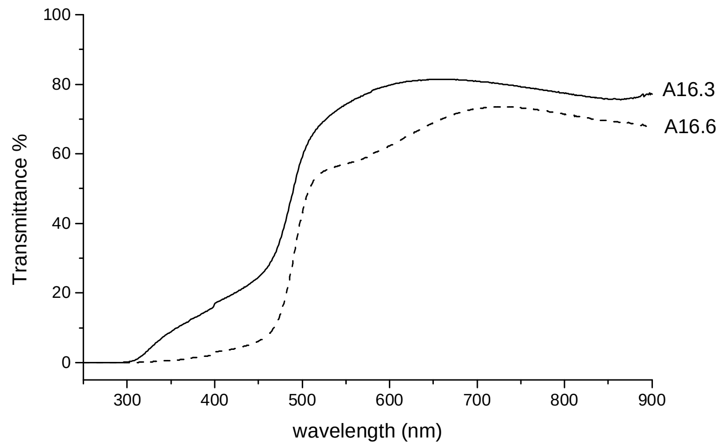

Fig. 1. Optical transmission of CdS/glass structures deposited from the standard chemical bath # 1. Thickness of the films: 135 nm (A16.3) and 261 nm (A16.6).

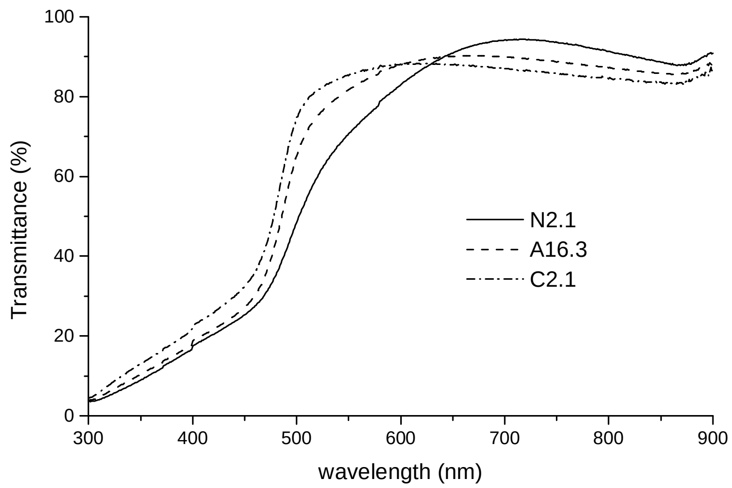

Fig. 2. Transmittance spectra (corrected for the glass absorption) of CdS films deposited from chemical baths of different composition.

The change of bath composition has a higher influence on the specular reflectance of CdS films. Again, the films prepared from bath # 3 have the best properties (Fig. 3). The partial replacement of sodium citrate with ammonium chloride (chemical bath # 2) produces reflectance decrease of CdS films.

In spite of the fact that during the annealing process the film thickness decreased, no improvement in the film transmittance of samples deposited from chemical bath # 1 or # 2 could be observed. The unusual dependence on wavelength of transmittance (Fig. 4) and also of specular reflectance (Fig. 5) for samples deposited from bath # 2 and annealed in air at 500 ^{o}C could be explained by the formation of some powdery layers between uniform adherent CdS layers. XRD analysis confirmed the formation of cadmium oxide, as illustrated by the additional reflexion lines at d = 2.6995 Å, 2.3411 Å and 1.6610 Å (Fig. 6).

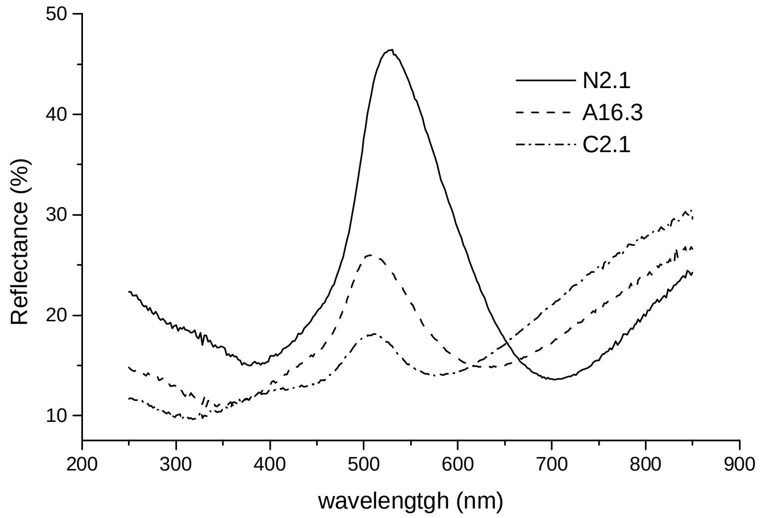

Fig. 3. Reflectance spectra at 8^{o} incidence angle of CdS/glass/CdS samples deposited from chemical baths of different composition.

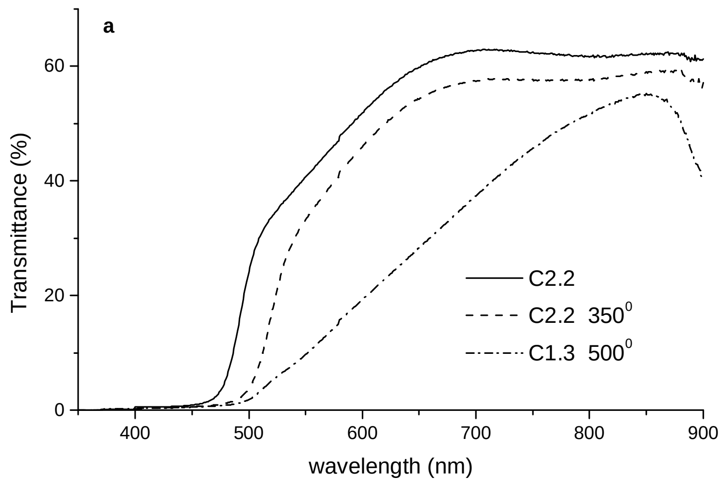

Fig. 4. Effect of air annealing on the transmittance spectra of CdS/glass/CdS samples grown by four successive depositions (chemical bath # 2).

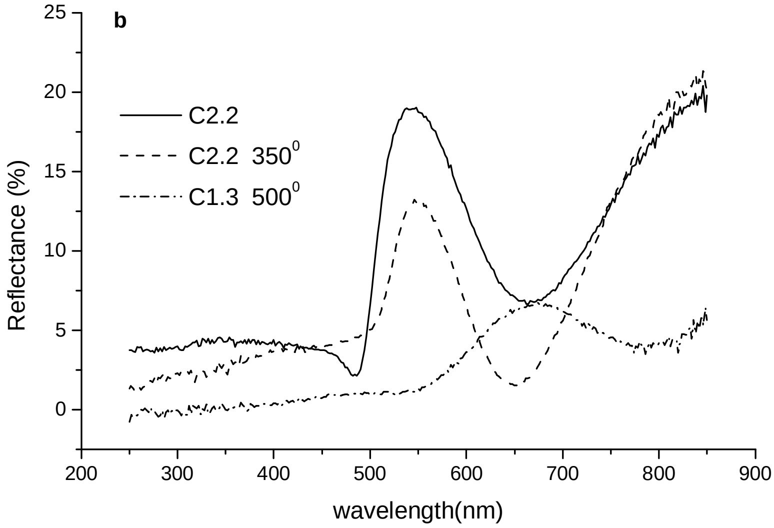

Fig. 5. Effect of air annealing on the specular reflectance i.e. reflectance measured at 8° incidence angle and corrected for diffuse reflectance of CdS/glass/CdS samples (chemical bath # 2).

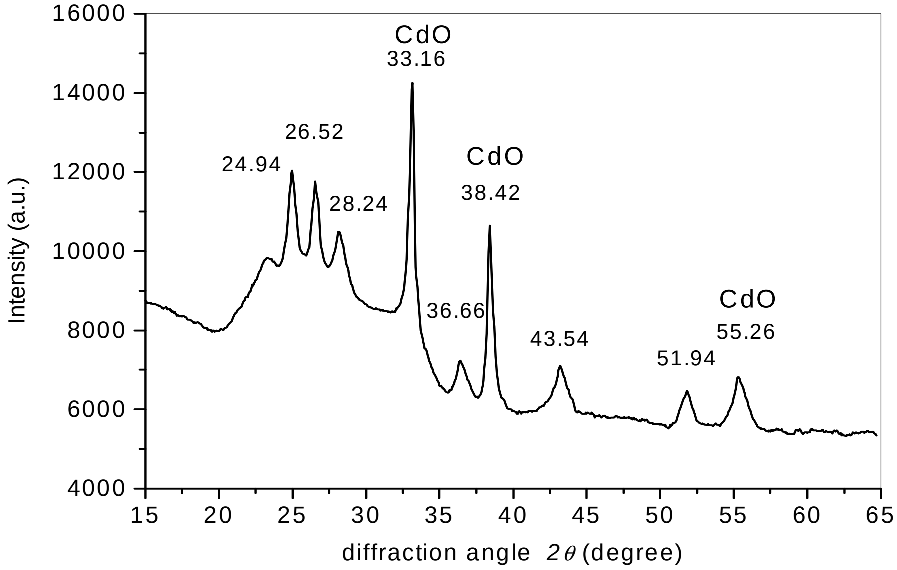

Fig. 6. XRD spectrum of CdS/glass/CdS sample annealed at 500 °C (CuKα radiation).

Optical constants of the films

Cadmium sulphide is a direct band gap semiconductor and a value of 2.42 eV is generally accepted for bulk CdS [7].

Absorption coefficient values associated with the strong absorption region of the films were calculated from transmittance data. The E_g value was estimated by extrapolation of the straight line of the plot of $(\alpha h\nu)^2$ *versus* photon energy (Fig. 7). The band gap of as-grown films is 2.41 eV for sample N2.1 and 2.50-2.52 eV for CdS deposited from chemical bath 1 or 2. The decreasing of band gap to 2.37 eV for sample C2.2 annealed at 350 °C and to 2.32 eV for sample C1.3 annealed at 500 °C confirms the powder nature of these films and suggests a possible contamination with cadmium hydroxide as source of CdO identified by XRD.

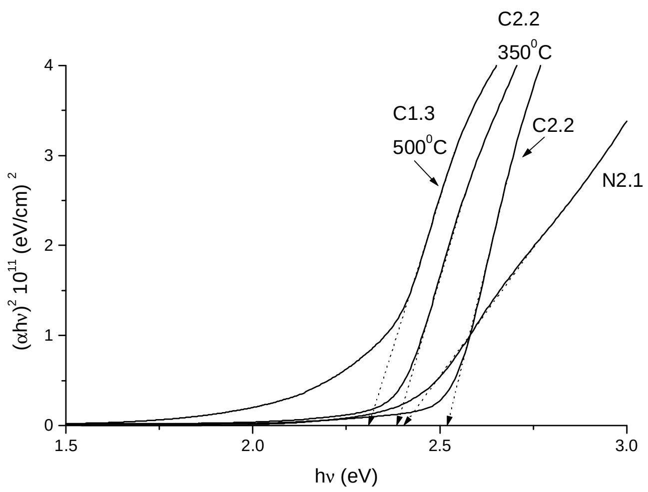

Fig. 7. Plot of $(\alpha h\nu)^2$ vs. hν for some cadmium sulphide films.

4. Conclusions

The replacement of sodium citrate with ammonium chloride influences the quality of CdS/glass samples modifying the growth rate and, consequently, the structural and optical properties of as grown and annealed films. Large ammonium chloride quantities are favourable to the formation of CdS films with good transparency and high reflectance values.

Acknowledgments

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