

The Effect Ultrasonication on CdS Thin Films Deposited By Using Ultrasonic Chemical Bath Deposition (UCBD) and (CBD) Chemical Bath Deposition

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Abstract: Uniform and adhesive cadmium sulphide (CdS) thin films were prepared by using ultrasonic chemical bath deposition (UCBD) and chemical bath deposition (CBD) techniques. Cadmium sulphate and thiourea were used as inorganic precursors. The deposited CdS thin films are extensively studied for characterization using X-ray diffraction (XRD), UV-Visible-NIR absorption spectroscopy, photoluminescence spectroscopy (PL) and scanning electron microscopy (SEM). The structural analysis is subjected to the XRD spectra which confirmed the formation of nanocrystalline CdS thin films with hexagonal closed packed structure. Absorption spectra revealed that, CdS films deposited by UCBD have high optical band gap values as compared to those with CBD. PL Spectra showed that, the band edge emission shifted towards blue region in case of UCBD which can be assigned as a formation of nanosonic thin films. Nanosonic is an emerging new field, which provides interlink and inter relation between ultrasound and nanomaterials. SEM analysis showed almost uniform grain on surface of the substrate.

1. Introduction

In the present scenario, nanocrystalline thin films of semiconducting materials have tremendous applications in the field of optoelectronic, photovoltaic, coating and sensor technology. However it was previously argued that nanoscale material properties can be tailored by means of chemical synthesis techniques routes and the change in crystallite size as well as film thickness. Now days nanoscale materials are of particular interest due to their innovative structural, electrical, surface morphology and optical properties. They are useful in bioelectronics, biosensing, optoelectronic devices [1]. The synthesis of chalcogenide of groups II-VI semiconductors has been obtained in the form of nanocrystalline thin films. Nanocrystalline thin films is a fast growing area of research because of their important non-linear optical, luminescent properties, reduction of dimension, quantum-size effect, surface and interface effects, other important physical and chemical properties[2]. CdS thin film act as a "Buffer" and "window" layer in heterojunction solar cell. It has numerous applications in optoelectronic, solar cells, light emitting diodes, etc [3]. Various techniques are used for the formation of CdS thin films, such as CBD, electrodeposition, spray pyrolysis, pulsed electrodeposition, sputtering, chemical vapor deposition, solid liquid interface reaction, etc.

Ultrasonication during CBD is found to be useful to change the properties of materials [4]. The present paper reports results of comparative study carried out on chemically deposited CdS thin films with and without sonications [5].

In the CBD technique, CdS thin films are formed by decomposition of thiourea in alkaline solutions of the salts of the corresponding cation. The physical properties of the thin films depend on different growth parameters such as the bath temperature, the relative concentrations of the reactants in the chemical bath and the pH value of the solution [7- 29].

In the present work, CdS thin films were prepared by CBD and UCBD. Cadmium acetate, ammonium acetate, and ammonium hydroxide are used as reagents.

2. Experimental Details

2.1. Preparation of CdS thin films

The CdS thin films were deposited on degreased and ultrasonically cleaned corning microscope glass slides. Aqueous solution of CdSO₄, NH₂-CS-NH₂ and complexing agent ammonia has been used. The CdS thin films are prepared at constant 60°C temperature into a glass container solution. The CdS thin films were deposited by two routes a) by magnetic stirring the solution with a magnetic agitator (REMI 2MLH) during the deposition and b) by using ultrasonic cleaner. The newly modified chemical bath container and glass substrates are dipped into an ultrasonic cleaner vibrating at 25 KHz with controlled bath temperature [30]. The schematic diagram of CdS thin films by UCBD and CBD method is shown in Fig. 1.(a). and Fig. 1. (b). respectively, well cleaned glass substrate was dipped in 100 ml beaker containing cationic precursor solutions of 0.1 M cadmium sulphate (CdSO₄), 0.05 M thiourea (NH₂-CS-NH₂) and 10

ml ammonia (NH₃) in 1:1/2 ratio, where Cd²⁺ and Sn²⁺ ions get adsorbed onto surface of substrate. The photograph of the UCBD and CBD unit is as shown in Fig. 1. (a) and 1.(b) respectively.

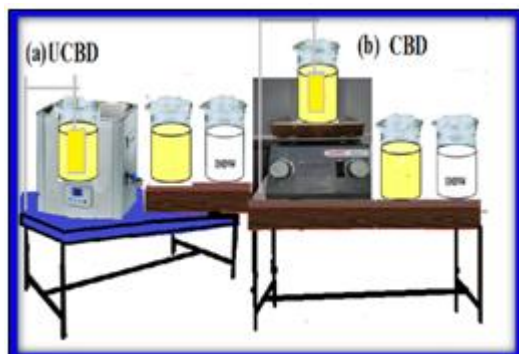


Fig.1. (a) The schematic diagram of UCBD and CBD method for the deposition of CdS thin films. Beaker 1 contains ultrasonically assisted CdS solution and beakers 2 contain De-ionised water in (a) UCBD and 3 contain magnetically stirred assisted CdS solution, 4 contain De-ionized water for (b) CBD method.

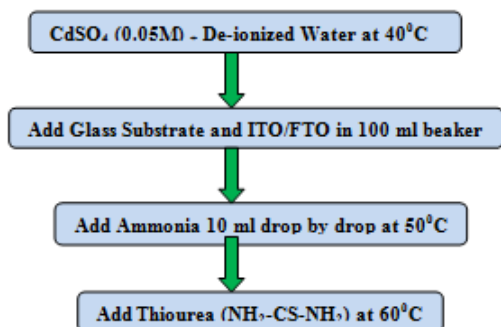


Fig.2. Schematic diagram of the solution-based chemical bath deposition for CdS thin films for UCBD and CBD respectively.

2.2 Characterization Techniques

The structural characterization of CdS thin films were carried out by analyzing D-8 Brooker X-ray diffractometer model. The Cu-K_α (K_α = 1.5418Å) wavelength is used for X-ray diffraction (XRD) patterns. The surface morphological analysis was carried out using scanning electron microscopy (SEM) JEOL JSM model 6360. The optical absorption study was carried out within a wavelength range 350–850 nm using a UV-1800 JASCO spectrophotometer.

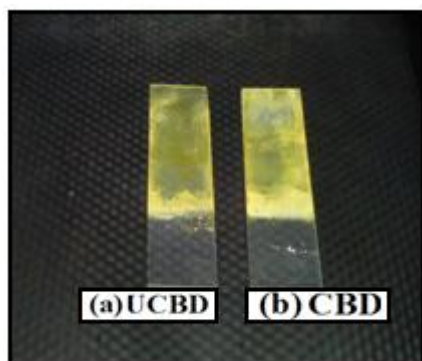
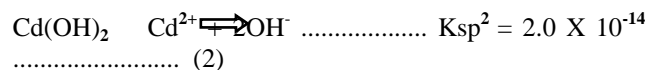
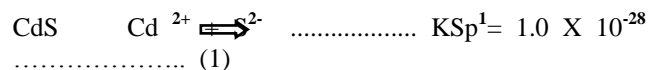


Fig. 3. Photographs of large area (2x7 cm²) CdS thin films deposited over glass (G) for UCBD and CBD method

3. Results and Discussion

3.1. CdS thin films formation and reaction mechanism

Chemical reaction of CdS thin films are same in many aspects, so it might be expected that deposition of their chalcogenides is also similar. However, there is a significant difference in their chalcogenide formation tendency. This difference is caused by the large solubility product difference for various compound formations by UCBD and CBD methods.



The tendency of cadmium ions to form hydroxides is almost two orders of magnitude higher as compared to that of cadmium ions as can be calculated by solubility products of Cd(OH)₂. Whereas sulfide formation tendency is higher for cadmium ion. The CdS thin films have at pH = 10 values for CdS deposition. However, if too low pH value is maintained, the very slow rates for hydrolysis of thiourea limit the reaction rates in magnetic agitations of CBD.

In this work sonochemistry has been employed with primary aim to develop synthetic method for deposition of two dimensional semiconductors thin films. An alkaline solution of CdS nanocrystalline thin films deposition is preferred over ion by ion mechanisms. For CdS deposition, the Cd(OH)₂ concentration must be much lower than free Cd²⁺ concentration in the solution in order Cd²⁺ to deposit CdS according to simple ionic product considerations. The strength of complexation (with NH₃) is almost comparable, therefore it is possible to adjust the complexant concentration such that there is no Cd(OH)₂ present in the solution. In that case, CdS deposition occurs by ion-to-ion mechanism, while Cd(OH)₂ deposition occurs by cluster mechanism.

The growth kinetics of a thin films deposition process is of the ion-by-ion type which involves the ion-by-ion deposition at nucleation sites on the immersed surfaces. According to Lundin and Kitaev [30], nucleation takes place by adsorption of the colloidal ions and growth takes place as a result of surface coagulation of these ions, giving thin and adherent film. The possible reaction mechanism for the formation of CdS thin films is already discussed in previous paper [20]. If an ionic product exceeds than solubility product, which shows the formation thin films on glass substrate. The ionic product is the [Cd²⁺ * S²⁻] concentration enhances nucleation growth mechanism, complex by complex ion due to the formation of more cationic species specific molar concentration of Complexing agents [Cd(NH₄)]⁺ cations. The prepared CdS thin films are uniform and well adherent to the substrate. Fig. 3[(a) and (b)] shows yellow colored CdS thin film having area 14 cm² area deposited over various substrates such as glass substrate confirming the

feasibility of chemicals method for large area deposition. The chemical method has no restrictions on substrate dimensions or its surface profile. Moreover, it is relatively inexpensive, simple and convenient for large area deposition.

2.3 Structural Studies

In order to remove cadmium hydroxide from during the deposition of thin film and to improve the crystallinity by UCBD process, the growth mechanism of CdS nucleation under were sonicated at 25 KHz for 20min. These films were used for further characterization. Fig. 4 shows the XRD patterns, which revealed that, as deposited CdS thin film is nanocrystalline for UCBD, while chemically bath deposited films are crystalline. The matching of observed 'd' with standard 'd' values confirmed that the deposited films are of CdS. The low intensity peaks show that less dense and crystallinity of as-deposited CdS thin films for CBD. Highly intense and broad full width half maxima of CdS thin films are nanocrystalline with

hexagonal closed packed (HCP) structure with maximum improvement in the crystallinity, whereas films are chemically as-deposited at 333 K become a crystalline with HCP structure. In case of UCBD, CdS thin films are nanocrystalline with a mixture of CdS and CdO phases, as the primary phases has a highest intense reflection found in 3-dimensional picture of XRD pattern. In the ultrasonicated temperature at 300 K, CdS films showed (0 0 2) peak with maximum intensity compared to other planes (100) and (200) planes of CdS [31], which are characteristic of the HCP structure. The diffraction peak positions are not shifted with high temperature in chemical bath deposition, suggesting that CdS phase is stable and its formation is independent of temperature. Similar type of results are obtained by as-deposited CdS thin films for CBD [31], where it has been concluded that CdS content of the films is difficult to ascertain because the lattice parameters of CdO are almost identical to those of CdS thin films.

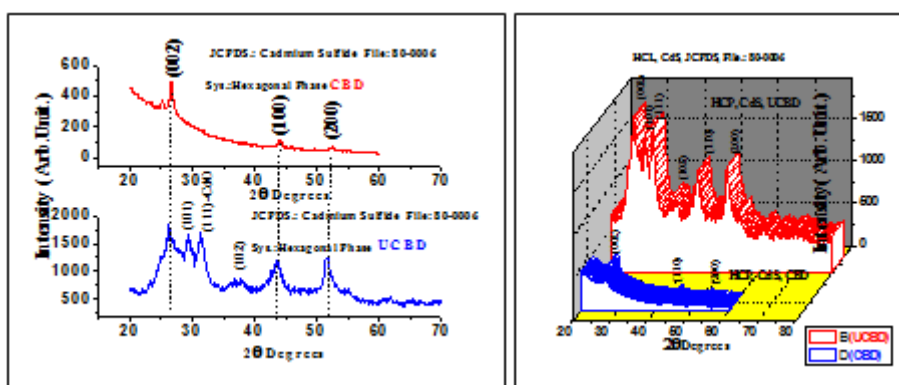


Fig.4. XRD spectra of CdS samples deposited by CBD and UCBD techniques in 2-dimensional and 3- dimensional picture.

The crystallites size was calculated using Scherrer's formula:

$$\text{Average crystalline size (d)} = 0.9 \cdot \lambda / \beta \cdot \cos(\theta_B) \quad (3)$$

Where d is the crystallite size, β is the broadening of the diffraction line measured at half of its maximum intensity (rad) (FWHM) and ' λ ' is the X-ray wavelength (1.5418 Å). 60nm of average crystallite size was estimated from highest intense (0 0 2) peak reflection. XRD pattern shows that crystallite size increases due to ultrasonically deposited CdS thin films from crystalline to

nanocrystalline HCP structure. The values of full width half maxima (FWHM) were calculated from XRD. It represents the grain size is small as per nanoscale for UCBD thin film. Reciprocal lattice of (002) plane orientation is observed in XRD pattern in fig.5. a), which is corresponds to the direct lattice of (002) plane orientation in hexagonally closed packed structure of shaded portion of (002) plane in fig.5. b). The unit cell of HCP structure shows the ABAB stacking of (002) planes with primitive lattice vectors made by 120° of bottom plane in fig.5. c) and d) respectively.

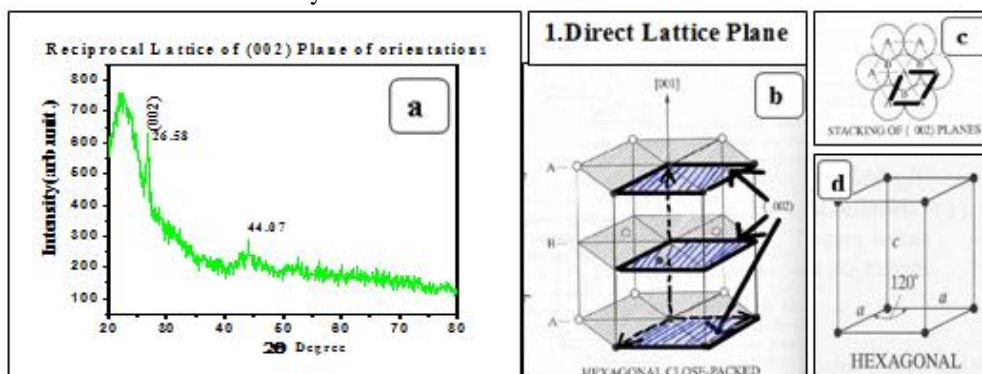


Fig.5. a) XRD spectra of CdS samples deposited by CBD in reciprocal lattice, b) (002) plane of orientations in direct lattice plane of HCP, c) stacking of (002) planes in HCP, d) unit cell of primitive lattice vectors made by 120°

2.4 Surface Morphological Study

The surface micrograph of CdS thin films deposited by using UCBD and CBD is shown in Fig. 6. Effect of sonications at 300 K temperature for 15min, surface looks more uniform with relatively smaller grains $\sim 60\text{nm}$ (Fig. 6(a)). In case of magnetic agitating at constant 333 K temperature for 15 min and 20 min causes the formation of larger grains $\sim 100\text{ nm}$ along with some coalescence and clusters of overgrowth (Fig. 6(b)). Such overgrowth can be explained on the basis of nucleation and coalescence process. At high 60°C temperature, well-covered irregular shaped grains interconnected with each other are seen from Fig. 6 (b) & (c).

Much bigger grain size morphology of CdS thin film instead of irregular shaped grains has been reported. It is well known that the efficiency of crystalline thin film solar cell increases with increasing grain size of the window layer [32-34].

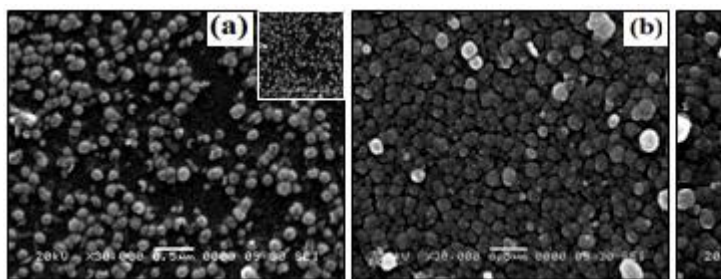


Fig. 6. The surface micrograph of as deposited CdS thin films at (a) 300 K for 15min by UCBD (b) 333 K for 15 min by CBD and (d) 333 K for 20min by CBD temperatures. Reference XRD patterns of bulk CdS, ZnS and SnS₂ materials are also shown for the comparison.

3.4. Growth mechanisms of CdS thin film

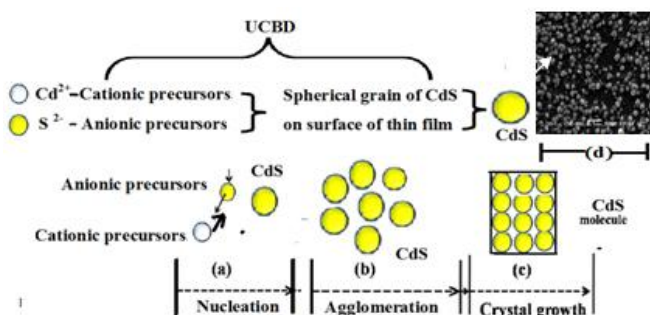


Fig. 7. The schematic representation of growth process of CdS thin film (a) Nucleation, (b) agglomeration and (c) crystal growth deposited by UCBD. [Inset (d) shows enlarge SEM image of as-deposited CdS for UCBD].

As-deposited CdS thin films surface is found to be as a smooth and compact. Also the film surface is covered with irregular shaped grains of random size without pinhole for UCBD and CBD respectively. This can be explained on the basis of nucleation growth mechanism in both chemical systems. Initially formation of very small tiny particles is known as nucleation, Cd^{2+} metal ions come

closer to each other resulting into cationic nuclei on the substrate surface. Further from the anionic precursor bath, S^{2-} ions are adsorbed over the cationic nuclei to form CdS molecule. This process is called as aggregation, which is shown in Fig.7. and Fig.8. for UCBD and CBD respectively. In the magnetic agitations, many such CdS molecules are grow with different size by means of coalescence. In Fig. 8(f). shows that, coalescence is appear on the surface substrate for CBD. $\text{Cd}(\text{OH})_2$ forms a cluster with overgrowth without sonication. Finally crystal growth take place by coalescence and Cluster of CdS molecule. The continuity in geometric orientation to give rise a smooth and compact morphology of deposited CdS thin film as shown in Fig. 8.(e). Inset Shows an enlarge fig 8. (f) and fig.8.(g) of SEM image of as-deposited CdS thin film by CBD. Similar type of growth mechanism of CdS thin film formation for UCBD except coalescence and Cluster avoid due to the ultrasonication, which leads to formation of nanosonic particles explained by suslick et al. [4].

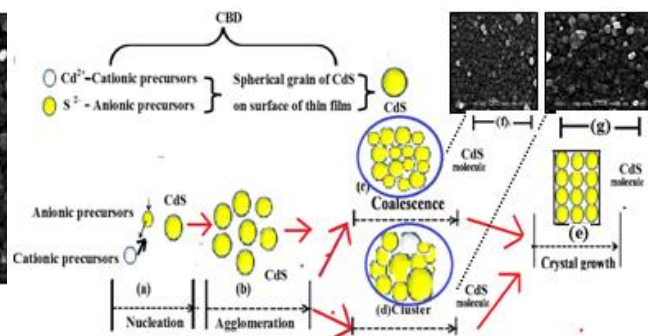


Fig. 8. The schematic representation of growth process of CdS thin film (a) Nucleation, (b) agglomeration, (c) coalescence, (d) cluster and (e) crystal growth deposited by CBD. [Inset (f) and (g) shows enlarge SEM image of as-deposited CdS for CBD].

3.5. Optical Study

Fig. 9 represents that, typical curves of the optical absorbance versus the wavelength (nm) for UCBD and CBD techniques. The band edge absorption of CdS thin films have corresponds to the λ (nm) is estimated by a linear interpolation of each curve to wavelength (nm) axis. An optical spectrum has accuracy up to 0.02 nm. The band edge absorption of CdS thin films has found to be in visible regions, Bulk materials of CdS thin films has been reported a longer wavelength ($520\text{ nm} \pm 534\text{ nm}$) for CBD [37,- 39]. The band gap of CdS films prepared by CBD, both with magnetic agitation and ultrasonic vibration, are shown in the first two curves of Fig. 9. Note the differences, the optical spectra obtained for CdS thin films prepared by CBD and UCBD techniques are shown in figure 9. The values of band edge absorption observed for CdS films grown by CBD and UCBD are 534 nm and 476 nm respectively. The smaller wavelength of band edge absorption is obtained from the films with ultrasonication imply that CdS grown under ultrasonication cause a stable nucleation, which can stop further growth mechanism. The band edge absorption shifted towards the lower

wavelength region caused by acoustic cavitations process, which leads to the formation of nanosonic particle and other hand higher wavelength regions, which could be due to the formation of bulk materials, band edge absorption of spectrum in the longer wavelength region (≥ 520 nm) is usually caused by coalesces and cluster (cadmium hydroxide) crystalline defects such as grain boundaries and dislocations as early reported. The change in band gap occurs due to the change particle size or improvement in crystallinity for UCBD as compared to the CBD.

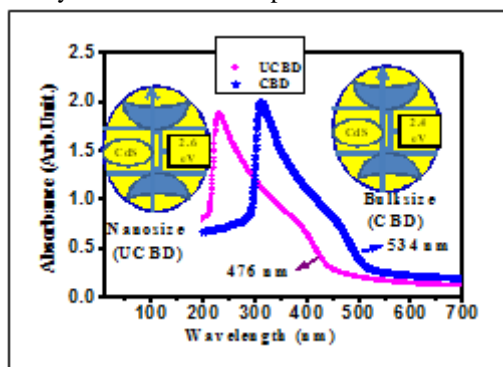


Fig 9. UV visible absorption spectra of CdS thin film deposited by CBD and UCBD technique

3.6 PL Studies:

The study of photoluminescence (PL) spectra of CdS thin films for UCBD and CBD method, which reveals various peaks as shown in fig.10. The PL spectra of CdS thin films excited at 460 nm to determine the band edge emissions of semiconductors in the visible region. since the most common radiative transition is occurred in the semiconductor, the forbidden difference from the states of bottom of the conduction band and the top of the valence band both lie on the same energy axis versus wavelength (nm) also with some non radiative transitions from trapping states of vacancies and defects[41].

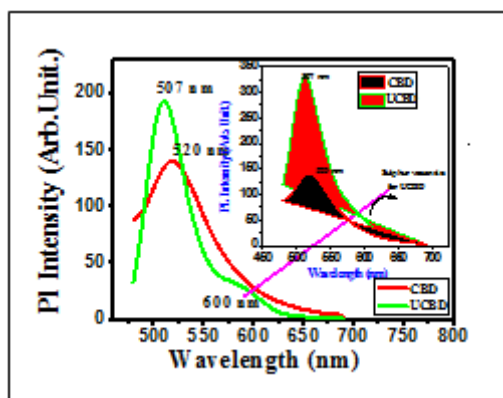


Fig: 10. The photoluminescence (PL) spectra of CdS thin film deposited by CBD and UCBD techniques.

Different agitations on CBD method, ultrasonically thin films show a very high intense peak at 507 nm (2.44 eV), which is leads to the formation nanocrystalline thin films and also with sulphur vacancies of small hump at 590 nm [35-36]. The magnetically agitated thin films shows small intense peaks of band edge emissions at 520 nm reveals a bulk materials. PL spectra of CdS thin films were appeared in the range of 2.3 – 2.54 eV [42-44].

4. Conclusions

The Nanocrystalline transparent CdS thin films are successfully prepared by UCBD and CBD techniques. The sonication and magnetic agitations impact is observed as follows, both films are compact and well adhesive to the substrate. Uniform and adhesive films were observed with improved crystallinity by using UCBD technique. Hexagonally closed packed structure of CdS thin films have a single crystalline phase obtained by both techniques. Coalescence and cluster can be avoided by using sonication method. The band edge absorption found to be at smaller wavelength 476 nm for UCBD and higher wavelength band edge absorption was observed for bulk materials in case of CBD process. The blue shift observed in PL spectra of CdS thin film for UCBD method, which is due to formation of nanosonic particles of CdS.

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