

A Study on the Effect of the Complexing Agent on Particle Size of CBD Deposited Cds Layer

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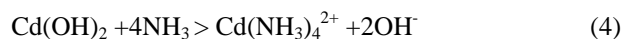
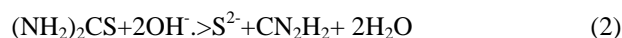
Abstract- Semiconductor compounds with n-type conductivity and band gaps between 2.0 and 3.6 eV have been applied as buffer for CIGS solar cells. However, CdS remains the most widely investigated buffer layer, as it has continuously yielded high-efficiency cells. CdS for high-efficiency CIGS cells is generally grown by a chemical bath deposition (CBD), which is a low-cost, large-area process. Thus Cds buffer layer plays a important role in forming the heterojunction in the CIGS solar cell. In this study dependence of CdS particle size is shown on two complexing agents i.e. TEA (Tri ethanol amine) and NH₄Cl. It is found that the rate of ion-ion exchange is strongly influenced by the presence of these complexing agents, which in turn affects the growth rate of the film. It is further found that NH₄Cl is a much better complexing agent than TEA. The resulting film was characterized by AFM (Atomic force microscope), GIXRD (Glancing Incidence X ray diffractometer) and spectrophotometer.

Keywords- CdS, CIGS, Complexing agent

1. Introduction

Cadmium sulphide, due to its wide band gap (2.42 eV), photoconductivity, and high electron affinity, is known to be an excellent heterojunction partner for p-type CdTe [1,2], CIS [3,4,5], CIGSe [6,7], CIGS [8,9], and CZTS [10] films. It has also been used in other applications including electronic and opto-electronic devices [11]. In the past few decades, several techniques such as thermal evaporation, RF sputtering, physical vapor deposition, pulsed laser evaporation, molecular beam epitaxy, electro deposition, spray pyrolysis, MOCVD, screen printing and CBD (chemical bath deposition) have been used for CdS deposition [12]. In all of the above "Chemical bath deposition" (CBD) is a simple, low temperature and inexpensive large-area deposition technique and thus is probably most widely used for this process. CdS film deposited through CBD is known to enhance the performance of chalcopyrite solar cells [13]. Deposition of CdS using CBD is based on the slow release of Cd²⁺ and S²⁻ ions in an aqueous alkaline bath and the subsequent condensation of these ions on substrates suitably mounted in

the bath. Details equations for the formation of CdS thin film is shown below.



The S²⁻ ions are supplied by the decomposition of thiourea or sodium thiosulfate [12]. Release rate of Cd²⁺ ions can be altered by adding a complexing agent (ligand) to the solution containing the Cd salt to form cadmium complex species, which upon dissociation, results in the release of changed concentrations of Cd²⁺ ions [12]. Different groups have used different complexing agents. Their summary is beautifully covered in the work of H .Khallaf [12]. In his work J Barman [14] has used NH₄Cl and TEA both for the deposition of CdS film using CBD process. TEA is also used for the deposition of NiS and ZnS thin films in the work of

Anuar Kassim [15, 16]. In another article M.A Barote [17] mentioned the use of triethanolamine as a complexing agent in the deposition of Cd_{1-x}Pb_xS thin films. M Rami [18] has worked on Cadmium chloride and cadmium acetate as cadmium sources and found that the deposition of CdS using cadmium chloride gives non-uniform deposition and larger grain size. T Nakanishi [19] has also used NH₄Cl as a complexing agent in the deposition of CdS thin film from CdCl₂ as a cadmium source.

It as been reported that for the application of CdS thin films in solar cells, it is necessary to have layers with the following characteristics: i) uniformity, ii) transparency, and iii) crystallinity [20]. There is a strong tendency of agglomeration of Cd(OH)₂ formed in the solution on substrate surface in the form of large particles, thus resulting in a CdS layer with poor surface coverage [21]. As a heterojunction partner in thin film solar cells, CdS layers must fulfill two contrasting requirements. They should not only provide uniform surface coverage but should be thin enough (typically 50-100 nm for CIGS cells) also to minimize light absorption losses. Inherently rough nature of chalcopyrite absorber surfaces further makes uniform coverage difficult while keeping the CdS layer thickness small at the same time. In such a tricky situation CdS particle size becomes an important parameter which critically influences the surface coverage provided by the CdS layer. CdS layer with large particles (> 100 nm) resulting from conglomeration of smaller grains during film growth provides poor surface coverage. On the other hand, a CdS layer with very small grains (few nm) is likely to provide

excellent surface coverage but will hamper electrical transport due to large number of grain boundaries. Typically the particle size should be of the order of CdS layer thickness to get decent surface coverage as well as electrical transport properties. CdS particle size is generally affected by the reaction kinetics in the CBD process. As stated earlier, use of a complexing agent during CBD process alters reaction kinetics and thus particle size by controlling the availability of Cd²⁺ ions in the solution. However, very few studies are available about the particle size dependence of CdS particles with the use of complexing agent. Our study here shows the impact of complexing agent in reducing the conglomeration of grains to form bigger particles and also the impact on the uniformity, transparency and crystallinity of the CdS film. So in this paper we have studied the impact of two different complexing agents on the CdS particle size using cadmium chloride as the cadmium source.

2. Experiment:

The optimum CdS thickness for chalcopyrite solar cells is 50-100 nm as higher film thickness leads to recombination. In our experiments, the process optimization is done to achieve the two basic requirements of the CdS films i.e. ~ 90 nm thickness & band gap of ~ 2.4 eV. Figure 1 shows the schematic diagram of the CBD setup. Magnetic stirrer is used for uniform mixing of the solution. All the stock solutions were prepared in DI water having resistivity > 18 Mohm.cm [21]. Details of each deposition process are summarized in Table 1.

Table 1. Summary of CdS film processing conditions

Complexing agent	Bath Temp.	pH	Thiourea molarity	CdCl ₂ Molarity	Complexing agent Molarity	NH ₄ OH molarity	Deposition time
NH ₄ Cl	80° C	10.5-11	0.075	0.01	0.02	0.2	40 min
TEA	70° C	11.5-12	0.10	0.01	0.75	0.27	10 min
No complexing agent	70° C	11.5-12	0.10	0.01	-	0.27	10 min

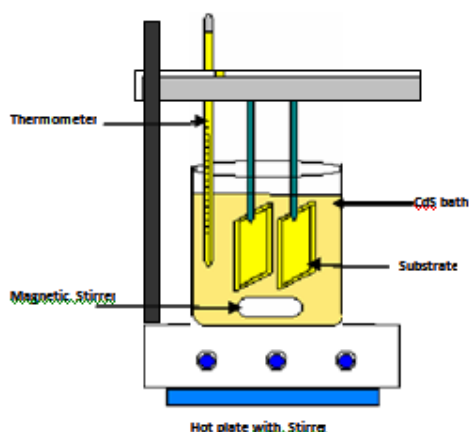


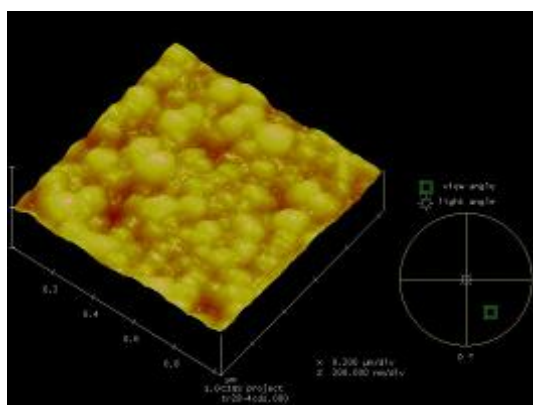
Fig. 1. Schematic diagram of the CBD Set up

CdS coated substrates are characterized for crystal structure using XRD [Rigaku Ultima IV] and surface morphology using AFM [VEECO 3100]. Optical measurements were done using spectrophotometer [Sun Angstrom Tech. SR500].

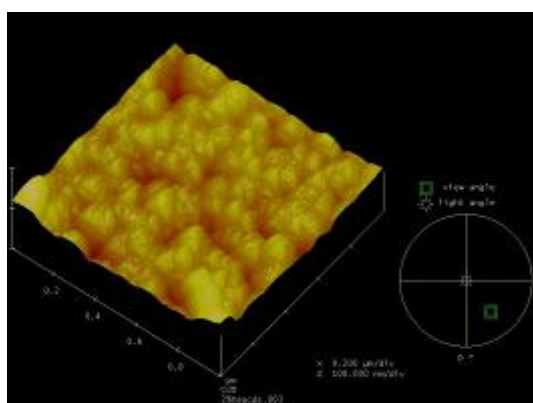
3. Results and discussion:

3.1. Surface Analysis using AFM:

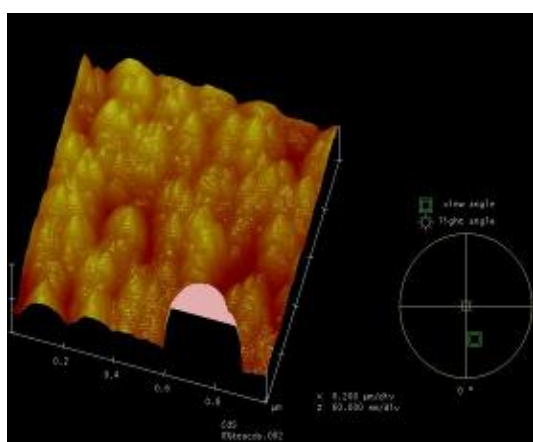
Different CdS samples were subjected to tapping mode AFM and sample area of 1x1 mm was scanned. AFM images of different samples are shown in figure 2. The impact of complexing agent on CdS particle size is clearly highlighted in these images. The particle size is ~ 60 nm in case of NH₄Cl, ~110 nm in case of TEA and ~200 nm in the case of no complexing agent. Also the uniformity of CdS layers deposited with complexing agents (fig 2a and 2b) is relatively better compared to the one deposited without a complexing agent (fig 2c). Consequently, the CdS layer of fig 2c is likely to result in relatively poor coverage of absorber surface.



(a)



(b)



(c)

Fig. 2. AFM image of CdS film of 1mmx1mm area (a) NH₄Cl as complexing agent, (b) TEA as complexing agent, (c) no complexing agent

Table 2. CdS film performance

CdS Film	FWHM (rad.)	Crystallite Size, D (nm)	Band Gap (eV)	Avg. T (%) (500-800 nm)	Particle Size by AFM (nm)	Ra by AFM (nm)
No complexing agent	0.0668	2.22	2.39	81.46	200	4.9
TEA as complexing agent	0.0645	2.30	2.45	76.32	110	4.7
NH ₄ Cl as complexing agent	0.0284	5.24	2.41	82.13	60	12.6

3.2. GIXRD Study:

The GIXRD spectra of as deposited CdS film are shown in fig 3. The peak observance is same for the all three type of samples. The spectra indicate that the films have cubic crystal structure with identified peaks corresponding (111), (220) and (311) planes of the material with cubic phase matched with standard JCPDS data card 80-0019. The intensity of (111) peak for CdS film with NH₄Cl as complexing agent is the highest, which indicates better crystallinity of the film. When we compare the FWHM of different samples we observe a trend i.e. FWHM is reducing when we move from no complexing agent, to samples with TEA and samples with NH₄Cl as complexing agent. This means that the crystallite size is increasing from samples with no complexing agent to samples with NH₄Cl as complexing agent. The crystallite size is determined by Scherer's equation [22].

$$D = 0.94\lambda / \beta \cos(\Theta)$$

Where, λ is the wavelength of X-ray used, β is the FWHM in radian, and q is the Bragg's diffraction angle. The CdS crystallite size of different process conditions is listed in table 2. The particle size for all three CdS films as apparent in AFM images are much larger and seem to be the result of conglomeration of smaller crystallites. It shows that by using a suitable complexing agent like TEA or NH₄Cl the effect of conglomeration can be reduced and CdS films with desired smaller particles can be obtained.

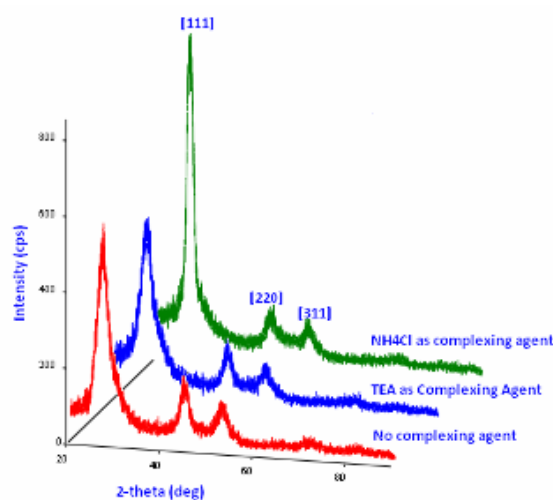


Fig. 3. XRD Spectra of different CdS films

3.3. Optical Properties (Transmission & Band gap):

UV- visible spectra of as deposited CdS samples are shown in figure 4. Here we observe lower transmission values of 76.32 % for CdS film deposited using TEA as complexing agent whereas films with NH4Cl and no complexing agent have transmission >80%. The fundamental absorption, which corresponds to electron excitation from valence to conduction band, can be used to determine the nature and value of optical band gap, which is calculated using the Tauc formula [23].

$$(a hn) = A (hn - E_g)^n$$

Where a is the absorption coefficient, hn is the incident photon energy, A is a constant, and the exponent “n” assumes the values 1/2, 2, 3/2 and 3 for allowed direct, allowed indirect, forbidden direct and forbidden transitions, respectively. Linear nature of the plots at absorption edge confirmed that CdS is semiconductor with direct band gap and so n takes the value of 1/2. The band gap has been calculated by extrapolating the linear region of (ahn)² vs hn plots on the energy axis as shown in figure 5. The calculated band-gap for different films is given in table 2. In his work, A. Cortes [24] has shown an inverse square relation of band gap with crystallite size on the film, however we did not see such relation in our data.

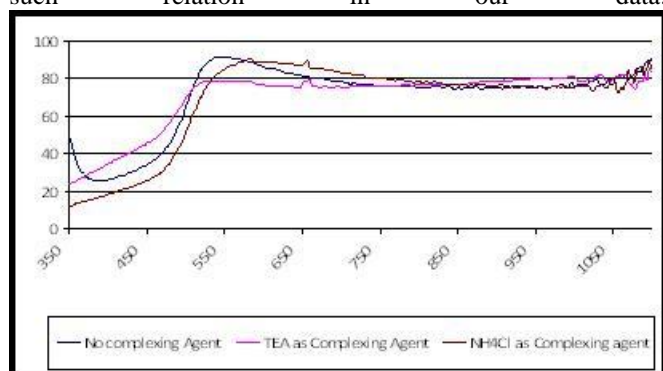


Fig. 4. Transmission graph of different CdS films

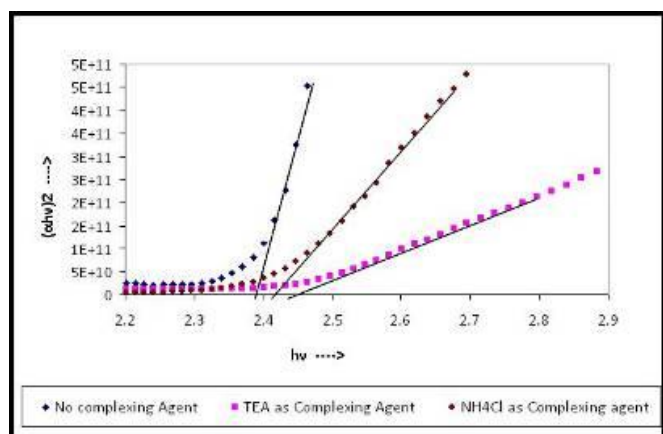


Fig. 5. Plot of (ahv)² vs. hv of different CdS films

4. Conclusion

Use of complexing agent affects CdS film properties by reducing the conglomeration of smaller CdS crystallite to form larger particles. The reduction in particle size results into a film with uniform coverage. The crystalline nature of films made using complexing agent is also higher than the films with no complexing agent that is confirmed by XRD. The use of NH₄Cl as complexing agents reduces the Cd²⁺ release to a large extent i.e. the rate of reaction of formation of CdS on the substrate is reduced. The use of NH₄Cl as a complexing agent helps in achieving a CdS film with good uniformity, transparency and crystallinity. These properties are achieved at a particle size of 60 nm as observed under AFM. In this study, it is also demonstrated that CdS film deposited using CdCl₂ as cadmium source and NH₄Cl as complexing agent meets the criteria of n-type heterojunction partner required for chalcopyrite solar cells.

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