

# Optimization of chemical bath deposited CdS thin films using nitrilotriacetic acid as a complexing agent

Hani Khallaf<sup>a</sup>, Isaiah O. Oladeji<sup>b</sup>, Lee Chow<sup>a,\*</sup>

<sup>a</sup> Department of Physics, University of Central Florida, Orlando, FL 32816, USA

<sup>b</sup> SOLMAX TECHNOLOGIES, 1209 West Gore St., Orlando, FL 32805, USA

Received 24 February 2007; received in revised form 8 October 2007; accepted 15 October 2007

Available online 22 October 2007

## Abstract

We report a design of experiment approach for the optimization of CdS thin films grown by chemical bath deposition using nitrilotriacetic acid (NTA) as a complexing agent. With the help of this approach, we developed a set of experiments that enabled us to maximize the growth rate. In comparison with works reported earlier, a much faster growth rate is achieved. Two different cadmium precursors; CdSO<sub>4</sub> and CdCl<sub>2</sub> were used in this work. Only NTA was used as a ligand for all films deposited on transparent conducting oxide coated soda lime glass substrates. CdS films deposited on quartz glass using only NTA peeled off, and became patchy. However, with the addition of hydrazine monohydrate, high quality CdS films were obtained on quartz glass.

© 2007 Elsevier B.V. All rights reserved.

**Keywords:** CdS; Thin films; Chemical bath deposition; Nitrilotriacetic acid

## 1. Introduction

Cadmium sulfide (CdS), 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 cadmium telluride (CdTe), p-type copper indium diselenide (CuInSe<sub>2</sub>), and/or Cu(In,Ga)Se<sub>2</sub> (CIGS). It has been widely used as a window material in high efficiency thin film solar cells based on CdTe or CIGS [1,2]. CdS has also been used in other applications including electronic and optoelectronic devices [3–5]. In the past few decades, several techniques such as thermal evaporation [6], radio frequency sputtering [7], physical vapor deposition [8], pulsed laser evaporation [9], molecular beam epitaxy [10], electrodeposition [11], spray pyrolysis [12], metal organic chemical vapor deposition [13], successive ionic layer adsorption reaction [14], screen printing [15], close spaced vapor transport [16], and chemical bath deposition (CBD) [17–28] have been used in the deposition of CdS thin films. However, CBD has the advantages of being a simple, low temperature, and inexpensive large-area deposition technique. In fact, compared to all other

techniques mentioned earlier, CBD is known to greatly enhance the performance of CdS windows used in the above mentioned solar cells. The highest efficiencies reported for both CdTe and CIGS solar cells were obtained when chemical bath deposition was used to grow the CdS window [29,30].

Chemical bath deposition is the analog in liquid phase of the well-known chemical vapor deposition technique in the vapor phase. In CBD, deposition of thin films takes place from aqueous solutions at low temperatures (near room temperature) by a chemical reaction between dissolved precursors, with the help of a complexing agent (or ligand). CBD has been used in the deposition of CdS thin films for over forty years [17]. Several ligands have been utilized in the deposition of CdS, such as NH<sub>3</sub> [17–20], triethanolamine [21], ethylenediamine [22], ethylenediaminetetraacetic acid [23], nitrilotriacetic acid (NTA) [24,25], cyano-complex [26], citrato-complex [27], and more recently tartaric acid [28].

However, the usage of NTA was reported only few times in the literature. Gorer and Hodes [25] reported the usage of NTA as a complexing agent in the deposition of CdS thin films using CBD, but with very few details. Němec et al. [24], on the other hand, studied the dependence of the film thickness on the deposition time, the deposition temperature, and the pH of the

\* Corresponding author. Tel.: +1 407 823 2333; fax: +1 407 823 5112.

E-mail address: [chow@ucf.edu](mailto:chow@ucf.edu) (L. Chow).

final solution. No attempt to study the effect of changing the [Cd]/[S], [NTA]/[Cd], [NTA]/[S] ratios on the CdS film thickness and optical properties, was reported. We believe that combined changes of the [Cd]/[S], [NTA]/[Cd], [NTA]/[S] ratios in the bath, the bath temperature, and the concentration of the KOH, which was used as the OH<sup>-</sup> source, will affect the film thickness and optical properties, and studying this will be very useful to optimize the whole deposition process of CdS using NTA.

In this work, two cadmium sources, namely, CdSO<sub>4</sub> and CdCl<sub>2</sub> were used in the deposition of CdS, while only thiourea was used as sulfur source. In each case, the film thickness, transmission, and optical band gap were studied as a function of the [NTA]/[Cd] ratio. The [NTA]/[Cd] ratio was then kept constant at the value corresponding to the maximum thickness, and the effect of the KOH concentration on the film thickness, transmission, and optical band gap was studied. This served as a starting point to a more comprehensive approach to optimize the deposition process as a whole by simultaneous changes of the bath temperature as well as the concentration of all reagents. Thickness and transmission measurements as well as optical band gap calculations were carried out for all films obtained. Films were deposited on soda lime glass with SnO<sub>2</sub> layer on one side. All measurements were carried out on films deposited on the SnO<sub>2</sub> layer side.

In addition, two sets of films were deposited on quartz, one set using CdSO<sub>4</sub> and the other using CdCl<sub>2</sub> as the Cd source. We found that using NTA alone as a complexing agent results in high quality films only when soda lime glass/SnO<sub>2</sub> substrates were used. However, in the case of quartz, when hydrazine was added to NTA, adherent, specularly reflecting, and high quality CdS films were obtained. In the absence of hydrazine, films deposited on quartz glass peeled off, and the films became patchy. In addition to the thickness and optical measurements, further measurements using Scanning Electron Microscopy (SEM), Rutherford Back Scattering (RBS), and X-Ray Diffraction (XRD) for both films deposited on quartz were carried out.

## 2. Experimental details

Each bath contained 100–120 ml of stirred de-ionized water (resistivity ~ 18 MΩ cm) at a desired fixed temperature. Substrates of 38 mm × 38 mm × 3 mm of SnO<sub>2</sub> coated soda lime glass (TEC 8 glass, supplied by Libbey Owens Ford, Pilkington Inc.) were used in this work, except for two sets of films that were deposited on quartz substrates of similar dimensions (supplied by Quartz Scientific Inc.). The cleaning steps of the substrate were reported elsewhere [19]. The same cleaning steps were followed in cleaning both types of substrates. With the help of Teflon holders, all substrates were held vertically in the solution. All substrates were placed in the bath prior to the addition of any of the reagents. Only one deposition for 30 min was carried out, except for the deposition on quartz where two successive depositions for 8 min each, were executed. Three different bath temperatures; 55 °C, 70 °C, and 85 °C were studied. Two different Cd sources, CdSO<sub>4</sub> and CdCl<sub>2</sub> were used as Cd precursors, with only thiourea as sulfur precursor. KOH (assay 45% w/w) was used as the OH<sup>-</sup> source,

and NTA was used as the complexing agent. Deposition time was recorded immediately after adding thiourea. Alpha-step 500 surface profilometer (Tencor) was used to determine the film thickness. Transmission spectra were measured using UV/VIS Cary (Varian) spectrophotometer. Only specular transmission was carried out in this work. The optical absorption coefficient  $\alpha$  was calculated for each film using the equation:

$$I_t = I_0 \exp(-\alpha t) \quad (1)$$

where  $t$  is the film thickness,  $I_t$  and  $I_0$  are the intensity of transmitted light and incident light, respectively.

The absorption coefficient  $\alpha$  is related to the incident photon energy  $h\nu$  as:

$$\alpha = \frac{K(h\nu - E_g)^{n/2}}{h\nu} \quad (2)$$

where  $K$  is a constant,  $E_g$  is the optical band gap, and  $n$  is equal to 1 for direct band gap material such as CdS.  $E_g$  was determined for each film by plotting  $(\alpha h\nu)^2$  versus  $h\nu$  and then extrapolating the straight line portion to the energy axis.

SEM micrographs were obtained using JEOL 6400F SEM at an acceleration voltage of 10 kV. RBS measurements were done using 2.25 MeV  $\alpha$ -particles IONIX 1.7 MV Tandemtron, with a surface barrier detector with energy resolution  $\leq 15$  keV (full width at half maximum—FWHM), positioned at a scattering angle of 165°. XRD Rigaku D (with 40 kV, 30 mA CuK $\alpha$  radiation,  $\lambda = 0.15406$  nm) was used for XRD measurements. The sample was mounted at 2.5° and scanned from 25°–70° in steps of 0.02° with a scan rate of 1.2° min<sup>-1</sup>.

## 3. Results and discussion

### 3.1. CdSO<sub>4</sub>-based CdS films

#### 3.1.1. Effect of changing [NTA]/[Cd] ratio

Fig. 1(a) shows the dependence of film thickness on [NTA]/[Cd] ratio, with [CdSO<sub>4</sub>]=0.2 mmol, [CS(NH<sub>2</sub>)<sub>2</sub>]=0.4 mmol, KOH=1.5 ml, bath temperature=70 °C, and 30 min deposition time. The film thickness increases with the [NTA]/[Cd] ratio until it reaches its maximum at a ratio of 4, and then decreases. We found that there's no deposition at all when [NTA]/[Cd] ratio reaches 7.

It's worth noting that, till now, it was typically believed that with NTA as a complexing agent, the CdS deposition mechanism is mainly based on the formation of Cd(NTA)<sup>-</sup> or Cd(NTA)<sub>2</sub><sup>-4</sup> complex in the solution [24,25]. However, according to our findings we believe that this is not always the case. As shown in Fig. 1(a), the film thickness increased by a factor of three or more when the [NTA]/[Cd] ratio increased from 2 to 3, and then increased by a factor of 4 or more when this ratio increased from 2 to 4. We believe this suggests that the main deposition mechanism is based on the presence of Cd(NTA)<sub>3</sub><sup>7-</sup> and/or Cd(NTA)<sub>4</sub><sup>10-</sup> complexes in the solution. It was noticed that when the [NTA]/[Cd] ratio was less than 3, homogeneous reaction dominated the deposition process within a few minutes which in turn lead to a quick depletion of the Cd ions in the solution, and very thin films were obtained. This indicates that for a ratio less than 3, the

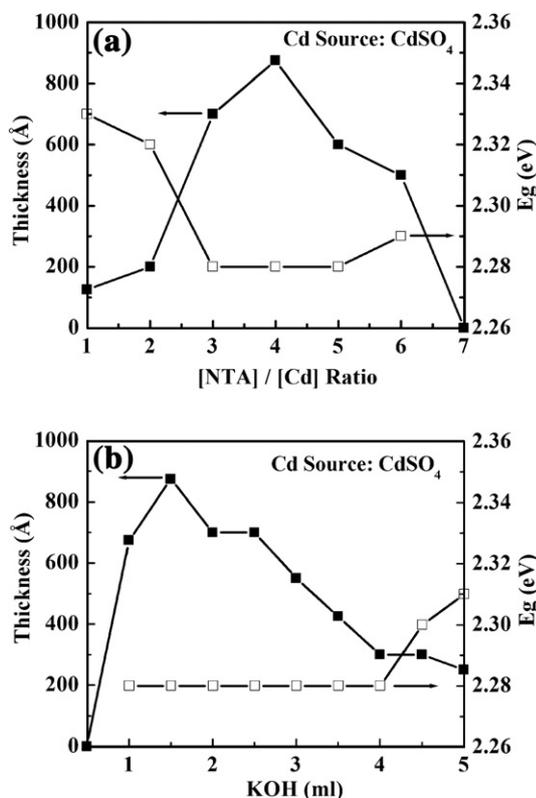


Fig. 1. Film thickness/ $E_g$  dependence on (a) [NTA]/[Cd] ratio, (b) KOH concentration. (Films were deposited on  $SnO_2$  coated soda lime glass).

stability constant of the Cd complex formed in the solution is too low to ensure the slow release of Cd ions in the main bath. This may explain why the undesirable homogeneous reaction dominated the deposition process.

It was also noticed that when this ratio goes beyond 4, the solution remains clear with no homogeneous reaction during most of the deposition time indicating a very limited release rate of Cd ions in the solution. Apparently, the stability constant of the  $Cd(NTA)_x^{y-}$  complex, where  $x$  is larger than 4, is too high. This means fewer Cd ions are available for CdS deposition. This was confirmed by allowing this ratio to increase till it reached 7, at which the solution remained colorless with no deposition at all during the whole 30 min of deposition time and no film was obtained. Obviously, the stability constant of the Cd complex formed when the [NTA]/[Cd] ratio is about 4 seems to have a moderate value so that the growth rate is maximum at this particular ratio, and as a result, this ratio is optimum. The stability constants  $K_1$  and  $K_2$  for  $Cd(NTA)^-$  and  $Cd(NTA)_2^{4-}$  complexes at 25 °C are given by [31]:

$$K_1 = \frac{[Cd(NTA)^-]}{[Cd^{2+}][NTA^{3-}]} = 10^{9.78} \text{ mole}^{-1} \text{ liter} \quad (3)$$

$$K_2 = \frac{[Cd(NTA)_2^{4-}]}{[Cd^{2+}][NTA^{3-}]^2} = 10^{14.39} \text{ mole}^{-2} \text{ liter}^2 \quad (4)$$

Stability constants for higher order  $Cd(NTA)_x^{y-}$  complexes, where  $x$  is larger than 2, are not available in the literature.

The transmission spectra for all these films are shown in Fig. 2(a). It's clear that there's a red shift, towards longer wavelengths, in the absorption edge once the [NTA]/[Cd] ratio exceeds 2. This is reflected by the optical band gap drop shown in Fig. 1(a). It's worth noting that at [NTA]/[Cd]=4.0, where the film thickness is maximum, the optical band gap is minimum. This may be attributed to lattice strain in films. The average grain size, in general, increases with increasing film thickness which in turn reduces the strain in the film (smaller the grain size more the stress in films). Rakhshani and Al-Azab [32] reported that such stress in CdS films causes a relative change in optical band gap  $\Delta E_g/E_g$  that is proportional to the extent of strain in film (the more stress the higher  $E_g$ ). They reported an inverse relationship between  $E_g$  and grain size. This actually agrees with our observation (Fig. 1a) where band gap is maximum when thickness is minimum ([NTA]/[Cd]=1.0) and minimum when thickness is maximum ([NTA]/[Cd]=4.0). However, no XRD measurements were carried out for these films to determine the grain size.

### 3.1.2. Effect of changing KOH concentrations

With  $[CdSO_4]=0.2$  mmol,  $[CS(NH_2)_2]=0.4$  mmol,  $[NTA]=0.8$  mmol ([NTA]/[Cd]=4.0), bath temperature=70 °C, and 30 min deposition time, CdS films were grown at different KOH concentrations (from 0.5 ml to 5.0 ml). As shown in Fig. 1(b), the film thickness increases dramatically from almost zero (no deposition observed) at 0.5 ml KOH to ~900 Å at 1.5 ml KOH,

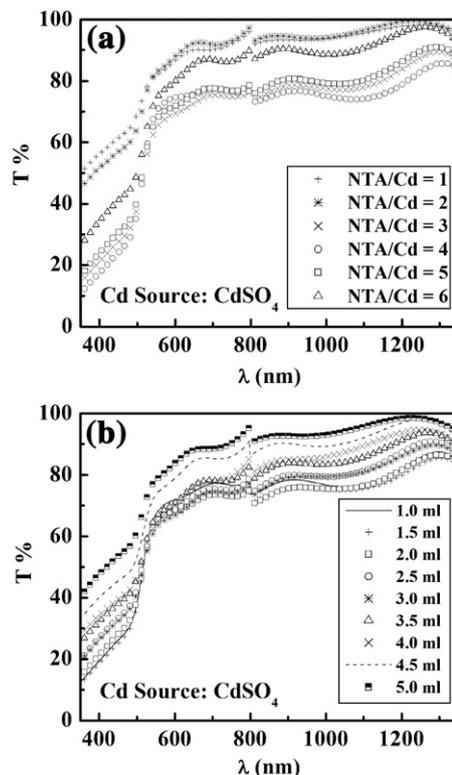


Fig. 2. Transmission spectra of films deposited at different (a) [NTA]/[Cd] ratios, (b) KOH concentration. (Films were deposited on  $SnO_2$  coated soda lime glass).

after which the film thickness decreases rapidly with KOH concentration. This, in fact, agrees with the observations of Němec et al. [24], where they studied the dependence of the film thickness on the pH of the final solution. The transmission spectra of the grown films, Fig. 2b, show blue shifted band edge once the KOH concentration exceeds 4.0 ml. This is reflected by the rise in  $E_g$ , as shown in Fig. 1(b).  $E_g$  remains relatively constant until the KOH concentration exceeds 4, and then it starts to increase with KOH concentration (smaller film thickness), which confirms the inverse relationship between  $E_g$  and film thickness observed in Fig. 1(a).

### 3.1.3. Optimization of $CdSO_4$ -based CdS films

After analyzing the data we acquired from these 17 different CdS films, we used a design of experiment to optimize CdS film growth. We used the conditions that gave the maximum film thickness as the center point and did a two-level, five-factor based experiment around this. Here, the five factors are the bath temperature, the Cd concentration, NTA concentration, sulfur concentration, and the KOH concentration. The two levels for each factor are the minimum and the maximum concentration or temperature about the centre value that gave maximum thickness in the previous set of experiments. Statistically the number of experiments possible that will combine these two-level factors is  $2^5$  or 32 experiments. Since some of the experiments may not provide additional information, fractional factorial design of experiment that resulted in 14 experiments was used. This enabled us to optimize the deposition process by allowing the bath temperature, the Cd concentration, NTA concentration, sulfur concentration, as well as the KOH concentration to vary simultaneously, in a carefully controlled fashion. Thickness and  $E_g$  of the grown films were used as the experimental response. The details of the experiment and results are summarized in Table 1. Out of 14 attempts, four attempts lead to films with higher thickness than the maximum thickness we obtained in the other 17 experiments. The thickness of the film labeled #19 was almost twice the maximum thickness obtained before. In other words, the growth rate almost doubled.

Table 1  
Thickness and  $E_g$  of optimized  $CdSO_4$ -based CdS films

Sample #	$CdSO_4$ (mmol)	Thiourea (mmol)	KOH (ml)	NTA (mmol)	Temperature (°C)	Thickness (Å)	$E_g$ (eV)
18	0.31	0.26	2	0.6	55	200	2.26
19	0.31	0.65	1	1.0	55	1550	2.32
20	0.12	0.65	2	1.0	55	1000	2.30
21	0.12	0.26	2	0.6	55	1000	2.30
22	0.12	0.26	1	0.6	55	250	2.32
23	0.31	0.65	1	0.6	55	200	2.30
24	0.31	0.26	1	1.0	55	500	2.29
25	0.12	0.65	2	0.6	85	225	2.23
26	0.31	0.26	2	1.0	85	1100	2.33
27	0.31	0.65	2	1.0	85	450	2.25
28	0.31	0.26	2	0.6	85	200	2.27
29	0.31	0.65	1	0.6	85	250	2.23
30	0.12	0.65	1	0.6	85	650	2.25
31	0.12	0.26	1	1.0	85	200	2.2

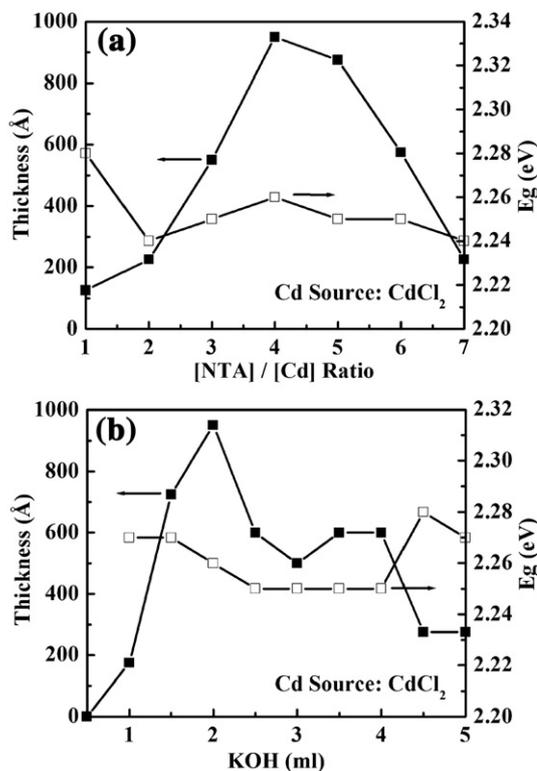


Fig. 3. Film thickness/ $E_g$  dependence on (a)  $[NTA]/[Cd]$  ratio, (b) KOH concentration. (Films were deposited on  $SnO_2$  coated soda lime glass).

## 3.2. $CdCl_2$ -based CdS films

### 3.2.1. Effect of changing $[NTA]/[Cd]$ ratio

Fig. 3(a) shows the dependence of film thickness on  $[NTA]/[Cd]$  ratio, with  $[CdCl_2]=0.2$  mmol,  $[CS(NH_2)_2]=0.4$  mmol,  $KOH=2.0$  ml, bath temperature =  $70^\circ C$ , and 30 min deposition time. It's worth noting that the film thickness becomes maximum (950 Å) at  $[NTA]/[Cd]$  ratio of 4, which is more than four times the film thickness (200 Å) at  $[NTA]/[Cd]$  ratio = 2. This proves that regardless of the Cd precursor used, the presence of  $Cd(NTA)_4^{10-}$  complex in the solution is essential for higher thickness and faster growth rate of CdS films. The transmission spectra of these seven films are shown in Fig. 4(a). Once the  $[NTA]/[Cd]$  ratio exceeds 1, a red shift in the absorption edge of the CdS films grown is observed. This reflects on  $E_g$  of these films as shown in Fig. 3(a).

### 3.2.2. Effect of changing KOH concentrations

With  $[CdCl_2]=0.2$  mmol,  $[CS(NH_2)_2]=0.4$  mmol,  $[NTA]=0.8$  mmol ( $[NTA]/[Cd]=4.0$ ), bath temperature =  $70^\circ C$ , and 30 min deposition time, CdS films were again grown at different KOH concentrations, from 0.5 ml to 5.0 ml. A behavior similar to that of  $CdSO_4$ -based films is observed (Fig. 3b), but with film thickness being maximum at  $KOH=2.0$  ml instead of 1.5 ml. No deposition was observed at  $KOH=0.5$  ml. Transmission spectra as well as  $E_g$  calculated for all 9 films are shown in Figs. 3(b) and 4(b), respectively.  $E_g$  was found to be minimal for KOH concentrations between 2.5 ml and 4.0 ml.

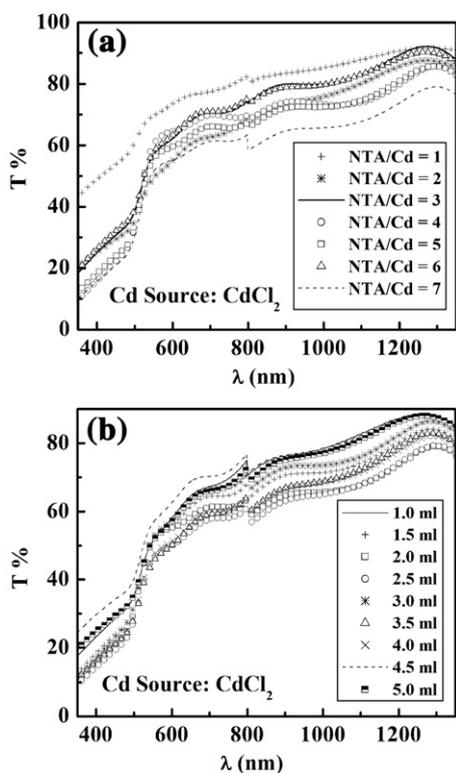


Fig. 4. Transmission spectra of films deposited at different (a) [NTA]/[Cd] ratios, (b) KOH concentration. (Films were deposited on SnO<sub>2</sub> coated soda lime glass).

### 3.2.3. Optimization of CdCl<sub>2</sub>-based CdS films

With the help of the results we obtained, a set of 14 more experiments were devised. Thickness and  $E_g$  of all 14 films are shown in Table 2. Out of 14 experiments, two experiments resulted in CdS films with a thickness higher than the maximum thickness obtained in the other 17 experiments. The thickness of the film labeled #54 was about 26% higher than the maximum thickness obtained in the other 17 experiments.

### 3.3. Deposition on quartz

Using only NTA as a ligand, we tried to deposit two sets of CdS films on quartz, one using CdSO<sub>4</sub> and the other using

Table 2  
Thickness and  $E_g$  of optimized CdCl<sub>2</sub>-based CdS films

Sample #	CdCl <sub>2</sub> (mmol)	Thiourea (mmol)	KOH (ml)	NTA (mmol)	Temperature (°C)	Thickness (Å)	$E_g$ (eV)
48	0.055	0.13	1.5	0.6	55	No film	–
49	0.055	0.65	1.5	0.6	55	225	2.25
50	0.33	0.13	1.5	0.6	55	350	2.26
51	0.33	0.13	1.5	1.0	55	175	2.23
52	0.055	0.65	2.5	0.6	55	275	2.22
53	0.055	0.13	2.5	1.0	55	No Film	–
54	0.33	0.65	2.5	1.0	55	1200	2.32
55	0.055	0.13	1.5	1.0	85	No Film	–
56	0.055	0.65	1.5	1.0	85	275	2.27
57	0.33	0.65	1.5	0.6	85	250	2.25
58	0.33	0.65	1.5	1.0	85	1000	2.28
59	0.055	0.65	2.5	0.6	85	175	2.24
60	0.055	0.13	2.5	1.0	85	200	2.19
61	0.33	0.13	2.5	0.6	85	200	2.24

CdCl<sub>2</sub>. Unfortunately, in contrast to what was reported earlier by Gorer and Hodes [25] and Němec et al. [24], all films obtained on quartz glass were patchy due to peeling during deposition. We believe that this may be due to the stress the CdS film suffers on glass. In the earlier part of this work, it was observed that when soda lime glass substrates were used, CdS deposition takes place on top of the SnO<sub>2</sub> side only with little or no deposition occurs on the glass side of the substrate. We believe that the SnO<sub>2</sub> layer acts as nucleation sites for the Cd<sup>2+</sup> and S<sup>2-</sup> ions resulting in formation of Cd film only on the SnO<sub>2</sub> side of the substrate.

However, when hydrazine monohydrate was added, adherent, specularly reflecting, high quality CdS films were obtained. Two successive depositions, for 8 min each, were carried out on 38 mm × 38 mm × 3 mm quartz substrates at 70 °C for both films. In the case of CdSO<sub>4</sub>-based film, we had [CdSO<sub>4</sub>]=0.2 mmol, [CS(NH<sub>2</sub>)<sub>2</sub>]=0.4 mmol, [NTA]=0.4 mmol, ([NTA]/[Cd]=2.0), KOH=0.5 ml, and 2.0 ml of hydrazine monohydrate (assay 100%). Similarly, in the case of CdCl<sub>2</sub>-based CdS film, the same conditions were used except for the Cd source, where 0.2 mmol of CdCl<sub>2</sub> was used instead of 0.2 mmol CdSO<sub>4</sub>.

High quality films were obtained with thickness of 0.10 μm in the case of CdSO<sub>4</sub>-based film, and 0.12 μm in the case of CdCl<sub>2</sub>-based film. This shows that the growth rate is high, bearing in mind that only two depositions were done, each for 8 minutes only. Apparently, in addition to reducing the film stress on glass, we believe that using hydrazine monohydrate

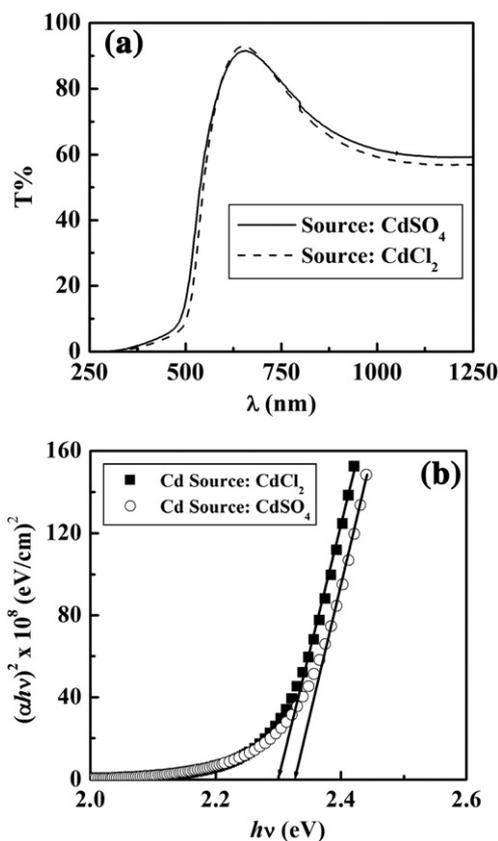


Fig. 5. Transmission spectra (a) and  $E_g$  (b) of CdS films deposited on quartz using two different Cd sources.

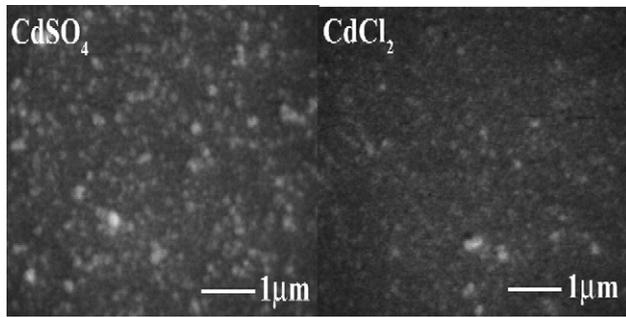


Fig. 6. SEM micrographs of CdS films deposited on quartz using two different Cd sources.

with NTA also reduced the stability constant of the Cd complex formed in the solution achieving the hydroxide line where Cd(OH)<sub>2</sub> was adsorbed on the glass substrate and then CdS was formed by adsorption of thiourea on the Cd(OH)<sub>2</sub> followed by decomposition of Cd(OH)<sub>2</sub>-thiourea complex to CdS [17]. This in turn may have increased the release rate of Cd ions in the solution, and yielded a higher growth rate.

Transmission spectra for both films are shown in Fig. 5(a). The CdCl<sub>2</sub>-based film shows similar transmission to the CdSO<sub>4</sub>-based films, although it has a 20% higher thickness than that of the CdSO<sub>4</sub> one. This can be explained by considering the SEM micrographs (Fig. 6) for both films showing the CdCl<sub>2</sub>-based film to have a much smoother surface than the CdSO<sub>4</sub>-based film. Typically, the less rough the surface, the less the light will be scattered, and the higher the transmission will be for photons with energy lower than the band gap. This in fact may explain why the CdCl<sub>2</sub>-based film, although thicker, shows similar transmission to the CdSO<sub>4</sub>-based films.  $E_g$  of both films was calculated and shown in Fig. 5 (b). CdSO<sub>4</sub>-based film has a relatively higher  $E_g$  (2.32 eV) than that of CdCl<sub>2</sub>-based film (2.30 eV).

XRD patterns of both films are shown in Fig. 7. Both films are cubic with a strong (111) reflection at  $2\theta=26.5^\circ$ , and two

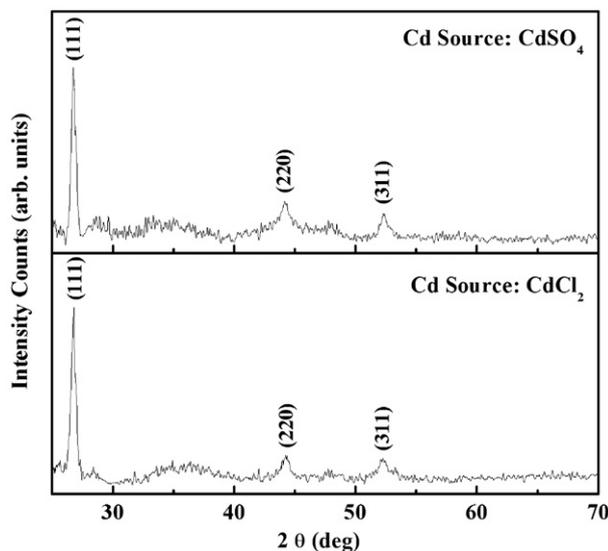


Fig. 7. XRD patterns of CdS films deposited on quartz using two different Cd sources.

weaker (220) and (311) peaks that confirmed the cubic phase of both films. The average crystallite size was calculated using the Debye–Scherrer formula. The grain size was about 176 nm in the case of the CdSO<sub>4</sub>-based film, and about 172 nm in the case of the CdCl<sub>2</sub>-based film. Since the growth rate was relatively high, we believe that this may indicate that the deposition process was dominated by cluster-by-cluster deposition and not by ion-by-ion deposition [18,25]. This may explain why such large grain size was obtained in both films, compared to crystallite size of few nanometers obtained by Němec et al. [24].

RBS spectra of both films are shown in Fig. 8. It seems that in both cases, there's more cadmium in the film than sulfur. The ratio of sulfur to cadmium was found to be higher in the CdCl<sub>2</sub>-based film (S: Cd = 1: 1.08 ± 0.01) than in the CdSO<sub>4</sub>-based film (S: Cd = 1.00: 1.05 ± 0.01). These ratios agree with the reduction in the stability constant of the Cd complex due to the presence of hydrazine as we explained earlier. In other words, the lower the stability constant of the Cd complex, the more Cd<sup>2+</sup> ions in

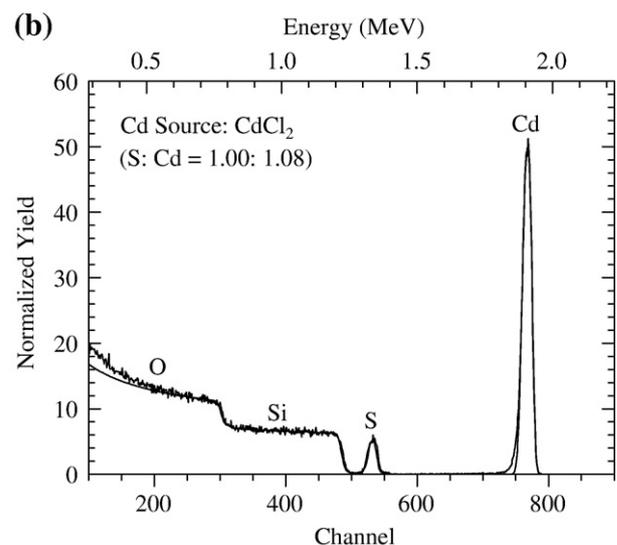
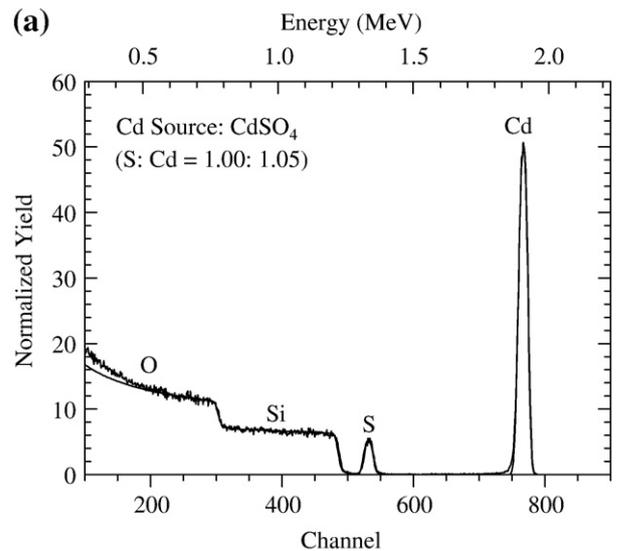


Fig. 8. RBS spectrum of CdS films deposited on quartz using two different Cd sources.

Table 3

A summary of properties of CdSO<sub>4</sub>-based and CdCl<sub>2</sub>-based CdS films deposited on quartz

Film type	CdSO <sub>4</sub> -based CdS film	CdCl <sub>2</sub> -based CdS films
Thickness	0.10 μm	0.12 μm
Optical band gap	2.32 eV	2.30 eV
Crystal structure	Cubic	Cubic
Grain size	176 nm	172 nm
S: Cd ratio	1.00:1.05	1.00:1.08

the growth solution end up as excess Cd in the CdS film. Table 3 summarizes some of the differences observed between both CdS films grown on quartz.

#### 4. Conclusion

High quality CdS thin films were deposited onto SnO<sub>2</sub> coated soda lime glass using only NTA as a complexing agent. The growth rate is highly dependent on the [NTA]/[Cd] ratio in the solution, achieving a maximum value at a ratio of 4, regardless of the Cd source used. This suggests that the existence of Cd(NTA)<sub>4</sub><sup>10-</sup> complex in the solution is necessary to maximize the deposition rate. A design of experiment approach to optimize the deposition process was tested and proved to be effective. Deposition of CdS films on quartz using NTA alone led to porous, non-adherent films. With the addition of hydrazine monohydrate, high quality CdS films were obtained. Both films were found to be highly transparent, with  $E_g$  of 2.32 eV and 2.30 eV for CdSO<sub>4</sub>-based, and CdCl<sub>2</sub>-based CdS films respectively. XRD showed that both films are cubic with grain size of about 176 nm for CdSO<sub>4</sub>-based, and 172 nm CdCl<sub>2</sub>-based films. RBS showed that both films have higher content of cadmium than sulfur, with higher cadmium to sulfur ratio in the case of CdCl<sub>2</sub>-based film. Finally, SEM surface morphologies of both films showed that the CdCl<sub>2</sub>-based film has a much smoother surface than the CdSO<sub>4</sub>-based film resulting in higher transmission.

#### Acknowledgements

We thank K. Scammon and M. Klimov of the Advanced Materials Processing and Analysis Center (AMPAC), University of Central Florida, for their help with the XRD, RBS, and film thickness measurements. This work was partially supported by Apollo Technologies, Inc. and Florida High Tech. Corridor Council.

#### References

- [1] I. Oladeji, L. Chow, C. Ferekides, V. Viswanathan, Z. Zhao, Sol. Energy Mater. Sol. Cells 61 (2000) 203.

- [2] M. Contreras, M. Romero, B. To, F. Hasoon, R. Noufi, S. Ward, K. Ramanathan, Thin Solid Films 403/404 (2002) 204.
- [3] A. Davis, K. Vaccaro, H. Dauplaise, W. Waters, J. Lorenzo, J. Electrochem. Soc. 146 (1999) 1046.
- [4] O. Vigil-Galan, J. Larramendi, I. Riech, G. Rodriguez, A. Iribarren, J. Aguilar-Hernandez, G. Contreras-Puente, Semicond. Sci. Technol. 17 (2002) 1193.
- [5] O. Vigil-Galan, J. Ximello-Quiebras, J. Aguilar-Hernandez, G. Contreras-Puente, A. Cruz-Orea, J. Mendoza-Alvarez, J. Cardona-Bedoya, C. Ruiz, V. Bermudez, Semicond. Sci. Technol. 21 (2006) 76.
- [6] R. Buckley, J. Woods, J. Phys., D, Appl. Phys. 6 (1973) 1084.
- [7] C. Tsai, D. Chuu, G. Chen, S. Yang, J. Appl. Phys. 79 (1996) 9105.
- [8] R. Birkmire, B. McCandless, S. Hegedus, Int. J. Sol. Energy, 12 (1992) 145.
- [9] C. Dai, L. Horng, W. Hsieh, Y. Shih, C. Tsai, D. Chuu, J. Vac. Sci. Technol. A. 10 (1992) 484.
- [10] P. Boieriu, R. Sporcken, Y. Xin, N. Browning, S. Sivananthan, J. Electron. Mater. 29 (2000) 718.
- [11] M. Ilieva, D. Dimova-Malinovska, B. Rangelov, I. Markov, J. Phys., Condens. Matter 11 (1999) 10025.
- [12] Y. Ma, A. Fahrenbruch, R. Bube, Appl. Phys. Lett. 30 (1977) 423.
- [13] H. Uda, H. Yonezawa, Y. Ohtsubo, M. Kosaka, H. Sonomura, Sol. Energy Mater. Sol. Cells 75 (2003) 219.
- [14] M. Sasagawa, Y. Nosaka, Electrochim. Acta 48 (2003) 483.
- [15] S. Al Kuhaimi, Vacuum 51 (1998) 349.
- [16] J. Aguilar-Hernandez, G. Contreras-Puente, A. Morales-Acevedo, O. Vigil-Galan, F. Cruz-Gandarilla, J. Vidal-Larramendi, A. Escamilla-Esquivel, H. Hernandez-Contreras, M. Hesiquio-Garduno, A. Arias-Carbajal, M. Chavarria-Castaneda, G. Arriaga-Mejia, Semicond. Sci. Technol. 18 (2003) 111.
- [17] G. Kitaev, A. Urtskaya, S. Mokrushin, Russ. J. Phys. Chem. 39 (1965) 1101.
- [18] I. Kaur, D. Pandya, K. Chopra, J. Electrochem. Soc. 127 (1980) 943.
- [19] I. Oladeji, L. Chow, J. Electrochem. Soc. 144 (1997) 2342.
- [20] C. Voss, Y. Chang, S. Subramanian, S. Ryu, T. Lee, C. Chang, J. Electrochem. Soc. 151 (2004) C655.
- [21] P. Nair, J. Campos, M. Nair, Semicond. Sci. Technol. 3 (1988) 134.
- [22] P. O'Brien, T. Saeed, J. Cryst. Growth 158 (1996) 497.
- [23] H. Zhang, X. Ma, D. Yang, Mater. Lett. 58 (2003) 5.
- [24] P. Němec, I. Němec, P. Nahálková, Y. Němcová, F. Trojáněk, P. Malý, Thin Solid Films 403/404 (2002) 9.
- [25] S. Gorer, G. Hodes, J. Phys. Chem. 98 (1994) 5338.
- [26] R. Call, N. Jaber, K. Seshan, J. Whyte, Sol. Energy Mater. 2 (1980) 373.
- [27] M. Nair, P. Nair, R. Zingaro, E. Meyers, J. Appl. Phys. 75 (1994) 1557.
- [28] P. Roy, S. Srivastava, Mater. Chem. Phys. 95 (2006) 235.
- [29] M. Contreras, B. Egaas, K. Ramanathan, J. Hiltner, A. Swartzlander, F. Hasoon, R. Noufi, Prog. Photovolt: Res. Appl. 7 (1999) 311.
- [30] X. Wu, J. Keane, R. Dhere, D. Dehart, D. Albin, A. Duda, T. Gessert, S. Asher, D. Levi, P. Sheldon, Proceedings of the 17th European Photovoltaic Solar Energy Conference, Munich, Germany, October 22-26 2001, p. 995.
- [31] A.E. Martell, R.M. Smith, Critical Stability Constants, vol. 1, Plenum Press, New York, 1974, p. 142.
- [32] A. Rakhshani, A. Al-Azab, J. Phys., Condens. Matter 12 (2000) 8745.