CHARACTERIZATION OF CdS THIN FILMS DEPOSITED BY CHEMICAL BATH DEPOSITION USING NOVEL COMPLEXING AGENTS

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Cadmium sulfide (CdS) thin films have been deposited by chemical bath deposition (CBD) at 70°C on glass substrates. In order to have a better control of deposition rate in CdS synthesis, Sodium borohydride and hydrazine were demonstrated as novel complexing agents. The structural, optical and electrical characteristics of the CdS thin films obtained were analyzed. Sodium borohydride as complex agent increased the deposition rate while hydrazine reduced the deposition rate due to higher complexation and slow generation of Cd^{2+} while improving the morphology of CdS films. Homogeneous CdS thin films with hexagonal crystalline structure and energy band gap of 2.4 eV were obtained. The deposited thin films showed a good electrical conductivity with resistivity values in the order of 10-300 Ω-cm, suggesting a low metal-semiconductor contact resistivity as well.

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1. Introduction

II–VI compound semiconductor deposition from aqueous solution has gained attention due to the economical advantages and capability of large-area deposition [1-2]. Cadmium sulphide (CdS) is the most studied chalcogenide with a bandgap of 2.4 eV (in bulk) [3], additionally it was studied as the semiconductor active layer during the early development of Thin Film Transistors (TFTs) [4]. The application of CdS films as window layers in high efficiency solar cells based on cadmium telluride (CdTe) and copper indium gallium selenide $Cu(In,Ga)Se_2$ (CIGS) has recently increased the interest and studies on this material [5].

CdS thin films have been prepared by different methods (physical and chemical) such as electrostatic deposition [6], gas evaporation [7], micelles [8], chemical bath deposition (CBD) [9] etc. Among those, CBD process is attractive due to the simplicity and low cost, the technique can yield homogeneous, adherent, transparent, and highly stoichiometric CdS thin films [10,11]. In particular chemical bath deposition is a technique used to obtain thin inorganic semiconductor films from most cations of transition metals and metalloids, with anions of group VI, and more often, with sulphide and selenide ions. This technique is also known as solution growth, controlled precipitation, or simply a chemical deposition. CBD can be used to deposit any compound that satisfies four basic requirements: the material must be prepared by simple precipitation, the compound is highly insoluble in the solution, the compound is chemically stable in the solution

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and the reaction should proceed with a free anion that is slowly generated [12]. Most CBD reactions are carried out in alkaline solution. To prevent the precipitation of metal hydroxides, a complexing agent is added. The complexing agent also reduces the concentration of free metal ions, which helps to prevent rapid bulk precipitation of the desired product.

Typically, CdS films are formed from the reaction between a cadmium salt and thiourea in an alkaline solution. The slow release of Cd^{2+} ions are achieved by adding a complexing agent (ligand) to the Cd salt to form some cadmium complex species, which, upon dissociation, results in the release of small concentrations of Cd^{2+} ions. The S^{2-} ions are supplied by the decomposition of thiourea.

The aim of the present work is to study the effect of sodium borohydride and hydrazine as novel complexing agents in CdS synthesis to deposit CdS thin films by chemical bath deposition method and to understand the growth mechanism and its impact in the electrical properties for electronics device applications. The films were characterized using X- ray diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM) to understand the CdS structure and morphology. The optical band gap was determined from UV-Vis absorption edges. The electrical characterization was carried out in order to obtain the resistance of the material, and the behavior of the current-voltage characteristics.

2. Experimental details

a) Substrate preparation

The CdS films were deposited on glass slide substrates (soda lime glass). The substrates were cleaned in an ultrasonic bath with acetone followed by isopropanol and finally rinsed with distilled water and dried under a N_2 flow.

b) Cadmium sulphide deposition

The CdS films were deposited by immersion of the substrates in a CBD solution prepared from cadmium nitrate ($Cd(NO_3)_2$), sodium borohydride ($NaBH_4$)/hydrazine (N_2H_4), pH 10 ammonia buffer and thiourea ($SC(NH_2)_2$) in a volumetric ratio of 4 ml (0.1M): 5 ml (0.5 M/30%): 4 ml: 5 ml (1M). The total reaction volume was adjusted with water to 62 ml. The temperature of the solution was maintained at 70 °C +/- 1°C for 12 minutes. After deposition, the CdS films were cleaned in an ultrasonic bath with methanol followed by distilled water rinse and dried with N_2.

The crystalline structure of the CdS films was analyzed in a Rigaku Ultima III X-ray diffractometer with CuKα (λ)= 1.54 Å, operated at 40kV and 44mA. The 2ϴ scan rate was 0.5°/min. The morphology was studied in a SEM Zeiss SUPRA 40 with operating voltage of 5 kV. The optical properties were studied using an Ocean optics UV-Vis spectrophotometer. Finally, 100 nm thick Al contacts were deposited by e-beam evaporation to form, through a shadow mask process, the source and drain contacts to determinate the electrical characteristics of CdS films. The electrical characteristics of the thin films were determined using current–voltage (*I-V*) measurements at room temperature in a 4200 Keithley semiconductor characterization system under dark conditions.

3. Results and discussions

The deposition of the film on glass surface is an adsorption phenomenon. Film formation occurs by combination of released metal ions from complex metal ion source and chalcogenide source. In the present study sodium borohydride and hydrazine were used as complexing agents on the synthesis of CdS thin films by CBD.

The X-ray diffraction patterns in Figure 1a show the crystallinity of the films deposited with different complexing agents. CdS films deposited with $NaBH_4$ solution shows an increase in the degree of crystallinity. The X- ray diffraction peak at 2ϴ= 26.5° evidenced the preferential orientation along the (002) hexagonal plane.

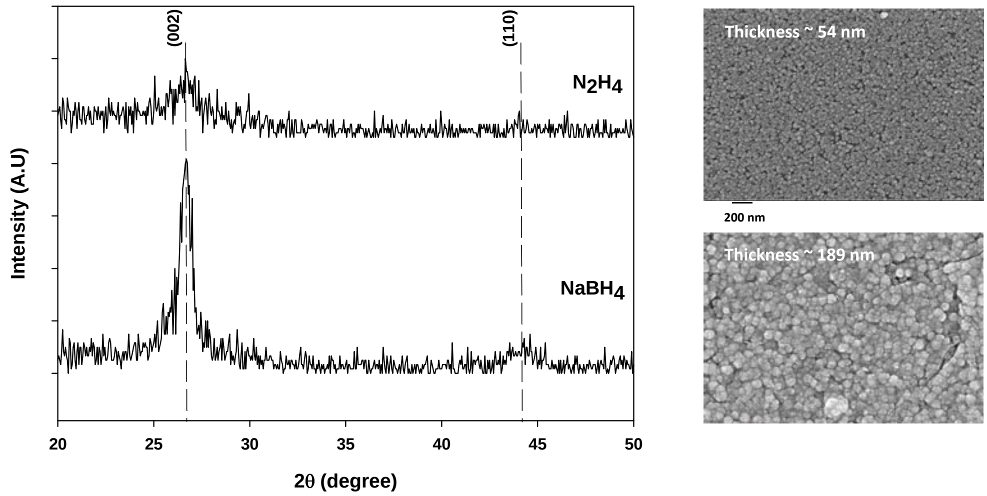

Fig. 1. a) XRD patterns and b) SEM for CdS films deposited with different complexing agent.

SEM yields microscopic information of the surface (Figure 1b). This technique was helpful to identify the growth mode, determining the complexing agent effect on the film morphology.

Average CdS thicknesses were obtained by cross-section SEM. In the film deposited with $NaBH_4$ solution cracks formation is appreciated due to the higher deposition rate. Homogeneous CdS film is observed for low deposition rate with the use of N_2H_4 solution during the synthesis. At low deposition rate, Cd $^{2+}$ free ions concentration is less due to high complexation, resulting in thinner film. CdS film grown at high deposition rate showed denser film with stress which results in cracks on the surface. Figure 4 show the deposition rate vs. complexing agent for CdS films.

Figure 2 shows the AFM characterization for films deposited with $NaBH_4$ and N_2H_4 solution. Film deposited with $NaBH_4$ solution showed roughness of ~ 9.33 nm (Fig. 2a), whereas film deposited with N_2H_4 solution showed roughness of ~ 6.33 nm (Fig. 2b). The smooth surface of the films deposited with N_2H_4 solution exhibits a well- defined granular structure with nanometric-size grains.

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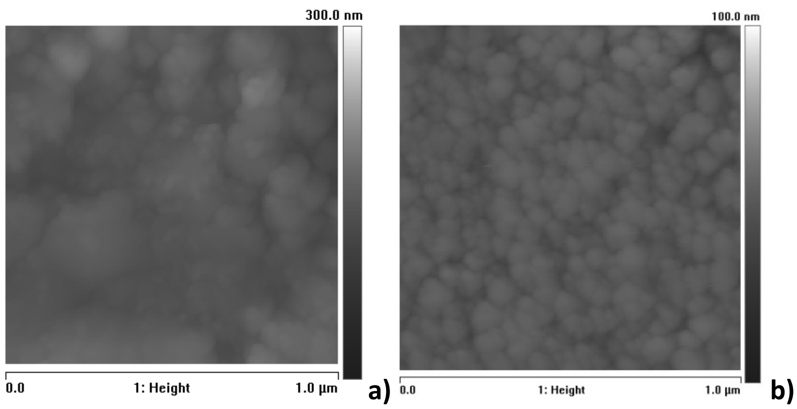

Fig. 2. AFM images for a) CdS film deposited with $NaBH_4$ solution, b) CdS film deposited with N_2H_4solution.

Figure 3 shows the optical properties of CdS thin films, measured using UV/Vis spectrometer. Due the low roughness of thin films deposited with N_2H_4 solution the optical transmission increase in the visible region (Figure 3a).

The Tauc method was used to obtain the optical band gap of the semiconductor compound (CdS thin films). The absorption measurement at various wavelengths (UV-Vis) of CdS films deposited on glass substrate was used to estimate the optical band gap. A plot of $(OD\ X\ E)^2$ versus E is shown in the Figure 3b. Here, OD is the optical density and E is the photon energy. Extrapolation of the linear portion of the curve to $(E^{*}OD)^{\wedge 2}=0$, gives the estimated optical band gap ~ 2.43 eV for CdS film deposited with $NaBH_4$ solution (high deposition rate) and 2.35 eV for CdS film deposited at with N_2H_4 solution (low deposition rate)). Measured band gap values are comparable with previously reported values (2.43 eV) [13-14].

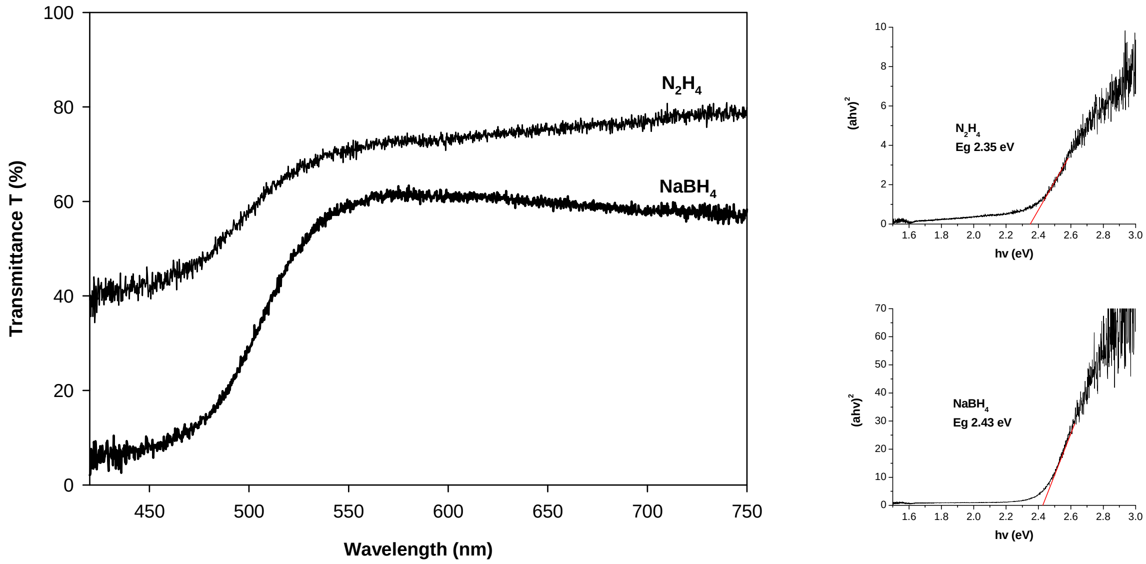

Fig. 3. a) Transmission spectra and b) Estimated band gap from optical absorption spectrum for CdS films deposited with different complexing agent.

Figure 4 shows the variations in resistivity with complexing agent and deposition rate. The results show that the resistivity diminishes as the deposition rate decreases.

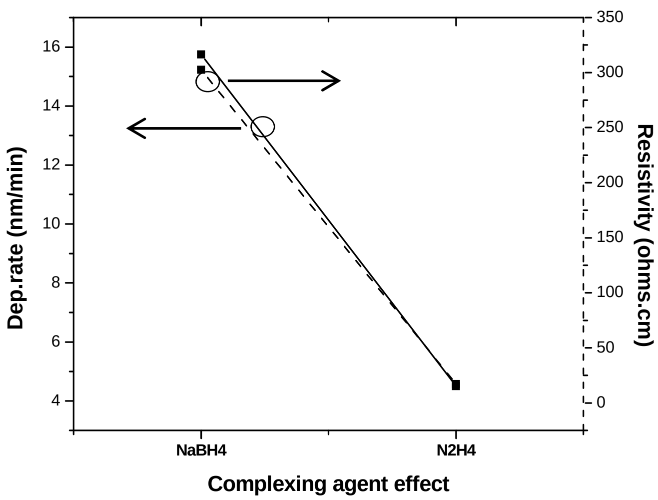

Fig. 4. Effect of complexing agent on the resistivity of CdS films.

On the other hand, it increases with thickness. The two films exhibit semiconducting behaviors with resistivity in the order of Ω-cm. The values of the resistivity in the materials studied in this work are very promising for the application of the semiconductor in electronic devices.

5. Conclusions

CdS films were obtained using the chemical bath deposition method, which is a low cost, low temperature and simple technique to growth chalcogenides compounds. With the use of novel complexing agents as hydrazine or sodium borohydride is possible to obtain CdS thin films with good properties when we used these compounds.

CdS film deposited at low deposition rate or with hydrazine used as complex agent was found to be polycrystalline with a hexagonal phase and optical band gap of around 2.35 eV. At low deposition rate the free cadmium ions concentration was low due to high complexation, thus reducing the degree of precipitation and yielding on resulting homogeneous deposition process showed through microstructural characterization obtained from SEM and AFM. However hydrazine and sodium borohydride are affective complexing agents for the cadmium ions in the CBD processes. The deposited thin film showed a good electrical behavior in the interface metal-semiconductor with values in the order 10-300 Ω-cm.

These characteristics in the CdS films make them a suitable candidate for various optoelectronic and device applications.

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References

[1] D.K. Kaur, K.L. Pandya, J. Chopra, Electrochem Soc. **127,** 43 (1980).
[2] P.K. Nair, M.T.S. Nair, V.M. Garcia, O.L. Arenas, Y. Pena, A. Castillo, I.T. Ayala, O. Gomezdaza, A. Sanchez, J. Campos, H. Hu, R. Suarez, M.E. Rincon, Solar Energy Mater. and Solar Cells **52,** 313 (1998).
[3] J. I. Pankove, Optical Processes in Semiconductors, Ed Dover (1971).
[4] W. E. Howard, in Thin Film Transistors, C. R. Kagan, P. Andry, Editors, Marcel Dekker, New York (2003).
[5] A. Romeo, M. Terheggen, D. Abou Ras, D. L. Batzner, F.J. Haug, M. Kalin, D. Rudmann, A.N. Tiwari, Prog. Photovolt: Res. Appl. **12:93,** 111 (2004).
[6] O.V. Salata, P.J. Dobson, P.J. Hull, J.L. Hutchinson, Thin Solid Films **251,** 1 (1994).
[7] T. Arai, T. Yoshida, T. Ogawa, J. Appl. Phys. **26,** 396 (1987).
[8] W. Hoheisel, V.L. Colvin, C.S. Johnson, A.P. Alivisatos, J. Chem. Phys. **101,** 8455 (1994).
[9] M.G. Sandoval Paz, M. Sotelo Lerma, A. Mendoza Galvana, R. Ramirez Bon, Thin Solid Films **515**, 3356 (2007).
[10] R. Ramírez-Bon, M.A. Quevedo- López, R.A. Orozco Terán, F.J. Espinoza Beltrán and M. Sotelo Lerma, J. Phys. Chem. Solids **59**, 145 (1998).
[11] R.A. Orozco Terán, M. Sotelo Lerma, R. Ramirez Bon, M.A Quevedo López, O. Mendoza González and O. Zelaya Angel, Thin Solid Films **587,** 343 (1999).
[12] G.Hodes, Physical Chemistry Chemical Physics **9,** 218 1 (2007).
[13] S. M. Sze. Physics of Semiconductor Devices, Ed John Wiley (1981).
[14] J. Santos Cruz, R. Castanedo Pérez, G. Torres Delgado, O. Zelaya Angel, Thin Solid Films **518,** 1791 (2010).