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A New Route for the Synthesis of CdS Thin Films from Acidic Chemical Baths

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Abstract: Well adherent nanocrystalline cadmium sulphide thin films have been successfully deposited from acidic chemical baths by employing tartaric acid and hydrazine as complexing agents for the first time. The pH of the bath was about 2.35 and the depositions were carried out at bath temperatures of 60 °C and 70 °C. The films were characterized by a variety of techniques. Powder X-ray diffraction patterns of the films exhibited a well crystallized hexagonal structure with a preferred orientation along the (002) plane. Scanning electron microscope investigation showed that the films are formed from spherically shaped grains. The EDAX result revealed that the deposited films had very good stoichiometry. The band gap of the thin films obtained by optical absorption spectroscopy, were 4.12 eV for the films deposited at 60 °C and 3.89 eV for films deposited at 70 °C. This unusual large band gap could be attributed to size quantization effects obtained by this new synthesis route.

Keywords: Cadmium Sulphide thin films; acidic chemical bath; deposition temperature; crystal structure; optical properties.

1 Introduction

Cadmium sulphide (CdS) is II-VI semiconductor which exists in two crystal forms; the more stable hexagonal wurtzite structure and the metastable cubic zinc blende structure. It has a direct optical band gap of ~2.42 eV[1], and has proven potential in industrial applications which include fabrication of electronic and optoelectronic devices [2]. It is an environmentally stable compound and the most promising photovoltaic material available for low cost high-efficiency solar cells[3]. Thin films of CdS have been prepared by various methods such as vacuum deposition, sintering, spray pyrolysis, chemical bath deposition and others. Among these techniques, chemical bath deposition (CBD) has been widely used because of its simplicity, cost-effectiveness and conducive for applications involving large area deposition such as fabrication of solar cells [4, 5].

The technique is sensitive to deposition parameters which include bath temperature, deposition time, type of precursors and their concentrations, and bath pH. The pH of the bath influences a number of factors, such as; the action of complexing agents and hydrolysis of nonmetallic precursors. However it is not always simple to predict its particular effect [6]. Chemical bath deposition of CdS begun as early as the 1960s [6], and available literature indicates that these depositions were mostly carried out in alkaline chemical baths using the thiourea and ammonia system [7, 8].

There are available reports, where the chemical bath deposition of CdS was carried in an ammonia free system. One such report is by Roy and Srivastava [9], who reported the deposition of CdS in an alkaline medium using thiourea as the sulphur source and tartaric acid as the complexing agent. Few authors have also reported the deposition of CdS from acidic chemical baths, using no complexing agents[4, 8]. Complexing agents have significant influence in controlling the rate of reaction, reaction mechanism and microstructure of the films [9].

In this work, we report on the deposition of CdS thin films from acidic chemical baths with pH as low as 2.35, using tartaric acid and hydrazine as complexing agents, thioacetamide as the sulphur ions source and cadmium acetate dihydrate as the source of cadmium ions. As far as the authors are aware, there is no report on the deposition of CdS thin films from acidic chemical baths using a combination of tartaric acid and hydrazine as complexing agents. Such low pH is also not common in the acidic bath deposition of CdS thin films.

2 Experimental Details

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Aqueous solutions of 20 ml (0.1M) cadmium acetate dihydrate was mixed with 5 ml (60 %) hydrazine in a 100 ml beaker and stirred for few minutes. 20 ml of deionized water was added followed by an appropriate amount of 1 M tartaric acid. The pH of the solution was adjusted to 2.35 by drop wise addition of 2 M hydrochloric acid. Finally 7.5 ml of 1 M thioacetamide solution was added under continuous stirring. The colourless solution changed to green yellow immediately after the addition of thioacetamide. Silica glass substrates, which were cleaned using the procedure reported in [10],were then immersed vertically in the stock solution. The vessel was sealed with a special cover which also served as a substrate holder.

The stock solution was continuously stirred, and placed in a water bath. Two CdS samples were deposited at temperatures of 60 °C and 70 °C, keeping all the other deposition parameters the same. After 100 minutes the thin films were taken out of the bath and washed thoroughly with de-ionized water. Samples were dried under ambient conditions and kept inside the desiccator before characterization. The thin films were well adherent, smooth, transparent and green yellow in colour. It is worth mentioning that the color of the bulk CdS is either orange or orange yellowish [11] whereas the color of quantum sized CdS is yellow to green yellow [12, 13].

Hydroxide ion is normally responsible for film growth through cluster-by-cluster mechanism. However, the presence of hydroxide ion is very limited in acidic chemical bath. Therefore deposition in acidic medium normally takes place through ion-by-ion mechanism. Thioacetamide in acidic medium can release S^{2-} either through the formation of H_2S by hydrolysis decomposition or directly by complex decomposition [6]. A general thioacetamide decomposition reaction through sulphide formation may be written as:

$$H_3C.C(S)NH_2 + 4H_2O \leftrightarrow CH_3COOH + NH_3 + 2H_2O^+ + S^{2-} \qquad (1)$$

The Cd^{2+} ion is released from cadmium acetate dihydrate:

$$Cd(CH_3COO)_2.2H_2O \leftrightarrow Cd^{2+} + 2CH_3COO^- + 2H_2O \qquad (2)$$

The Cd^{2+} ion released from the cadmium acetate dihydrate should be complexed by tartaric acid and/ or hydrazine.

$$[Cd(tartaric\ acid)]^{2+}/[Cd(hydrazine)]^{2+} + S^{2-} \longrightarrow CdS + tartaric\ acid/hydrazine \qquad (3)$$

Thioacetamide decomposition at intermediate pH values, particularly in weakly acidic solutions (pH $\geq$ 2), has also been suggested to occur through a thioacetamide complex decomposition in parallel with acid hydrolysis of thioacetamide through intermediate formation of sulphide [6]. The formation of CdS by complex decomposition of thioacetamide can be represented as:

$$[Cd\text{-}(CH_3CSNH_2)]^{2+} \leftrightarrow CdS + H_2 + CH_3CN \qquad (4)$$

The method used to prepare a material can profoundly affect the phase composition, thermal stability, and morphology, which in turn can influence the functional behaviour of the material [14], hence the need for characterization. Structural characterization of the thin films was carried out by a PANalytical X'Pert PRO X-ray diffractometer with Cu K_α monochromatic radiation (λ=0.15406 nm) operating at (45 kV, 40 mA). Optical absorbance of the samples was measured by a Shimadzu UVmini-1240 UV/Vis single beam spectrophotometer. The surface morphology and composition of the thin films were investigated using a field emission scanning electron microscopy (FESEM, Zeiss, sigma) integrated with an energy dispersive X-ray analyzer (EDX) device.

3 Data Analysis

3.1 Structural Analysis of CdS Thin Films

Structural characterization of the CdS thin films was carried out by adjusting the diffractometer to step size of 0.08° with 20 seconds scan time per step for 2θ values over 20–55°. Fig. 1 shows the X-ray diffraction patterns of CdS thin films deposited at 60 °C and 70 °C. The diffraction patterns of both samples have six discernable peaks with 2θ values around, 24.9°, 26.5°, 28.2°, 43.7°, 47.9° and 52.0°.

Table 1: Some standard and observed structural parameters of CdS

Standard values (JCPDS file code 00-042-1049)			Observed values for sample deposited at 70 ˚C				Observed values for samples deposited at 60 ˚C			
2θ (deg)	d-spacing (nm)	Relative intensity (%)	2θ (deg)	d-spacing (nm)	Relative intensity (%)	Texture coefficient	2θ (deg)	d-spacing (nm)	Relative intensity (%)	Texture coefficient
24.808	3.5861	62	24.902	3.5728	31	0.85	24.947	3.5665	28	0.83
26.507	3.3599	91	26.575	3.3516	100	1.87	26.558	3.3536	100	2.03
28.183	3.1638	100	28.231	3.1585	46	0.78	28.205	3.1614	43	0.8
43.682	2.0705	48	43.795	2.0654	30	1.06	43.85	2.063	26	1.02
47.84	1.8998	50	47.95	1.8957	18	0.61	47.961	1.8953	16	0.58
51.825	1.7627	31	52.017	1.7567	15	0.82	51.924	1.76	13	0.75

The hexagonal phase of CdS is formed under most film growth conditions [14]. The XRD patterns were matched with hexagonal CdS (JCPDS file code 00-041-1049) and the peaks were indexed as (100), (002), (101), (110), (103) and (112) planes of the hexagonal CdS structure. A low intensity peak was also observed at 36.60° for both samples due to (102) plane of hexagonal CdS. The broad hump in the 2θ range of 20° to 35° is due to the glass substrate [15].The samples deposited at 70 ˚C have higher peak intensities, indicating better crystallinity.

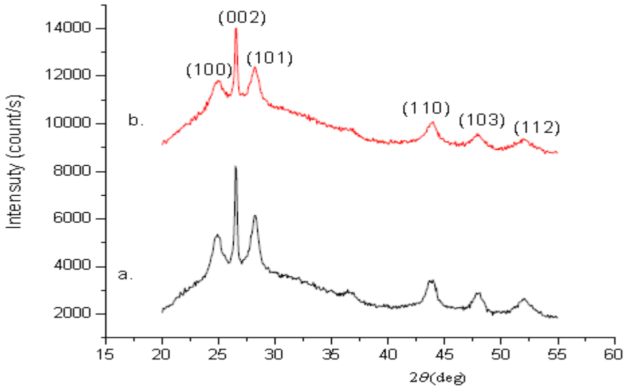

Fig.1: XRD patterns of CdS thin films deposited at (a) 70 ºC and (b) at 60 ºC

The average crystallite size estimated from the Debye-Scherrer's formula [16] was 11.27 nm for samples deposited at 70 ˚C, and 10.91 nm for samples deposited at 60 ˚C. The d-spacing values were calculated from Bragg's law [17], and from which the lattice constants were calculated from the relation:

$$\frac{1}{d_{hkl}^{2}}=\frac{4}{3}\left(\frac{h^{2}+hk+k^{2}}{a^{2}}\right)+\frac{l^{2}}{c^{2}} \tag{5}$$

where h, k, l are miller indices; *a* and *c* are lattice constants calculated from (100) and (002) planes respectively. The calculated values of $a_{(100)}$ for films deposited at 60 ˚C and 70 ˚C are 4.1182 nm and 4.1255 nm and that of $c_{(002)}$ are 6.7072 nm and 6.7031 nm, respectively. Some standard and observed structural parameters of the films are shown in Table 1. There are slight variations between the standard and calculated structural parameters as shown in the table.

From Fig.1, the relative intensity of the (002) reflection is high, which is an indication that the deposits are preferentially oriented with the c-axis perpendicular to the substrate [18]. This is supported by the calculated values of the texture coefficients given in Table 1. Such growth is particularly sought after as it is epitaxial with the (112) planes of $CuInGaSe_2$ and Cu_2ZnSnS_4 active layers used in thin film solar cells [18].

3.2 Investigation of Optical Properties of CdS Thin Films

The optical properties of the CdS thin films were investigated by measuring the absorption in the wavelength range of 200 to1100 nm (inset in Fig. 2). From inset in Fig. 2,the fundamental absorption edge of the CdS thin films are anomalously shifted towards the shorter wavelength values. The occurrence of such blue shifts in the optical spectra is usually observed with CdS particles of size about 6 nm [6]. The appreciable blue shift observed in this work could be attributed to quantum size effects due to the new deposition conditions.

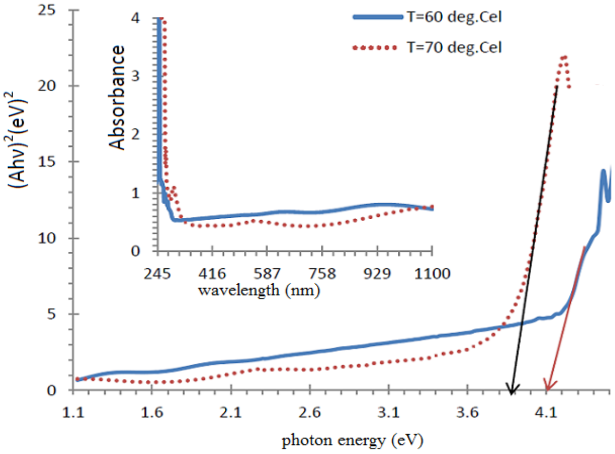

Fig. 2: A plot of energy square (A*hν*)^2 versus photon energy (*hν*) for CdS thin films (Inset: Absorbance versus wavelength of the films).

The band gaps of the films were obtained using the Stern relation[19].

$$A=[K(h\nu-E_g)]^{n/2}\Big/h\nu \tag{6}$$

where *A* is absorbance, *v* is the frequency, *h* is the Planck's constant, *k* is a constant while *n* carries the value of either 1 for direct transition or 4 for indirect transition. CdS is a direct band gap material[20], hence n is assigned the value 1. Fig.2 shows *(Ahν)²*as a function of *hν.* The energy band gap is obtained by fitting a line to the linear portion of the graph and extrapolating the fitted line to the point where it intersects the *hν* axis, as shown in Fig.2. The linear nature of the graph at high *hν* indicates the presence of a direct transition[10].

From Fig.2, the band gaps are 3.89 eV and 4.12 eV for the films deposited at 70 ˚C and 60 ˚C, respectively. Vossmeyer et al., (1994) [21] reported a band gap of 4.68 eV for 0.64 nm colloidal CdS particles prepared by size selective method. However, such large band gaps are rarely reported in chemical bath deposited CdS thin films. Larger band gap CdS particles can be obtained in the presence of quantum size effect which is manifested as a blue shift in the optical spectrum of the particles [6, 22].

3.3 Morphological and Elemental analysis of CdS thin films

Fig. 3 shows the SEM micrographs of the CdS thin films deposited at 60 ˚C and 70 ˚C. The films are formed from spherically shaped grains with well define grain boundaries. Most of the grains are isolated from each other rather than forming aggregates and/or coalesce.

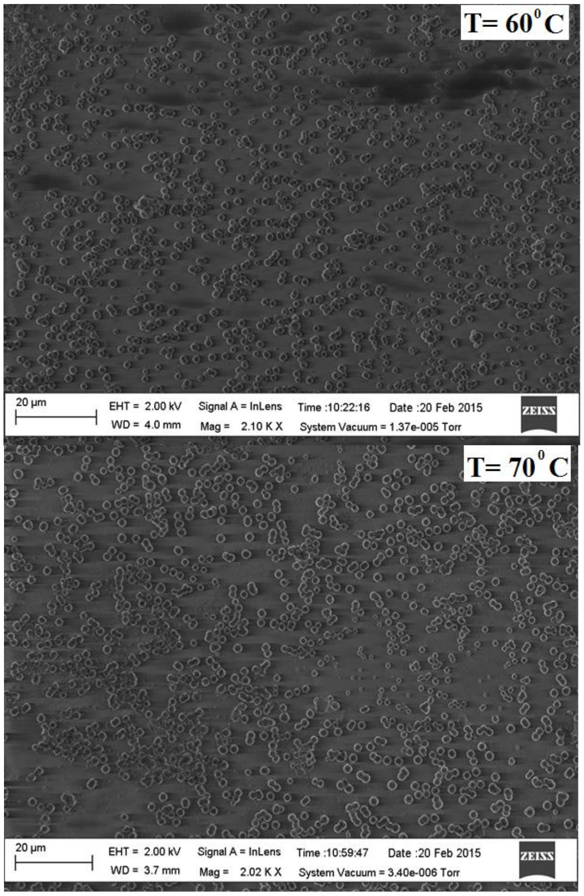

Fig.3: SEM micrographs of CdS thin films deposited at 60˚C and 70 °C.

The grains observed for films deposited at 70 ˚C appear to be more connected than that of films deposited at 60 ˚C. According to Hodes [6], some degree of electronic isolation between nanocrystals is required for size quantization to be exhibited. This is manifested by an increase in band gap and/or a blue shift in the optical spectrum as observed in this work. The isolation of grains observed in the present work could be a tangible evidence for electronic separation among the grains. This electronic separation in turn could be one of the possible reasons for the significant blue shift observed in the band gap of the CdS thin films.

The elemental analysis of the films was carried out by EDX attached to SEM. The EDX spectra of the CdS thin films (Fig. 4) confirmed the presence of Cd and S in the films. The atomic percentage ratios of Cd : S for samples deposited at 60 ˚C and 70 ˚C are 49.26:50.74 and 49.23 : 50.77 respectively, which show that the films had a good stoichiometry.

It is worth noting that most of the available literature on the chemical bath deposition of CdS suggests that the depositions were carried out in bath compositions with pH greater than 9, where the hydroxide concentration is high. For bath compositions with pH less than 9, powdery, non-adherent substandard films were predicted to form [23]. Thus, the success of depositing well adherent, crystalline and homogeneous CdS thin films from bath compositions with pH as low as 2.35 using the reagent described is surprising in that CdS deposition has in general been associated with baths which are supersaturated with respect to hydroxyl-cadmium species [24].

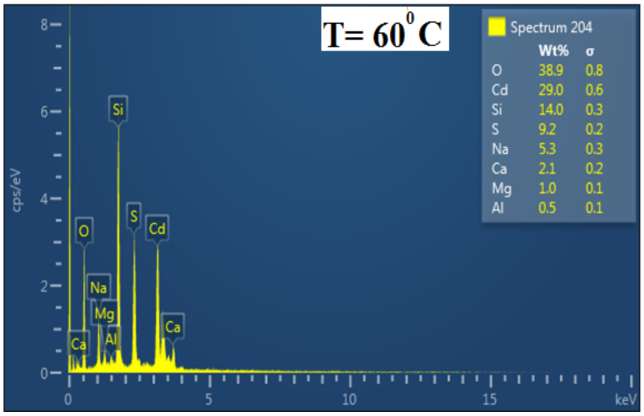

Fig. 4: EDX spectra of CdS thin film deposited at 60 °C

4 Conclusion

CdS thin films were successfully deposited on silica glass substrates from acidic chemical baths. The XRD analysis of the films revealed crystalline CdS thin films grown in the hexagonal structure with preferred orientation along the (002) plane. The samples deposited at 70 ˚C have higher peak intensities, indicating better crystallinity. The morphological investigation of the CdS films revealed that the films are formed from spherically shaped and electronically isolated grains. The films have very good stoichiometry with nearly 1:1 cadmium to sulphur ratio. The optical band gaps of the films were determined to be 3.89 eV and 4.12 eV for films deposited at 70 ˚C and 60 ˚C, respectively. The unusual large band gaps may be due to size quantization effects caused by the present deposition conditions. In our previous work, we reported on zinc sulphide thin films deposited from acidic chemical baths with deposition conditions very similar to that reported in this work. These similar deposition conditions opens up the possibility of depositing ternary films of (Cd,Zn)S under acidic conditions by this new route, and this activity is under investigation.

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