Research Paper

The Effect of Ammonia Salt Concentration on the Properties of Chemical Bath Deposited CdS Thin Films

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Abstract: *Cadmium sulphide films were grown on glass substrates by chemical bath deposition (CBD) from a bath containing $CdCl_2$, NH_4Cl, NH_4OH and thiourea. The effect of ammonium chloride on the deposition rate, structure and optical properties of the CdS thin films has been considered in this work. The XRD patterns show that the films have polycrystalline structure. The deposition time decreases with decreasing the concentration of NH_4Cl. The surface morphology, Optical properties and the band gap value reported in this work is in good agreement with that reported in the literature.*

Introduction

CdS thin films are widely used as n-type window/ buffer layers in thin film solar cells. Many preparation methods such as chemical bath deposition (CBD) [1–10], close spaced sublimation (CSS) [11], metal organic chemical vapor deposition (MOCVD) [12, 13], pulsed laser deposition [14], spray pyrolysis [15], sputtering [16, 17], are used to fabricate CdS thin films. Among them, the CBD technique has been proved to be the most suitable method to produce CdS thin films for photovoltaic applications because it is a cost-effective and large-area deposition method. Thin-film solar cells based on CdTe[18,19] and CIGS [20] have been achieved efficiencies in excess of 16.5% and 20.3% utilizing CdS films prepared via the CBD technique [9].
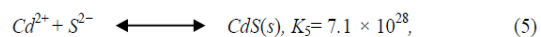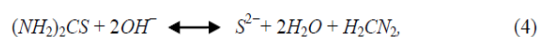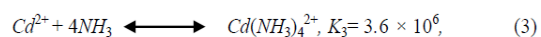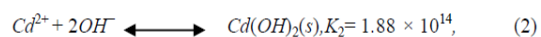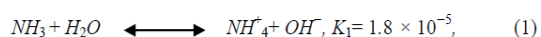
In the CBD technique, deposition parameters, such as the reaction temperature [21, 22], pH [23, 24] and composition of the starting chemicals [25, 26], control the stoichiometry and the structure of the films. In particular, the role of pH is extremely critical to the films formation. The pH of the solution is very sensitive to small concentrations of acids and bases and may change during the chemical reaction. It is a well known fact that the pH of the solution can be stabilized by using a buffer. Buffers are usually mixtures of weak acids or bases and their salts [27]. A common example in CBD-CdS is the use of an ammonium salt to control the pH of reaction solution. Several authors have reported the deposition of CdS films by varying the solutions composition [[25,26], its pH [23,24], and the reaction temperature [21,22]. Only few reports, Chu *et al* and Lee*etal*.[28,29] explain the properties of CdS films deposited with ammonium acetate as a buffer. Hence, there is ample of scope to the study the effect of buffer on the deposited films. NH_4Cl is also one of the buffer solutions in many chemical reactions. However, to the best of our knowledge, there are no reports on the effect of NH_4Cl buffer on the properties of CBD-CdS thin films. In this study, the CdS thin film was grown by using the CBD technique. In the present paper the structural, optical, and electrical properties of the CdS film were investigated as a function of the ammonium chloride concentration in order to optimize their physical and optical properties.

Material and Methods

CdS films were chemically deposited from an aqueous solution containing cadmium chloride ($CdCl_2$), thiourea (($NH_2)_2CS$), ammonia and ammonium chloride (NH_4Cl). Cadmium chloride of

0.05M and thiourea of 0.1M were employed as the cadmium and the sulfur sources, respectively. Ammonia was used as complexing agent to form a cadmium complex, which slowly releases Cd^{2+}ions for subsequent reaction with S^{2-}ions. Ammonium chloride was used as buffer. In the solution growth process, a cadmium complex (ammonia, cyanide, or triethanolamine) and an organic sulfidizing agent (thiourea or thioacetamide) provide very low concentrations of Cd^{2+} and S^{2-} in solution. In the presence of sufficient NH_3, the cadmium salt exists predominantly in the form of $Cd(NH_3)_4^{2+}$. The room-temperature equilibrium constant of the reaction in Eq. (4) is very small. When product of the concentrations of Cd^{2+} and S^{2-} in solution exceeds the solubility product of CdS, 1.4×10^{-29}at 25^0C, a chemical reaction takes place, precipitating CdS[28]. The reaction rate can be controlled by adjusting the pH, reaction temperature, and the relative concentrations of the various reactants in the solution [30]. The involved reactions and their equilibrium constants at room temperature are as follows [28]:

$$NH_3 + H_2O \longleftrightarrow NH_4^+ + OH^-, \quad K_1 = 1.8 \times 10^{-5}, \quad (1)$$

$$Cd^{2+} + 2OH^- \longleftrightarrow Cd(OH)_2(s), K_2 = 1.88 \times 10^{14}, \quad (2)$$

$$Cd^{2+} + 4NH_3 \longleftrightarrow Cd(NH_3)_4^{2+}, \quad K_3 = 3.6 \times 10^6, \quad (3)$$

$$(NH_2)_2CS + 2OH^- \longleftrightarrow S^{2-} + 2H_2O + H_2CN_2, \quad (4)$$

$$Cd^{2+} + S^{2-} \longleftrightarrow CdS(s), K_5 = 7.1 \times 10^{28}, \quad (5)$$

If an ammonium salt is added to the reaction solution, the NH_4^+concentration in the reaction in Eq. (1) is now dictated by the concentration of the ammonium salt rather than by that of ammonia due to the weak dissociation of ammonia. The buffering action of this solution can be understood by considering the equilibrium in Eq. (1). If extra $OH^-$is added to the solution, the equilibrium is shifted to the left. As a result, it tends to remove OH^-, and the pH of the solution is barely changed. Although it also removes NH_4^+, the reduction of the NH_4^+ion will not affect the pH greatly if the concentration of the NH_4^+ions is high to begin with. This is the reason that the combination of ammonia and ammonium ions is a better buffer than ammonia by itself [21].

The substrates used in this study were 76 mm x 26 mm x 1.3 mm glass slides. The cleaned substrates were mounted vertically using a teflon holder in a closed vessel, and a quantity of deionized water sufficient to make the total volume of solution 50 ml was transferred to the bath. This was followed by the addition of (i) $CdCl_2$ solution, (ii) ammonia, and (iii) NH_4Cl solution. The solution was mixed slowly at room temperature with continuous stirring. When the ammonia was added to the solution containing $CdCl_2$, the solution became milky color because of production of the $Cd(OH)_2$ via the reaction in Eq. (2). The addition of NH_4Cl made the reaction solution clear, indicating that the concentration of $Cd(OH)_2$ was decreased and the reaction in Eq. (3) had been promoted. An appropriate amount of thiourea was finally added to the reaction vessel. The solution was heated to the required temperature of deposition (75^0C). When the temperature of the solution had reached and was maintained at the same by means of a thermostatic water bath. The initial pH of the solution was about 11. The solution was vigorously stirred to facilitate the transport of Cd^{2+} and S^{2-}ions to the substrate's surface. The substrates were then taken out after a given time interval. All of the films were cleaned thoroughly with deionized water and then dried. For the purpose of optical characteristic measurements, we removed the CdS film on one side of the substrate by using cotton swabs dipped in diluted HCl. All of the CdS films had a thickness of about 200 nm, showing good reproducibility. Table 1 shows the growth conditions of CdS thin films.

Table 1: Growth conditions of the CdS thin films

S. No.	Parameters	Condition
1	Reaction temperature	75^0 C
2	Cadmium chloride ($CdCl_2$)	0.05 M
3	Thiourea (($NH_2)_2CS$)	0.1 M
4	Ammonia solution	2.0 M
5	pH	10.3 - 10.6
6	Ammonium chloride (NH_4Cl)	0 ~ 0.3 M

Film thickness measured by gravimetric weight difference method with the relation

$T = m / (\rho \times A)$

where, m is the mass of the film deposition on the substrate in gram, A the area of the deposited film in cm^2 and ρ the density of the deposited material (CdS $= 4.69$ g/cm³) in bulk form. The X-ray diffraction (XRD) patterns of the as-deposited CdS thin film were recorded in a D5005 Brucker X-ray diffractometer with CuK_α radiation $\lambda = 1.54056^\circ$ A, operated at 40 kV and 40 mA in Graging Incidence XRD (GIXRD mode. Scanning Electron Microscopy (SEM) micrographs were obtained using JEOL 6400F SEM at an acceleration voltage of 20 kV. Specular transmission measurements have been done at room temperature with unpolarized light at normal incidence in the wavelength range from 200 to 1000 nm using Cary 500 (Varian) double beam UV/VIS spectrophotometer. The optical absorption

coefficient α was calculated for each film using the equation:

$$I_t = I_o \exp(-\alpha t)$$

Where t is the film thickness, It and Io are the intensity of transmitted light and initial light, respectively. The optical absorption coefficient αvaries with photon energy (hν) according to the relation

$$(\alpha h \nu) = A(h \nu - E_g)^n$$

Where *n* is a factor which depends on the nature of the optical transition and $E_g$is the band gap. The values of n are ½, 2, 3/2 for direct-allowed, indirect-allowed and direct-forbidden transitions respectively. For direct-allowed transitions between parabolic bands, a plot of $(\alpha h\nu)^2$with photon energy (hν) is drawn for determination of optical band gap. The extrapolation of the linear region of the plot onto hν axis gives the direct optical band gap of the films.

Growth Characteristics
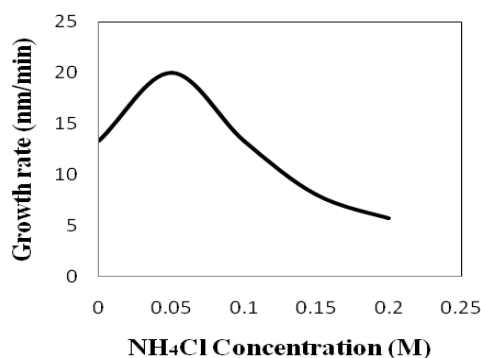
Figure 1: Growth rate of CdS films as a function of NH₄Cl Concentration

Figure 1 shows the growth rate of CdS films as a function of NH₄Cl concentration. In the absence of NH₄Cl, a rapid reaction in the solution gives rise to a number of CdS particulates that adsorb on the glass's surface, then reducing the thickness of the CdS film. When the NH₄Cl was added to the solution, the deposition rate increased rapidly. If the ammonium salt (in this case, NH₄Cl) is added, the slow release of $Cd^{2+}$and S^{2-}ions via the reactions in Eqs. (3) and (4) suppresses the homogeneous reaction in the solution and promotes a heterogeneous reaction on the substrate. Therefore, the growth rate of the CdS film increases. However, at concentrations of NH₄Cl higher than 0.05 M, the deposition rate was reduced. At a given temperature, the rate of formation of CdS is determined by the concentration of Cd^{2+}provided by $Cd(NH_3)^{2+}_4$and the concentration of S^{2-} produced by the hydrolysis of $(NH_2)_2CS$. The excess of NH₄Cl in the solution shifts the equilibrium position of the reaction in Eq.

(1), increasing the concentration $Cd(NH_3)_4^{2+}$ and reducing the concentration of Cd^{2+} ions. The equilibrium position of the reaction in Eq. (4) is also shifted; reducing the concentration of the S^{2-} ion [28]. Therefore, the rate of formation of CdS is reduced.

XRD Analysis
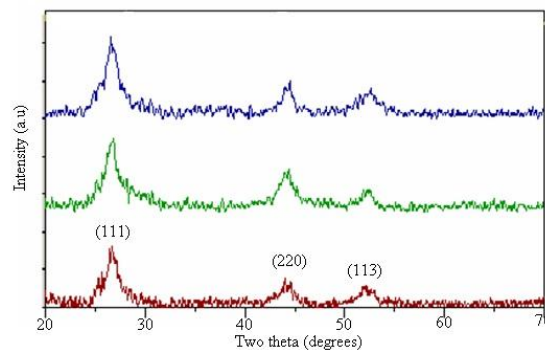
Figure 2: XRD patterns of CdS films with different NH₄Cl concentrations

Figure 2 shows the X-ray diffraction (XRD) patterns of CdS films prepared with different NH₄Cl concentrations. With no NH₄Cl There are no considerable diffraction peaks observed. As mentioned above, the addition of NH₄Cl can provide a slow release of Cd^{2+} and S^{2-}ions via the reaction in Eq. (3), promoting an ion by-ion reaction on the substrate's surface and the growth of a high-quality CdS film. As the NH₄Cl concentration was increased, peaks corresponding to the hexagonal (0 0 2) or the cubic (1 1 1) planes were observed peaks, in addition weak diffraction peaks which could be assigned to the hexagonal (1 1 0) or cubic (2 2 0) plane and to the hexagonal (1 1 2) or the cubic (3 1 1) plane, appeared in the XRD pattern. This result suggests that the crystallinity of CdS films is improved by the addition of an adequate amount of NH₄Cl.

Micro Structure

Figure 3.Shows the SEM micrographs of CdS films grown on glass substrates with different NH₄Cl concentrations. The CdS film prepared without NH₄Cl consists of a uniform layer of nano-crystallites less than 100 nm in size. In addition, a number of large particles were seen on the film's surface. Those were CdS particles, not impurities, because no impurity phase was observed in the XRD pattern. Those particles were quite likely colloidal particles formed in the solution and adsorbed on the substrate during the growth of the films. The formation of CdS can take place heterogeneously on the substrate's surface, depositing a CdS film, or homogeneously in the solution, producing CdS precipitation. The homogeneous process is highly undesirable because the adsorption of CdS particles on the substrate's surface yields powdery and non-adherent films. The

homogeneous process may be suppressed by using conditions for the formation of CdS at low rates, such as low concentrations of $CdCl_2$ and $(NH_2)_2CS$, high concentrations of NH_3 and NH_4Cl, low temperature, and so on [28]. As the NH_4Cl concentration was increased, the particulates on the surface decrease, and the grains in the film became larger. In the heterogeneous process, nucleation on the substrate surface results from the preferential adsorption of Cd^{2+} or S^{2-} ions, followed by the addition of S^{2-} or Cd^{2+} ions. The concentration of Cd^{2+} and S^{2-} ions in the solution is reduced by using the buffer. When the buffer is added, the slow release of these ions via the reactions in Eqs. (3) and (4) reduces the number of nucleation centers and promotes heterogeneous growth on the substrate.
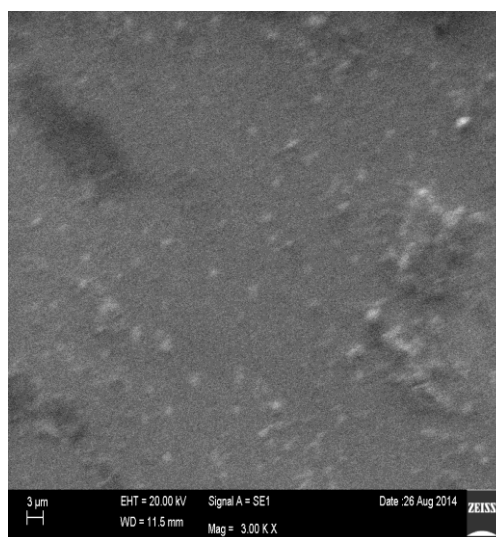

(C)

(A)
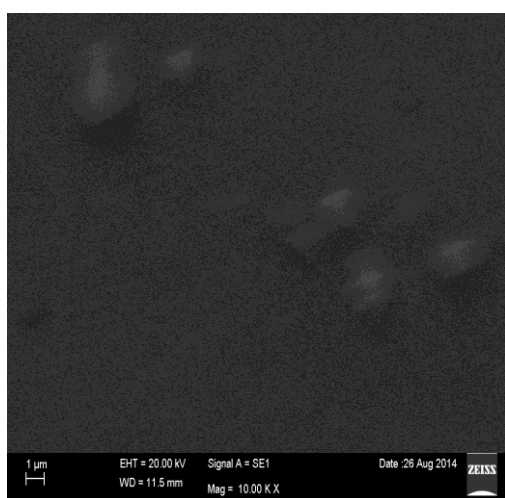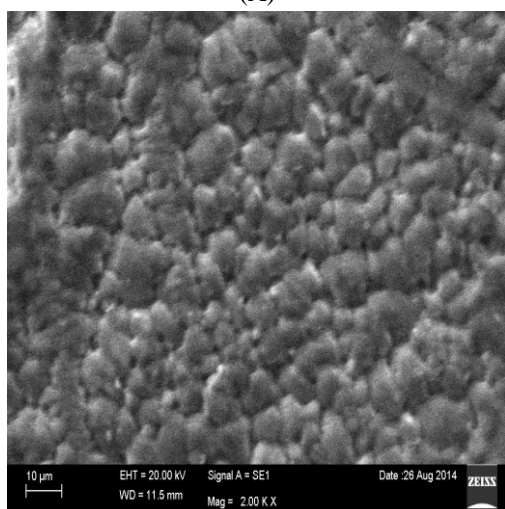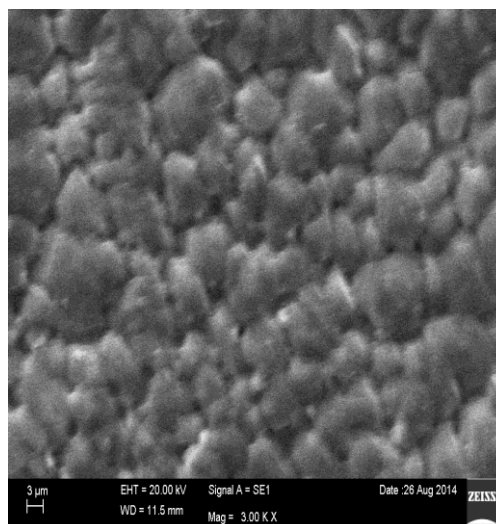
(D)

Figure 3: SEM images of A) NO NH₄Cl B) 0.1 M NH₄Cl C) 0.2 M NH₄Cl   D) 0.3 M NH₄Cl

Optical Properties

Figure 4 shows the optical transmittance of CdS films deposited with various NH_4Cl concentrations. For no or low NH_4Cl concentration, the sharp absorption edge near 550 nm was not observed, and tails were extended toward short wavelengths. In addition, relatively high transmittances were observed. This may be due to the small thickness and/or the poor crystallinity of the CdS film. As the NH_4Cl concentration was increased, a sharp absorption edge, which is generally observed for a direct semiconductor film, appeared in the transmittance spectrum. As the amount of the buffer solution was increased, the heterogeneous reaction on the substrate increased, the film became thicker, and its crystallization was improved, as shown Figs. 2 and 3.

(B)
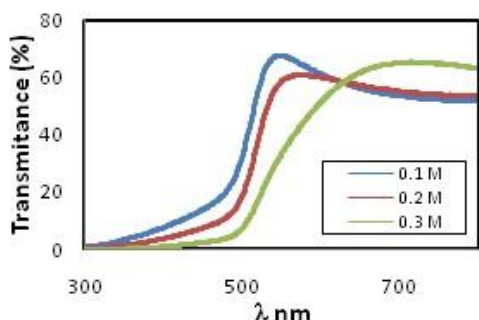
Figure 4: Optical transmission spectra as a function of λ for different NH₄Cl concentration
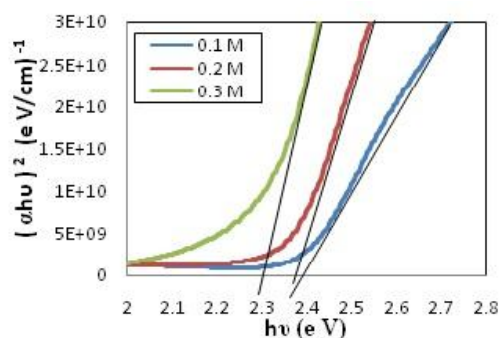
Figure 5: A plots of $(\alpha h\upsilon)^2$ versus $(h\upsilon)$ of CdS thin films at different NH₄Cl concentration

The plots of $(\alpha h\upsilon)^2$ versus $h\upsilon$ for CdS films are shown in Fig.5. The direct optical band gap of CdS films is found to 2.27 eV, 2.30 eV and 2.35 respectively. The decrease in optical band gap might be due to improvement in crystallinity with increasing buffer solution.

Conclusion

The deposition rate of the CdS films was greatly increased by using NH₄Cl as a buffer, and the crystallinity of the films was improved. Also, the number of CdS particulates adsorbed on the film's surface was decreased, and the grain size of the films was increased. However, the deposition rate was decreased as the concentration of NH₄Cl was increased. When more NH₄Cl was added to the reaction solution, the optical absorption edge shifted to longer wavelength, suggesting that the optical band gap of the films was lower. XRD analyses showed that the buffer played a significant role in the structural and optical properties of the CdS films.

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