

American Chemical Science Journal
4(2): 151-165, 2014

SCIENCEDOMAIN international
www.sciencedomain.org



Solution Based Cation-Exchange Process to Control Optoelectronic Properties of Cadmium Sulphide Thin Films

Uma Nerle¹ and M. K. Rabinal^{1*}

¹Department of Physics, Karnatak University, Dharwad - 580 003, Karnataka, India.

Authors' contributions

This work was carried out in collaboration between both authors. Both authors read and approved the final manuscript.

Original Research Article

Received 7th September 2013
Accepted 24th October 2013
Published 27th November 2013

ABSTRACT

The control of optoelectronic properties of cadmium sulphide films, by a simple solution based ion exchange process, is an important aspect for various applications. The effect of post doping of certain metal ions on chemical bath deposited cadmium sulphide thin films has been studied in this work. An alkaline bath has been developed to obtain highly homogeneous CdS films on various substrates. X-ray diffraction of these films reveals that as deposited material is amorphous. The energy dispersive x-ray analysis confirms that a reasonable amount of cations can be incorporated into these films without affecting its atomic structure. Optical absorption and electrical conductivity measurements suggest that there is a clear effect of cation-exchange with respect to lead, silver and copper ions. Electrical conductivity is significantly improved by copper ions, this change is close to five orders of magnitude with respect to intrinsic films. These results clearly show that both substitutional and interstitial mechanisms are involved in the cation-exchange process of these films.

Keywords: CdS; chemical bath deposition; post doping; amorphous; interstitial; substitutional.

*Corresponding author: Email: mkrabinal@yahoo.com;

1. INTRODUCTION

For the last few decades, there has been a growing interest in cadmium sulphide (CdS) thin films due to their interesting optoelectronic properties [1]. It possess a direct band gap (2.42 eV), high refractive index (2.5), superior optical absorption coefficient [2,3], a better life time of photo carriers and quite high on/off ratio ($\sim 10^9$) in photoconductivity [4]. As a result, this semiconductor has been looked as a better choice for many potential applications, such as photovoltaic window layer [5-8], active material for photodiode [9] and gas sensor [10] are few to quote here. In literature it has been shown that it is an excellent heterojunction partner for solar cells based on p-type semiconductors like CdTe [5], CuInSe₂ [9] and Cu(In, Ga)Se₂ (CIGS) [11]. With these interests, various techniques have been developed to grow CdS films [1,12]. Among these, the technique of chemical bath deposition (CBD) has been considered as the most prominent one [13]. It is simple, no sophistication, requires minimum materials, economical and permits deposition of large area films. These are essential aspects in the development of modern low cost solar cells [14].

Regardless of deposition conditions adopted in CBD, getting a uniform and chemically homogeneous film is still an open challenge that has to be appropriately addressed before the successful implementation of this material [15]. Further, electronic doping of these films is essential to control type and concentration of charge carriers without which it becomes difficult to realize the potential applications. For example, a high electrical conductivity is required if it is used as a window layer in solar cells and low conductivity for photodiode applications. Generally, the CBD technique yields less conducting films of CdS for stoichiometric composition, this aspect is critically controlled by chemical composition, temperature and pH of chemical bath [16]. Broadly there are two different approaches of doping CdS films deposited by CBD methods. One is in situ doping, here dopant ions are incorporated into a chemical bath prior to the deposition of films. There has been a considerable work in this direction, the in situ doping of copper (Cu), silver (Ag), indium (In) and other metal ions has been studied [17-21]. Second is post doping of as grown films, wherein as prepared CdS films are treated with the ionic solutions of dopants under different conditions [18,19]. Generally it is believed that there is displacement of Cd ions in the film by respective metal ion of solution by displacement reaction, hence a phase conversion of basic CdS to respective metal-sulphide has been proposed. Recently this simple technique has been used to convert a layer of CdS to Cu₂S by treating with aqueous solution of Cu ions at room temperature to form a solar cell [22]. This clearly suggests that the solution phase post doping is appealing and promising method to control optoelectronic properties of CdS. The literature in this direction clearly lacks on a systematic study of solution phase doping of as prepared CdS films and its possible conversion to other phases. The present work aims to study this effect to establish whether there is electronic doping or a phase conversion of initial CdS that is grown by CBD by choosing certain metal ions as dopants.

2. EXPERIMENTAL DETAILS

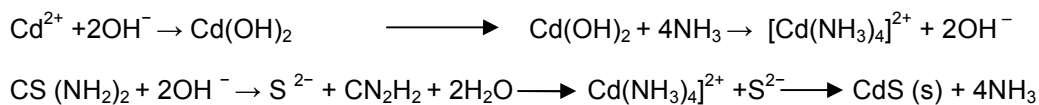
2.1 Materials

All the chemicals used in the present work were of analytical grade, cadmium chloride monohydrate (CdCl₂·H₂O), lead nitrate (Pb₂NO₃) and copper (II) chloride dihydrate (CuCl₂·2H₂O) were obtained from (Himedia), thiourea NH₂·CS·NH₂ (Thomas Baker), ammonia solution 25% (sd-Fine Chemicals, India) and silver nitrate (Sigma-Aldrich) were

used for the deposition of cadmium sulphide thin film by CBD. All the solutions were prepared by dissolving appropriate quantity of material into de-ionized water.

2.2 Chemical Bath Deposition of CdS Films

Here the chemical bath has been set to deposit CdS films using cadmium chloride and thiourea as a source of cadmium and sulphur ions respectively. Prior to optimizing the bath conditions, a large number of trials for different conditions with respect to temperature, concentration of ions and pH were carried out. The condition that yielded superior films, with respect to continuity, smoothness and adherence, was chosen to deposit the final films for further studies. A brief recipe of the present deposition is as follows. The substrates used to deposit films are both commercial glass slides and ITO coated glass slides (Xin Yan Technology LTD, Hong Kong) of typical size 70 × 25 mm². Prior to deposition the glass slides were cleaned by standard procedure. First it was cleaned with soap solution then boiled in soap solution for 30 minutes and finally rinsed with copious amount of distilled water and followed by sonication in water for 10 minutes. In two separate beakers solution of cadmium chloride (5 mM) and Thiourea (10 mM) were prepared. Aqueous ammonia (NH₃) was added to cadmium solution under constant stirring till a white precipitate of Cd(OH)₂ gets dissolved and the solution becomes clear, here ammonia also acts as a complexing agent in the chemical bath. The measured pH of final solution was close to 11.5. Quickly the solution of thiourea was added to the solution of cadmium in 100 ml beaker under stirring and the temperature of solution was raised to 60 °C, a special heat bath is designed to achieve a uniformly heating of bath well above the solution level. Once the required temperature is reached the cleaned glass/ITO slides were inserted vertically along the wall of the beaker and are left undisturbed for chemical bath deposition of CdS films for two hours. Initial colourless solution starts turning slowly to pale yellow with time and at the end of required time a clear deposition of CdS is observed both on glass slides and on the wall of beaker. The deposited slides were cleaned thoroughly with distilled water and later sonicated to remove unadherent material, finally these slides were dried for further characterization. The resulting films were yellowish, homogeneous, spectacularly reflecting with good adherence. Films after sonication which are completely free from adherent material are referred as intrinsic CdS (in-CdS). A photograph of such film is shown in Fig. 2a as an inset, it can be seen that these films are homogeneous and bright yellow in colour. The following chemical reaction is responsible for the deposition of these films.



2.3 Solution Phase Doping of as Prepared CdS Films

The solution phase doping of in-CdS films was studied by immersing these films in different cationic solutions at ambient condition. 5 mM solution of Pb, Cu and Ag were prepared using Pb₂NO₃, CuCl₂-H₂O and AgNO₃, respectively in water. Then in-CdS films were completely immersed in these solutions at room temperature for a longer duration (1 minute) to ensure that there is saturated diffusion of cations, as a result the original films are completely doped. At the end of this, films were thoroughly washed with distilled water and dried in air for further measurements. It is important to note that the solution doping clearly shows visible change in the colour of original film.

2.4 Experimental Characterization

Structural characterization of these films is carried out using X-ray diffractometer (Ultima-4 Rigaku co-operation Japan) operating at 25 kV and 20 mA with Cu $K\alpha$ radiation (1.54056 Å) and scanning rate 0.01°/s. Optical measurements were performed in the wavelength range 300-1100 nm using Analytikjena specord 200 plus (Germany). Surface morphology and elemental analysis was recorded by scanning electron microscope (SEM) (Model JEOL JSM-6360A). The film thickness was measured by thin filmetrics (F20-UV thin- film analyzer) and current-voltage curves were recorded on films deposited on ITO surface using Keithley 617 programmable electrometer at room temperature using our home made set up for conductivity measurements.

3. RESULTS AND DISCUSSION

3.1 Structural Analysis

X-ray patterns were recorded for all the samples, Fig. 1 shows these spectra for pure CdS, CdS:Pb, CdS:Ag and CdS:Cu for comparison. It is observed that as prepared films do not appear smooth, there is inhomogeneous binding of loosely adherent material on the surface. On water sonication of these films the extra material detaches and film appears quite smooth (photograph in Fig. 1 is one such film). To understand the nature of loosely adherent material the x-ray diffraction is also recorded for just as deposited film. The bottom most x-ray pattern is for as deposited film and the next pattern is for in-CdS film. The as prepared film has slight crystallinity that gives main peak at $2\theta=27^\circ$ and a weak peak at $2\theta=45^\circ$, which are nothing but (111) and (220) peaks of cubic phase. The pattern of in-CdS is completely absent from any crystalline peaks, but there is a broad hump around $2\theta=25^\circ$. These spectra clearly indicate that as deposited films (smooth film + adherent particulates) start with an amorphous form of CdS that is quite smooth and the packets of crystallites as loosely adherent particles grow at selected areas. Further, the starting amorphous phase is quite adherent to the glass substrate. In order to check the conversion of amorphous to crystalline state, the sonicated films of CdS were annealed at 300°C for 20 minutes under vacuum furnace ($\sim 10^{-3}$ torr). The x-ray pattern of this sample is shown in the Fig. 1 as (c). It remains same that is material is still amorphous. Further, x-ray patterns of solution doped films of Pb, Ag and Cu are shown Fig. 1 as (d) to (f). It is noticed that all these patterns also exhibit amorphous nature. Hence, the diffusion of above ions into amorphous CdS does not affect the structure of original film. A vast literature is available on the characterization of optoelectronic properties of CBD CdS films [23-26]. Both a highly crystalline and non-crystalline phases have been observed depending on the bath conditions. For example, Khallaf et al. have done a comprehensive study on the effect of cadmium sources on CBD deposited CdS films [24]. In this report, authors also summarize others results on pH, temperature and reagent effects on crystallinity of these films. For variation of pH from 7.8 to 13.5, CdS goes from cubic to hexagonal and to amorphous and sometime even it posses a mixture of both cubic and hexagonal phases together. Interestingly, these authors report that irrespective of cadmium sources the CdS goes to highly crystalline cubic phase. Recently, Kariper et al. studied exclusively the effect of pH on CBD films of CdS, it is noticed that pH of chemical bath has significant effect on the atomic structure of CdS films. It is concluded that low pH gives more crystalline structure and high pH (above 11) always gives more amorphous structure [27]. Under low pH (acidic bath) a natural deposition of films vanishes and hence a deriving force, like electrochemical, has to be applied to deposit the material. In fact, the effect of chemical bath conditions on the structure of films is a bit complex issue due

to numerous parameters such as nature of reagents, pH, temperature and pre-treatment of substrate surfaces.

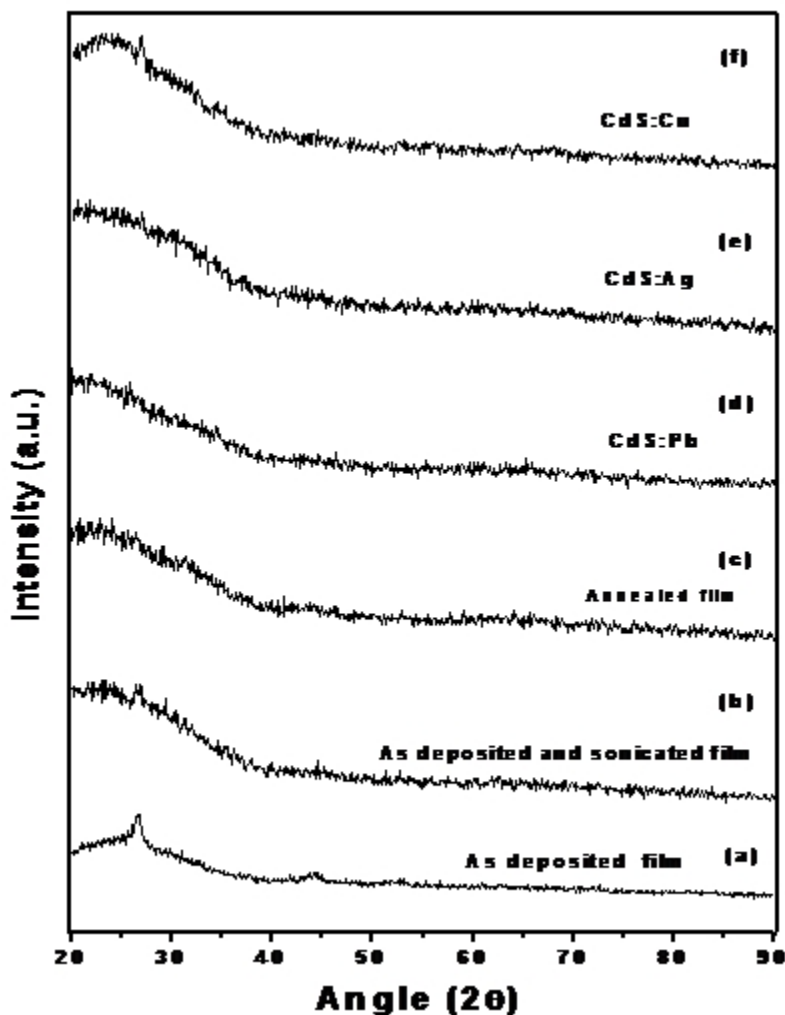


Fig. 1. XRD patterns of as deposited, as deposited and sonicated, annealed at 300°C for 20 minutes under vacuum furnace, Pb doped, Ag doped and Cu doped CdS thin films

3.2 Optical Properties

Optical properties of undoped and doped CdS films were recorded in the wavelength range between 300 and 900 nm and these plots are shown in Figs. 2(a, b) as normalized curves. Undoped film shows a well defined optical absorption whose tangent is close to 525 nm that gives optical band gap 2.39 eV. This number is quite close to its bulk band gap of crystalline CdS. In amorphous semiconductors optical band gap is quite close to their crystalline counter parts, it is a well established fact due to similar short and medium range orders in these two materials [28]. The internal strains in chemical bond length, bond angle and local variation in chemical composition would lead to the tailing and slight shift in the absorption

curve towards lower energy, generally known as Urbatch edge. With Ag doping the absorption curve shifts towards higher wavelength that is at 586 nm ($E_g = 2.11$ eV), further there is more shift in a same direction for Pb doping, whose absorption edge is at 850 nm and ($E_g = 1.4$ eV). A opposite trend, that is blue shift, has been observed in case of Cu doping, absorption edge is at 447 nm ($E_g = 2.77$ eV). The numerical values of critical absorption wavelength and their respective band gap for different films are given in Table 1.

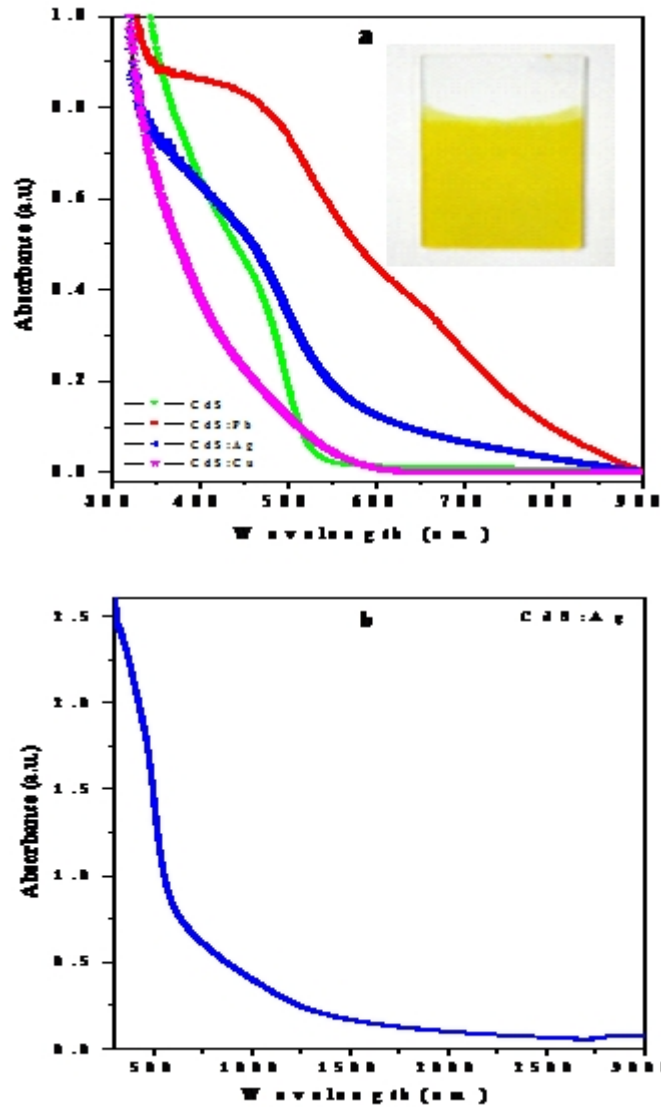


Fig. 2. Optical absorption spectrum of (a) as deposited and sonicated and various ion exchanged CdS films in UV-VIS range (inset shows the room light photograph of as deposited and sonicated CdS film deposited on a glass slide) and (b) UV-VIS-NIR for CdS: Ag film

Table 1. Numerical values of critical absorption wavelength and energy gap of in-CdS and doped CdS films

Thin film	Critical absorption wavelength (nm)	Energy gap (eV)
in-CdS	525	2.39
CdS:Pb	850	1.40
CdS:Ag	586	2.11
CdS:Cu	447	2.77

A decrease in band gap of CdS films with doping of certain metal ions has been attributed to the fact that these ions create donor levels quite close to conduction band (shallow levels) and these levels become highly degenerate with more percentage of doping and hence merge into the conduction band [29-30]. However, the increase in band gap of undoped CdS with Cu doping can be accounted to the Moss-Burstein shift (effect) [31,32]. This effect has been accounted to the fact that the absorption edges shift to higher energy due to over population of charge carriers as compared to the density of states in valence and conduction bands [33]. A solar cell has been formed on chemical bath deposited CdS film by converting it to Cu_2S by ion-exchange process, these cells were formed in multilayer with wide band gap semiconductor TiO_2 [22(a)]. Here also a blue shift in optical absorption of Cu_2S cell is reported as compared to intrinsic CdS cell.

The ion exchange doping of CdS may lead to conversion of original CdS to respective metal-sulphides. Then there can be formation of Cu_2S , PbS and Ag_2S within CdS phase due to Cu, Pb and Ag doping respectively. In order to confirm this, optical absorption measurements were extended upto 3000 nm to notice the absorption edges associated with above phases. The critical absorption of Cu_2S is 1033 nm, PbS is 3000 nm and Ag_2S is 1361 nm, these are the estimated values based on their respective bulk band gaps. The absorption spectrum of above films did not show the sign of these edges. A typical absorption curve of Ag_2S is shown as in Fig. 2(b) as a representative for other films. Hence, it can be concluded that in the present films there is no phase conversion but it is alloying of dopant material with amorphous matrix of CdS.

3.3 Surface Morphology and Chemical Analysis

Fig. 3 illustrate the SEM images of intrinsic and postdoped thin films of CdS at 30,000 magnifications. The growth of the films was observed to be uniform that covers substrate close to 100%. The surface in all the four films shows granular structure with well defined grain boundaries. The formation of these grains is quite typical of CBD technique. It is well known that there are two growth mechanisms in CBD, namely, ion-by-ion and cluster-by-cluster [34]. It is reported that the films deposited from ammonia (alkaline) bath is controlled by means of cluster-by-cluster mechanism [34]. In electrochemical induced ion-by-ion growth of CdS films a high crystallinity of hexagonal phase with preferential orientation has been reported in acidic bath [35]. Here, the hexagonal facets perpendicular to substrate can be clearly seen, which indicates growth rate is limited by surface reaction. In the present case, the individual grains are more or less spherical in nature (mean diameter about 45 nm) and there is good degree of aggregation of these particles. The X-ray diffraction clearly reveals that these films are completely amorphous in nature and the grain size seen in SEM pictures may not be the size of crystallites but grains of aggregated particles. The ion-by-ion growth process suppose to give more ordered (crystalline) state and cluster-by-cluster process

gives less ordered (amorphous) state. Hence, it can be believed that the present films are grown by cluster method. Further, from SEM pictures it is observed that upon doping of CdS there is swelling of grains, which is more in Pb films as compared to Ag films. The reason for this is yet to be established.

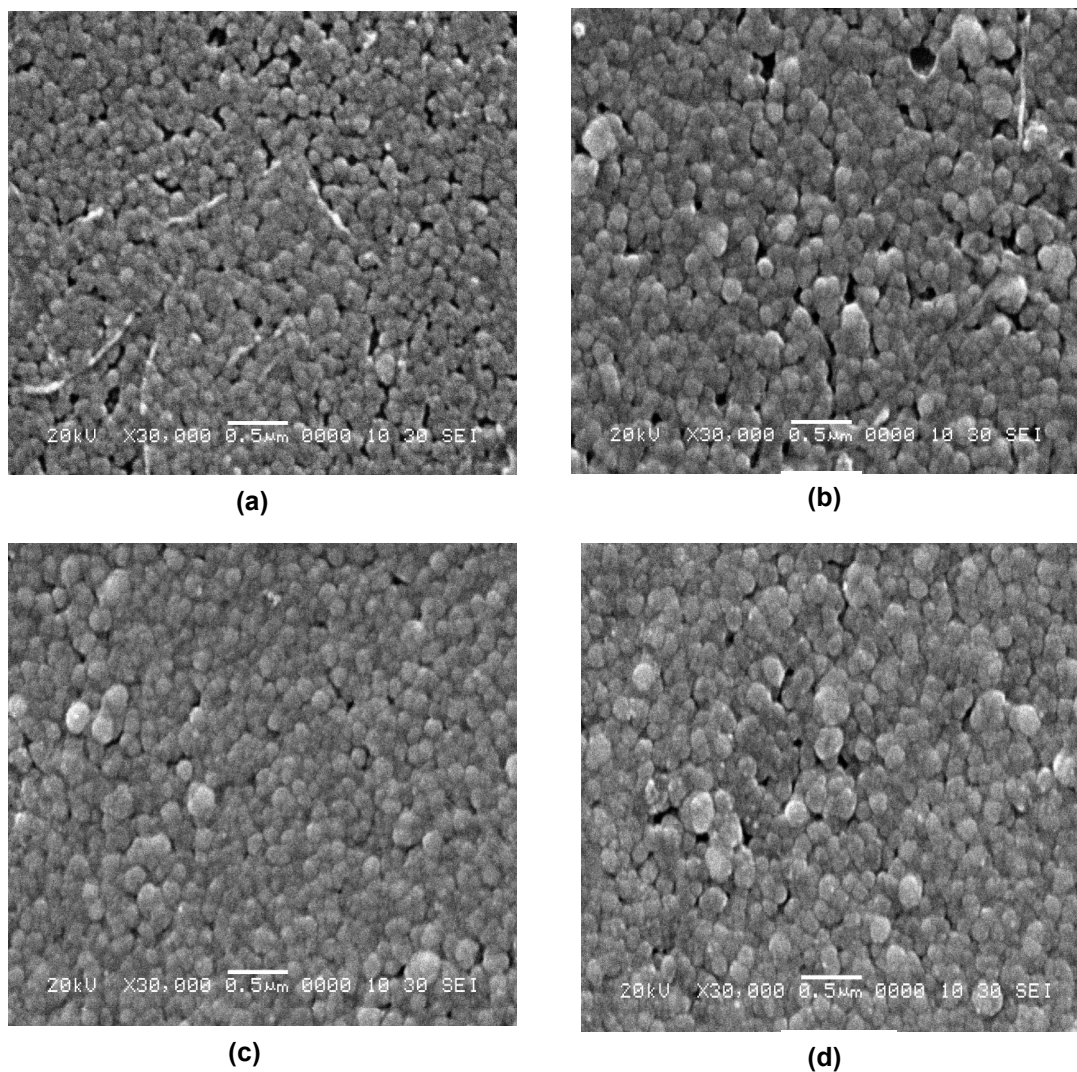


Fig. 3. Scanning electron micrographs of (a) as deposited and sonicated CdS, (b) CdS: Pb, (c) CdS: Ag and (d) CdS: Cu thin films

Table 2. Compositional analysis of different CdS films by Energy Dispersive X-ray analysis

Thin film	Element	Atomic wt (%)	Atomic ratio (Cd/S)
in-CdS	Cd	53.43	1.14
	S	46.57	
CdS:Pb	Cd	38.32	0.76
	S	50.23	
	Pb	11.45	
CdS:Ag	Cd	12.74	0.35
	S	36.13	
	Ag	51.13	
CdS:Cu	Cd	34.84	0.72
	S	48.25	
	Cu	16.90	

Chemical composition of these films was studied by energy dispersive x-ray analysis (EDX) measurements, these data are summarized in table 2. All the films are free from impurity atoms signals. The chemical composition of undoped CdS films shows that Cd atomic % is 53.43 and that of S is 46.57 and Cd/S atomic ratio is 1.14. This indicates there is slight excess of Cd atoms that is 14%, this excess Cd ions would sit either at interstitial position of CdS matrix or at regular site by creating equivalent amount of sulphur vacancy. In either case it changes the electrical conductivity of intrinsic CdS films [36]. The excess Cd in these films gives n-type conductivity [37], we also observed n-type conductivity by hot-probe method in all the films. In case of Pb doping, almost 11.4 atomic % of Pb is incorporated by maintaining sulphur composition close to 50%, this shows that Pb ions displace Cd ions at cationic sites. Similar the case for Cu doping, 16.9 atomic % replaces Cd ions by maintaining sulphur close to 48%. Hence, it can be inferred that Pb and Cu can be incorporated into CdS matrix by substitution diffusion by kick-out mechanism at Cd sites, similar observations have been made by earlier works [18]. Interestingly, a different scenario is observed in case of Ag doping. A large atomic % of Ag goes into CdS matrix that is close to 51.13%, as shown in table-2. The silver cations can sit either by substitution or by interstitial or by both. The chemical composition of these films shows that close to 23% goes to substitution site, this is with respect to S wt %, and more amount 28% to goes to interstitial position. It is well known in case of many materials that silver has ability of easy diffusion, particularly in case of amorphous semiconductors it shows a good mobility under electric field, light and temperature gradients [38]. There are certain reports on the solution phase ion-exchange doping of CdS films prepared by different methods [39]. In case of silver, it is reported that there is partial to complete conversion of CdS to Ag₂S [19]. Ristova et al. studied XPS profile of Ag doping in chemical bath deposited films of CdS to study ion distribution profile [19]. It is concluded that silver diffuses to entire material. Similarly, the diffusion of silver is also studied in case of thermally evaporated CdS films [18], these films exhibit better crystallinity and Ag incorporation only upto 4.65 atomic % has been observed. In the present case the large amount of silver diffusion (51 atomic %) is observed which is never reported earlier. It is believed that this could be due to highly amorphous nature of these films, in which the constituent atoms satisfy their valency (Mott's 8-N rule) [40] and there is more free volume and these are the factors that are responsible for high incorporation of silver ions into CdS phase.

3.4 Electrical Characterization

Electrical conductivity of these films was measured by our home built two probe set up with soft electrical contacts, (It is gold coated copper PCB on flexible plastic that is commercially available). The two metal probes (stripes: 4 mm length, 0.7 mm width and 0.38 mm separation between the probes) loaded on a soft polymer pad (PDMS) that further loaded with spring pres-sure rests on CdS film surface, the setup a convenient method to measure electrical conductivity of soft materials, a lower version of this setup has been published by us elsewhere [41]. Current versus voltage data for different films is shown in Fig. 4 (as semi-logarithmic plots). The linear current-voltage plots of these films show that in the entire measurement range these curves are ohmic in nature. It is clear from these plots that for voltage of 20V, the current in intrinsic film is 2×10^{-7} A that increase quite a little in Pb doped and there is further increase in Ag doped films. Almost one order of enhancement has been observed in case Ag doping as compared to undoped film. But, there is significant change with respect to Cu doping. There is almost five orders of magnitude change in current for the above voltage in these films. From these data electrical conductivities were estimated for different dopants and this data is summarized in Table 3. There is no direct correlation of electrical conductivities of these films with respect to their optical absorption edge. For example, the Pb and Ag doping gives a slight red shift in absorption edge, which is more in case of former. On the other hand, Cu doping leads to a slight blue shift absorption edge. There are two different aspects with respect to the observed optical and electrical properties of these films that need to be addressed. One is, a correlation has to be made between the shift in optical absorption edge and change in electrical conductivity of these films with doping. Another is, the mechanism of charge transport in these films with respect to doping of ions. As per the first aspect is concerned, the above results clearly suggest that the change in electrical conductivity upon ion exchange doping in CdS films is not mainly due to shift in their absorption edge as compared to undoped CdS. But it is entirely related to electronic states created by the dopants. On the basis of band gap shift with doping, it is expected that Cu doping should be less conducting and Pb and Ag should be more conducting with respect to intrinsic CdS. But the observations show that opposite is true. To account this in case of Cu doping, the significant enhancement of conductivity could be related to the Moss-Burstein shift (effect), overpopulation of charge carriers in conduction band due to heavy doping [31,32]. This leads to increase in apparent band gap as compared to the intrinsic band gap by having high density of charge carriers. Regarding the second aspect, intrinsic CdS shows very low conductivity as compared to Cu doped films (Table-1), it is almost five orders of magnitude change. In case of intrinsic film, the mechanism is due to thermally activated process of excitation of electrons from valence band to conduction band that is quite common in intrinsic semiconductors. Due to high band gap of CdS (2.40 eV) thermally excited carriers at room temperature is low which gives low conductivity. Whereas, in case of Cu doping, CdS is heavy doped and the semiconductor becomes highly degenerate and hence there is a large density of free electrons in conduction band leading to the Moss-Burstein shift (effect). Hence, it is believed that in this case the thermal excitation process, transition of charge carriers from valence band to conduction band, becomes weak as compared to the doping density. Further, the work is under progress to investigate the type and concentration of charge carriers in these films using Hall effect measurements. It will be interesting to study the role of crystallinity of CdS and its effect on ion-exchange process and their subsequent effect on optoelectronic properties.

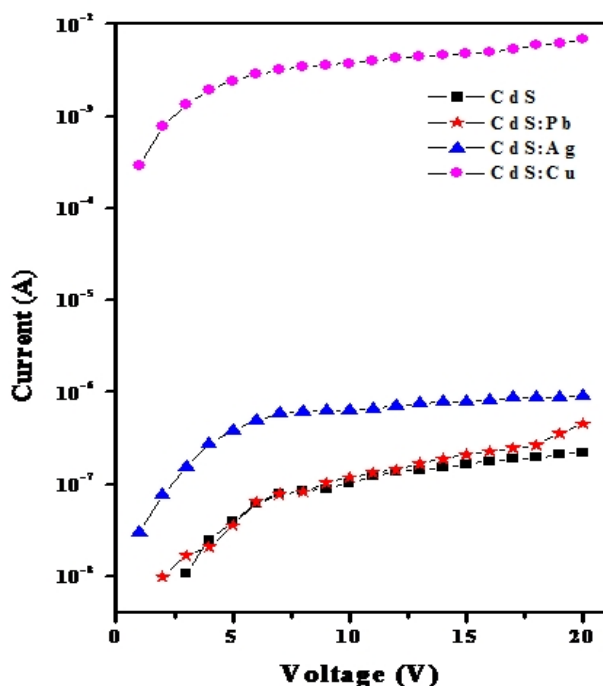


Fig. 4. Current-voltage measurements of as deposited and sonicated CdS, CdS: Pb, CdS: Ag and CdS: Cu films that were deposited on indium tin oxide (conducting) glass substrates

Table 3. Numerical values of room temperature electrical conductivity of intrinsic and doped CdS thin films

Thin film	Conductivity (Ωcm^{-1})
in-CdS	7.3×10^{-10}
CdS:Pb	1.4×10^{-9}
CdS:Ag	3.1×10^{-9}
CdS:Cu	2.4×10^{-5}

4. CONCLUSIONS

In summary, the solution based ion exchange is an interesting and a simple method to control the electrical conductivity of chemically bath deposited CdS films. In this work it is shown that highly alkaline chemical bath gives good homogeneous CdS films that are completely amorphous in nature. Upon ion exchange doping of these films with Pb, Ag and Cu there is visible change in optical properties, that is the optical band gap of CdS:Pb and CdS:Ag films was found to decrease while in case of CdS:Cu it decreases slightly. A reasonable amount of dopants can be incorporated in these materials by a natural diffusion process due to disordered structure. The XRD and SEM measurements suggest that internal structure and surface morphology almost remain same even after ion exchange doping of these films. But there is a significant enhancement in electrical conductivity, almost by five orders of magnitude, in case of Cu. At the end it can be concluded present measurements

that both doping (interstitial substitution) and phase conversion of intrinsic CdS happens in solution based cation-exchange process.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Dong D, Liu X, Li J, Shang C, Hu W. Effects of Growth Conditions on the Microstructure Characteristics of CdS Thin Films by AP-MOCVD, *Journal of Electronic Science and Technology*. 2010;8(2):149-153.
2. Cetinorgu E, Gumus C, Esen R. Effects of deposition time and temperature on the optical properties of air-annealed chemical bath deposited CdS films, *Thin solid films*. 2006;515(4):1688-1693.
3. Sandoval-Paz MG, Sotelo-Lerma M, Mendoza-Galvan A, Ramirez-Bon R. Optical properties and layer microstructure of CdS films obtained from an ammonia-free chemical bath deposition process, *Thin Solid Films*. 2007;515:3356–3362.
4. (a) Nair PK, Nair MTS, Campos J and Sansores LE. A critical discussion of the very high photoconductivity in chemically deposited cadmium sulfide thin films: Implications for solar cell technology, *Solar Cells*.1987;22(3):211–227. (b) Nair MTS, Nair PK and Campos J. Effect of bath temperature on the optoelectronic characteristics of chemically deposited CdS thin films, *Thin Solid Films*. 1988;161:21-34. (c) Nair PK and Nair MTS. Solar-assisted chemical deposition of highly photosensitive CdS thin films, *Solar Energy Materials*. 1987;15:431-440.
5. Durose K, Edwards PR, Halliday DP. Materials aspects of CdTe/CdS solar cells, *Journal of Crystal Growth*. 1999;197:733-742.
6. Cojocar-Miredin O, Choi P, Wuerz R, Raabe D. Atomic-scale characterization of the CdS/CuInSe₂ interface in thin-film solar cells, *Applied Physics Letters*. 2011;98:103504(1-3).
7. Hossain Md. A, Koh ZY, Qing Wang. PbS/CdS-sensitized mesoscopic SnO₂ solar cells for enhanced infrared light harvesting, *Phys. Chem. Chem. Phys*. 2012;14:7367–7374.
8. Lin H, Xia W, Wu HN, Tang CW. CdS/CdTe solar cells with MoO_x as back contact buffers, *Applied Physics Letters*. 2010;97:123504.
9. Pradhan B, Ashwani K Sharma, Ray AK. A simple hybrid inorganic-polymer photodiode, *J. Phys. D: Appl. Phys*. 2009;42:165308.
10. Hur S and Kim E, Lee J, Kim G, Yoon S. Characterization of photoconductive CdS thin films prepared on glass substrates for photoconductive-sensor applications, *J. Vac. Sci. Technol. B*. 2008;26(4):1334-1337.
11. Nakada T, Mizutani M, Hagiwara Y, Kunioka A. High-efficiency Cu(In,Ga)Se₂ thin-film solar cells with a CBD-ZnS buffer layer, *Solar Energy Materials & Solar Cells*. 2001;67(1-4):255-260.

12. (a) Kumar V, Sharma DK, Bansal MK, Dwivedi, Sharma TP. Synthesis and characterization of screen-printed CdS films, *Sci. Sinter.* 2011;43:335-341. (b) Goswami YC, Sharma R, and Rajaram Growth of CdS nanostructures by new sol gel route and its optical characterization, *Nanotechnology and Nanoscience.* 2011;2(1):38. (c) Lokhande CD, Sankapal BR, Pathan HM, Muller M, Giersig M, Tributch H. Some structural studies on successive ionic layer adsorption and reaction (SILAR) deposited CdS thin film, *Applied Surface Science.* 2001;181:277-282. (d) Anuar K, Zulkarnain Z, Saravanan N, Nazri M, Razak Sharin. Effects of Electrodeposition Periods and Solution Temperatures Towards the Properties of CdS Thin Films Prepared in the Presence of Sodium Tartrate, *Materials Science (Medžiagotyra).* 2005;11(2).
13. (a) Yamaguchi K, Yoshida T, Sugiura T, Minoura H A Novel Approach for CdS Thin-Film Deposition: Electrochemically Induced Atom-by-Atom Growth of CdS Thin Films from Acidic Chemical Bath, *J. Phys. Chem. B.* 1998;102:9677-9686. (b) Tec-Yam S, Patiño R, Oliva AI. Chemical bath deposition of CdS films on different substrate orientations, *Current Applied Physics.* 2011;11:914-920. (c) A Asikoglu and Yukselici MH. Evolution of the energy band structure in chemical-bath-deposited CdS thin films studied by optical absorption spectroscopy, *Semicond. Sci. Technol.* 2011;26:055012. (d) Lo YS, Choubey RK, Yu WC, Hsu WT, Lan CW. Shallow bath chemical deposition of CdS thinfilm, *Thin Solid Films.* 2011;520:217-223.
14. (a) Bayer A, Boyle DS, Heinrich MR, O'Brien P, Otway DJ, Robbe O. Developing environmentally benign routes for semiconductor synthesis: improved approaches to the solution deposition of cadmium sulfide for solar cell applications, *Green chemistry.* 2000;79-85. (b) Breen ML, John T. Woodward, IV, and Schwartz DK, Apblett AW. Direct Evidence For Ion by Ion Deposition Mechanism In Solution Growth of CdS Thin Films, *Chem. Mater. Chem. Mater.* 1998;10:710-717. (c) Oliva AI, Castro-Rodriguez R, Ceh O, Bartolo-Perez P, Caballero-Briones F, Sosa V. First stages of growth of CdS films on different substrates, *Applied Surface Science.* 1999;148(1-2):42-49. (d) Martinez MA, Guillen C, Herrero J. Morphological and structural studies of CBD-CdS thin films by microscopy and diffraction techniques, *Applied Surface Science.* 1998;136(1-2):8-16.
15. (a) Moualkia H, Hariach S, Aida MS. Structural and optical properties of CdS thin films grown by chemical bath deposition. *Thin Solid Films.* 2009;518:1259-1262. (b) Kozhevnikova NS, Rempel AA, Hergert F, Magerl A. Structural study of the initial growth of nanocrystalline CdS thin films in a chemical bath, *Thin Solid Films.* 517(8):2586-2589.
16. (a) Nemeč P, Nemeč I, Nahalkov P, Knizek K, Maly P. Ammonia-free chemical bath deposition of CdS films: tailoring the nanocrystal sizes, *Journal of Crystal Growth.* 2002;240(3-4):484-488. (b) Herrera S, Ramos CM, Patino R, Pena JL, Cauch W, Oliva AI. Analysis of the Chemical Bath and its Effect on the Physical Properties of CdS/ITO thin Films, *Brazilian Journal of Physics.* 2006;36(3B):1054-1057.
17. Petre D, Pintilie I, Pentia E, Pintilie I, Botila T. The influence of Cu doping on optoelectronic properties of chemically deposited CdS, *Materials Science and Engineering.* 1999;B58(3):238-243.
18. Shah NA, Nazir A, Mahmood W, Syed WAA, Butt S, Ali Z, Maqsood A. Physical properties and characterization of Ag doped CdS thin films. *Journal of Alloys and Compounds.* 2012;512(1):27-32.
19. Ristova M, Rostov M. XPS profile analysis on CdS thin film modified with Ag by an ion exchange 2001, *Applied Surface Science.* 2001;181(1-2):68-77.

20. Khallaf H, Chai G, Lupan O, Chow L, Park S, Schulte A. Investigation of aluminium and indium *in situ* doping of chemical bath deposited CdS thin films, J. Phys. D: Appl. Phys. 2008;41:185304 .
21. Atay F, Bilgin V, Akyuz I, Kose S. The effect of In doping on some physical properties of CdS films, Materials Science in Semiconductor Processing. 2003;6(4):197-203.
22. (a) Page M, Niitsoo O, Itzhaik Y, Cahen D and Hodes G. Copper sulfide as a light absorber in wet-chemical synthesized extremely thin absorber (ETA) solar cells, 2009 *Energy Environ. Sci.* 2009;2:220–223. (b) Wu Y, Wadia C, Ma W, Sadtler B and Alivisatos PA. Synthesis and Photovoltaic Application of Copper (I) Sulfide Nanocrystals, Nano letters. 2008;8(8):2551-2555. (c) Pan C, Niu S, Ding Y, Dong L, Ruomeng Yu, Liu Y, Zhu G, and Wang ZL, Enhanced Cu₂S/CdS coaxial nanowire solar cells by piezo-phototronic effect. Nano Letters. 2012;12: 3302-3307. (d) Tang J, Huo Z , Brittman S, Gao H, and Yang P. Solution-processed core-shell nanowires for efficient photovoltaic cells , *Nature Nanotechnology* . 2011;6:568-572.
23. Feitosa AV, Miranda MAR, Sasaki JM, Araujo-Silva MA. A New Route for Preparing CdS thin Films by Chemical Bath Deposition Using EDTA as Ligand. Brazilian Journal of Physics. 2004;34(2B):656-658.
24. Khallaf H, Oladeji IO, Chai G, Chow L. Characterization of CdS thin films grown by chemical bath deposition using four different cadmium sources , Thin Solid Films . 2008;516:7306–7312.
25. Archbold MD, Halliday DP, Durose K, Hase TPA, Smyth- Boyle D, Govender K. Characterization of thin film cadmium sulfide grown using a modified chemical bath deposition process , *IEEE* . 2005;476-479.
26. Karimia M, Rabiee M, Moztafzadeh F, Tahriri M, Bodaghi M. Controlled synthesis, characterization and optical properties of CdS nanocrystalline thin films via chemical bath deposition (CBD) route, Current Applied Physics. 2009;9:1263–1268.
27. Kariper A, Guneri E, Gode F, Gumus C. Effect of pH on the physical properties of cds thin films deposited by CBD , Chalcogenide Letters. 2012;9(1):27–40.
28. Chu J, Jin Z, Cai S, Yang J, Hong Z. An in-situ chemical reaction deposition of nanosized wurtzite CdS thin films, Thin Solid Films. 2012;520(6):1826-1831.
29. Roy P and Srivastava SK. *In situ* deposition of Sn-doped CdS thin films by chemical bath deposition and their characterization. J. Phys. D: Appl. Phys. 2006;39:4771–4776.
30. Santos Cruz J, Castanedo Perez R, Torres Delgado G, Zelaya Angel O. CdS thin films doped with metal-organic salts using chemical bath deposition, Thin Solid Films . 2010;518(7):1791–1795.
31. Ikhmayies SJ, Ahmad-Bitar RN. A Comparison between the Electrical and Optical Properties of CdS: In Thin Films for Two Doping Ratios. Jordan Journal of Mechanical and Industrial Engineering. 2010;4(1):111-116.
32. Rathore KS, Deepika, Patidar D, Saxena NS, Sharma KB . Effect of cu doping on the structural, optical and electrical properties of CdS nanoparticles. Journal of Ovonic Research. 2009;5(6):157-167.
33. Banerjee P, Lee W, Bae K, Lee SB, Rubloff GW. Structural, electrical, and optical properties of atomic layer deposition Al-doped ZnO films. Journal of Applied Physics. 2010;108:043504(7 pages)
34. Hernandez-Borja J, Vorobiev YV, Ramirez-Bon R. Thin film solar cells of CdS/PbS chemically deposited by an ammonia-free process, Solar Energy Materials and Solar Cells. 2011;95:1882-1888.
35. Yamaguchi K, Yoshida T, ugiura T, Minoura HJ. Phys. Chem. B. 1998;102:9677-9686.

36. Khallaf H, Chai G, Lupan O, Chow L, Park S, Schulte A. Characterization of gallium-doped CdS thin films grown by chemical bath deposition. *Applied Surface Science*. 2009;255:4129-4134.
37. Barote MA, Yadav AA, Masumdar EU. Synthesis, characterization and photoelectrochemical properties of n-CdS thin films. *Physica B*. 2011;406(10):1865-1871.
38. (a) Mitkova M, Kozicki MN. Ag-photodoping in Ge-chalcogenide amorphous thin films—Reaction products and their characterization. *Journal of Physics and Chemistry of Solids*. 2007;68:866–872. (b) Kozicki MN, Mitkova M. Mass transport in chalcogenide electrolyte films – materials and applications, *Journal of Non-Crystalline Solids*. 2006;352:567–577. (c) Mitkova M, Sakaguchi Y, Tenne D, Bhagat SK and Alford TL. Structural details of Ge-rich and silver-doped chalcogenide glasses for nanoionic nonvolatile memory, *Status Solidi A*. 2010;207(3):621–626.
39. (a) Mahdjoubi L, Derdouri M, Benmalek M. Preparation and analysis of CdS-Cu₂S solar cells, *Solar Cells*. 1982;5:205-212. (b) Bhide VG, Salkalachen S, Rastogi AC, Rao C N R and Hegde MS. Depth profile composition studies of thin film CdS:Cu₂S solar cells using XPS and AES. *J. Phys. D: Appl. Phys.* 1981;14:1647-56. (c) Bryant FJ, Hariri AK and Scott CG. Surface and Interface Processes Influencing The Stability of Cu₂S-CdS Thin Film Solar Cells *J. Phys. D: Appl. Phys.* 1983;16:2341-2348.
40. (a) Dongol M. Optical Absorption and Structural Properties of as-deposited and Thermally Annealed As-Te-Ga Thin Films, *Egypt. J. Sol.* 2002;25(1):33-47. (b) Mott NF. Electrons in glass, *Revue De Physique Appliquée*. 1977;12:619-630.
41. Hiremath RK, Rabinal MK, Mulimani BG. Simple setup to measure electrical properties of polymeric films, *Review of Scientific Instruments*. 2006;77(12):126106(1)-126106(3).

© 2014 Nerle and Rabinal.; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/3.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Peer-review history:

The peer review history for this paper can be accessed here:
<http://www.sciencedomain.org/review-history.php?iid=355&id=16&aid=2614>