The Effect of the Solution Concentration on Structural and Optical Properties CdS Thin Films Prepared by Chemical Bath Deposition Technique

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Abstract - Cadmium Sulphide (CdS) thin films were grown on glass substrates by chemical bath deposition technique. The effect of cadmium ion concentration on the structural and optical properties of the CdS films has been considered in this work. Structure of these films was characterized by X-ray diffraction ,where shown of CdS films deposited have polycrystalline structure cubic(zinc blend) and hexagonal (diamond) and the grain size increases with increasing cadmium ion concentration in solution. The optical properties shown of the CdS thin films have highly transmittance in visible region of spectrum and reach to more than 85% with wide band gap decreases from 2.45 to 2.35 eV with increasing of cadmium ion concentration in the solution.

Keywords - Cadmium Sulphide, chemical bath deposition, cadmium ion concentration, the structural and optical properties.

I. INTRODUCTION

Cadmium Sulphide (CdS) belongs to II-VI compound semiconductor with direct band gap of about 2.42 eV. CdS can exist in two crystalline modications: the hexagonal (wurtzite) phase and the cubic (zincblende) phase [1,2]. In the past years, the deposition and characterization of CdS thin films has a great application potential in the area of electronic and optoelectronic devices fabrications [3-6].

Many techniques have been reported for the deposition of CdS thin films. These include thermal evaporation [7], sputtering [8], chemical bath deposition [9], spray pyrolysis [10], metal organic chemical vapour deposition (MOCVD) [11], molecular beam epitaxial technique [12], electro deposition [13], photochemical deposition and chemical bath deposition [14].

Among of all methods, the CBD technique has many advantages such as simplicity, no requirement for sophisticated instruments, minimum material wastage, economical way of large area deposition, and no need of handling poisonous gases. The CBD method is a slow process, which facilitates the better orientation of the crystallites with improved grain structure [15].

Particularly, the CBD technique is an easy low-cost process, and useful for large-area industrial applications, reason for which it has been very used in the current days. CBD is a process to achieve high quality films, which are obtained by adjusting the pH, temperature and reagent concentrations. Normally, for obtaining CdS thin films by chemical bath deposition in aqueous solution a cadmium salt is used as the Cd ion source, thiourea as the sulfur source, a base to adjust the pH of solution, and a ligand to control the precipitation of chalcogenides and hydroxides[16].

II. EXPERIMENTAL

Cadmium sulfide thin films have been deposited on glass substrates using the chemical bath deposition technique. Glass slides (75×25×1 mm) were used as substrates. The substrates were degreased in HCl, washed in detergent and rinsed in distilled water dried in oven at 80°C. The CdS thin films was grown on glass substrate by using the cadmium nitrate salt[Cd(NO₃)₂.4H₂O] with molarity of 0.05 M to 0.2 M as a source of cadmium ions(Cd⁺²) and 0.1 M thiourea $[SC(NH_2)_2]$ as a source of sulphide ions (S^{2-}) . Ammonia hydroxide solution (NH₄OH) 25 % was added slowly to adjust pH to 10. The solution was stirred to ensure homogeneous dissolve about 10 minutes. The bath temperature was kept at 70°C for 3h and under unstirred condition. After the deposition, the CdS films were washed with methanol ultrasonically to remove the loosely adhered CdS particles on the film and annealed in air at 673 K for 1h using furnace model Yamato FM 27.

Film thickness is important parameter in the study of film properties. For thickness measurement, gravimetric weight difference method with the relation $t=m/(\rho \times A)$ where, *m* is the mass of the film deposition on the substrate in gram,*A* the area of the deposited film in cm² and ρ the density of the deposited material (CdS =4.69 g/cm³)in bulk form[17].The maximum thickness for CdS thin film was 680 nm.The X-ray diffraction(XRD) analysis was carried out using X-ray 6000(Shimadzu) diffractometer with Cuk_{α} radiation (α -1.541 Å) at 40 kV and 30 mA .The optical transmission spectra were investigated by UV-Visible Spectrophotometer (Cintra 5) GBC-Astrural).

III. RESULTS AND DISCUSSION

A. Reaction Mechanism

In the growth of the CdS thin film from chemical bath, ammonia as the complex agent to bind the Cd^{2+} ions. Formation of complex ion is essential to control the rate of the reaction and to avoid the immediate precipitation of the compound in the solution. The metal complexes hydrolyses slowly to generate the Cd^{2+} in the solution. Thiourea furnishes the necessary S^{2-} ions by hydrolysis. The reaction mechanism for the formation of CdS could be understood as follows[18].

Figure 1 shows the growth is strongly influenced by the molarity of cadmium nitrate. The deposition rate increases with increasing cadmium ion concentration , the terminal thickness increases with increasing cadmium ion concentration from 344 nm to 680 nm according to the concentration from 0.05 M to 0.2 M .The increase in deposition rate refers that in any chemical reaction the reaction rate is proportional to the concentration of the reacting species.



Fig. 1 Terminal thickness of CdS films as a function of the cadmium ion concentration

B. X-Ray Diffraction

Figure 2 shows X-ray diffraction pattern of CdS thin films deposited on glass substrate at different cadmium ion concentration. From the diffraction pattern, it can be seen that the diffraction peak is sharp and well defined indicating that the film is polycrystalline in nature. The diffraction peak existed at $2\theta = 26.5^{\circ}$ corresponding to either the (002) hexagonal or the (111) cubic planes. From the figure, it can be seen that the intensity of diffraction peak increases as the cadmium ion concentration of the film increase. This is an indication of the crystallinity improvement with increasing cadmium ion concentration. These values of 2θ and its crystal planes are comparable with standard data from CdS matches well (JCPDS file no .79-0043). Similar results have been observed by literatures [19, 20].



Fig. 2 The X-ray diffraction patterns of CdS thin films at different cadmium ion concentration

The average size of the crystallites was determined from X-ray diffraction data. We use the standard (002) H reflection at $2\theta=26.5^{\circ}$. The Scherer formula,

$$\mathbf{D} = \frac{\mathbf{k}\lambda}{\beta\mathbf{cos}\theta} \tag{1}$$

Where k is a constant taken to be 0.94, λ is the X-ray wavelength, β is the full-width at half-maximum (FWHM) of the peak, and θ is the reflection angle [21].The grain sizes of the CdS films increase from 23 nm to 44 nm with the increasing cadmium ion concentration, as shown in figure 3 where the diffraction peaks become more intense and sharper which indicated that the grains become larger and the crystal quality was improved. These results are consistent with other published results such as results [22, 23].



Fig. 3 Variation of crystallite size with cadmium ion concentration

C. Optical Properties

Figure 4 show the effect of cadmium ion concentration on the transmission spectra at the range 400 - 800 nm. The average transmittance of the CdS films in the visible region was found to be with a transmittance of more than 85%. We have found that film transmission with increasing the cadmium decreases ion concentration, where increasing cadmium ion concentration causes the increasing in grain size because of decreases in the density of nucleation centers thus a smaller number of centers start to grow, resulting in large grains.



Fig. 4 The optical transmission spectra as a function of wavelength of CdS thin films at different cadmium ion concentration

Optical band gap (E_g) of film was estimated from transmittance data. The photon energy (hv) and absorption coefficient (α) for direct optical transition are related by the following equation[24].

$$(\alpha h \nu) = B(h\nu - E_g)^{1/2}$$
⁽²⁾

Where hv is the photon energy, α is the absorption coefficient, E_g is the optical band gap and B is a constant. For calculation of the optical band gap of CdS film, the curve of $({}_{\alpha}\alpha hv)^2$ vs. hv was plotted. The E_g value of the CdS film was determined from Fig. 5 and it was found decreases from 2.45 eV to 2.35 eV with increasing the cadmium ion concentration , where increasing cadmium ion concentration causes to increasing in grain size. This decrease in the band gap is due to the improvement in the film crystallinity, i.e. the grain size and lattice parameters. Height concentration lead to sharp absorption edge because the films becomes more crystalline and the grain size increase with increase cadmium ion concentration. These values are in good agreement with the values reported by others [25, 26]. The band gap of the CdS thin films changed with increasing cadmium ion concentration, as shown in Figure 6. These show that with increasing cadmium ion concentration concentration, values of obtained band gap decreased.



Fig. 5 A plots of $(\alpha h \upsilon)^2$ versus $(h \upsilon)$ of CdS thin films at different cadmium ion concentration



Fig. 6 Variation optical band gap of CdS thin films with cadmium ion concentration

IV. CONCLUSIONS

From the obtained results, we can conclude the following. The deposition rate increases with increasing cadmium ion concentration .The X-ray diffraction studies showed that the films are polycrystalline in nature with a mixture of hexagonal and cubic phases. Grain size increases with the increasing cadmium ion concentration. The optical transmittance measurement showed that the CdS films has flat surface and high transmittance in the visible region with presence of direct band gaps decrease with increasing cadmium ion concentration.

V. REFERENCES

- [1] Britt J., Ferekides C., (1993). Appl. Phys. Lett. 62, 2851.
- [2] Feitosa V, Miranda M. A, Sasaki J. M, Ara´ujo-Silva M. A, (2004). Brazilian Journal of Physics, 34, 656-658.
- [3] Didden, H. Battjes, R. Machunze, B. Dam, R.Van de Krol, (2011). Appl. Physics ,110, 033717
- [4] Castillo S.J, Mendoza-Galvan A, Ramirez-Bon R, Espinoza-Beltran F.J, Sotelo-Lerma M, Gonzalez-Hernandez J , Martinez G, (2000). Thin Solid Films, 10,373.
- [5] Ullrich, H. Sakai and Y. Segawa, (2001). Thin Solid Films, 385, 220.
- [6] Birkmire R.W, Mc Candless B.E , Hegedus S.S, (1992).Sol. Energy ,12, 45 .
- [7] Mahmoud S.A, Ibrahim A.A , Riad A.S, (2000). Thin Solid Films, 372, 144.
- [8] Ullrich B, Sakai H, Segawa Y, (2001). Thin Solid Films, 385, 220.
- [9] Ashour H, El Akkad F, (2001). Phys. Status Solidi (a), 184 ,175. Sharma S N, Sharma R K, Sood K. N and Singh .S .M,(2005).Mater. Chem. Phys, 93,368.
- [10] Gibson. P. N, Özsan. M. E, Lincot. D, Cowache. P and Summa. D, (2000).Solid Thin Films, 34,361–362.
- [11] Bhattacharjee R,(2010). Assam University Journal of Science & Technology: Physical Sciences and Technology, 5,153-155.
- [12] Malandrino G, Finocchiaro S T, Rossi P, Dapporto P and Fragal I L, (2005) .Chem. Commun. 45 5681.
- [13] Kotkata M.F, Masoud A.E, Mohamed M.B, Mahmoud E.A, (2008).Chalcogenide Letters, 5, 209-217.
- [14] Sanap V. B, PawarA B. H,(2009). Chalcogenide Letters, 6, 415 – 419.
- [15] Khallaf H , Oladeji I.O, Chai G, Chow L, (2008) .Thin Solid Films ,516 ,7306–7312.
- [16] Mondal, T.K. Chaudhuri and P. Pramanik, (1983).Sol. Energy Mater. 7, 431.
- [17] Amlouk M, Dachraoul M. etal, (1987) .Solar Energy Materials, 15, 453.
- [18] Metin H, Sat F, Erat S, Ari M, (2008).Jou. OF Opto. Adv. Mater., 10,2622 – 2630.
- [19] Tran T, Tung Ngo D, Huong Vu T, Nguyen T.D, Ha C, (2010).Adv. Nat. Sci.: Nanosci. Nanotechnol. 1,015013 (1-4).
- [20] Feitosa A.V, Miranda M. A, Sasaki J. M, Ara´ujo-Silva M. A, (2004).Brazilian Journal of Physics, 34, 656-658.

- [21] Mahdi M. A, Kasem S. J, Hassen J. J, Swadi A. A, A l-Ani S. K. (2009). Int. J. Nanoelectronics and Materials, 2, 163-172.
- [22] Sanap V. B, Pawar B. H,(2010).Chalcogenide Letters, 7, 227-231.
- [23] Grecu R, Popovici E. J, dar M. L, Pascu L, Indrea E,(2004). Journal of Optoelectronics and Advanced Materials, 6, 127 – 132.
- [24] Hiie J., Dedova T., Valdna V., Muska K., (2006). Thin Solid Films 511, 443 – 447.
- [25] Ezenwa I.A., Ekpunobi J.(2010). Pacific Journal of Science and Technology, 11(2):435-440.
- [26] Perumal P., Manohari A.G., Valanarasu S., Kathalingam A., Rhee J., Soundaram N., Chandramohan R..(2012). JSEMAT, 2, 71-75.