Characterization of CdS thin films grown by chemical bath deposition using four different cadmium sources

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Abstract

A comprehensive study of the effect of cadmium sources on chemical bath deposited cadmium sulfide thin films is reported. Four different cadmium sources; cadmium sulfate, cadmium chloride, cadmium iodide, and cadmium acetate have been used. The effect of cadmium sources on film optical/electrical properties as well as film thickness, composition, crystal structure, and surface morphology was studied. Film growth rate and band gap were found to be sensitive to the Cd source used. Films were found to be highly stoichiometric when cadmium chloride and cadmium iodide were used. The lowest resistivity and highest mobility and band gap obtained were in the case of cadmium sulfate. All films were found to be cubic, regardless of the Cd salt used.
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1. Introduction

Chemical bath deposition (CBD) is known to be a simple, low temperature, and inexpensive large-area deposition technique. It has been used in the deposition of CdS semiconductor thin films since the 1960s [1,2]. CdS has been used as a window material in high efficiency thin film solar cells based on CdTe and Cu(In,Ga)Se$_2$ (CIGS) [3,4]. It has also been used in other applications including electronic and optoelectronic devices [5]. Although other techniques have been used in the deposition of CdS, chemical bath deposition is known to enhance the performance of cadmium sulfide window used in solar cell applications [6,7].

Deposition of CdS using CBD is based on the slow release of Cd^{2+} ions and S^{2-} ions in an aqueous alkaline bath and the subsequent condensation of these ions on substrates suitably mounted in the bath. The slow release of Cd^{2+} ions is achieved by adding a complexing agent (ligand) to the Cd salt to form some cadmium complex species which, upon dissociation, results in the release of small concentrations of Cd^{2+} ions. The S^{2-} ions are supplied by the decomposition of thiourea or sodium thiosulfate. Over the years, different cadmium sources have been used in this process, such as cadmium sulfate [8,9], cadmium acetate [10–14], cadmium iodide/nitrate [15–18], and cadmium chloride [11,18]. The effect of Cd source on the film properties has drawn attention for some time. Kitaev et al. [16] found that when CdCl$_2$ was used as a Cd source, the CdS film thickness was higher than when Cd(CH$_3$COO)$_2$, CdSO$_4$, or Cd (NO$_3$)$_2$ were used. They also reported the least thickness when CdI$_2$ was used. Similar results were obtained when Ortega-Borges and Lincot [17] studied the CdS growth rate dependence on the Cd salt. The latter, ranked the Cd salts based on the least film thickness, obtained from the lowest to the highest, in the following order: CdI$_2$, CdSO$_4$, Cd(NO$_3$)$_2$, Cd(CH$_3$COO)$_2$, CdCl$_2$. Other than film thickness, however, very few details were mentioned in both studies about the effect of Cd source on other film properties.

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Table 1
A summary of optical/electrical properties and crystallinity of CdS films reported in the literature and the corresponding Cd source used

	Cd source	Other reagents used in solution	pH	$T_{deposition}$ (°C)	Crystal structure	E_g (eV)	ρ_{dark} (Ω-cm)	Reference
1.	$CdCl_2$	$NH_4OH/NH_4Cl/TU$ [b]	11	80	Hexagonal	2.45	10^{6-7}	[11]
	$CdAc_2$ [a]				Amorphous	2.50	10^{6-7}	
2.	$CdCl_2$	$NH_4OH/NH_4Cl/TU$	11.5	>40	Cubic	2.45	10^{6-8}	[18]
	CdI_2	$NH_4OH/NH_4I/TU$		>60	Hexagonal	2.62	10^{8-10}	
3.	$CdSO_4$	NH_4OH/TU	–	60–85	Hexagonal	2.45	10^7	[8]
4.	$CdSO_4$	$NH_4OH/N_2H_4/TU$	–	60	Mixed	2.38–2.45	10^{10}	[9]
5.	$CdSO_4$	NH_4OH/TU	11–12	70	–	2.47	10^8	[19]
6.	$CdAc_2$	$NH_4OH/NH_4Ac/TU$	–	85	–	2.39	10^{3-4}	[10]
7.	$CdAc_2$	$NH_4OH/NH_4Ac/TU$	9	50–90	Mixed	2.35	10^{4-6}	[20]
8.	$CdAc_2$	$TEA+NH_4OH/TU$	–	30–85	–	–	10^9	[21]
9.	$CdAc_2$	$Na_3C_6H_5O_7/NH_4OH/TU$	–	50–90	–	2.58	10^8	[22]
10.	$Cd(NO_3)_2$	$NH_4NO_3/NaOH/TU$	7.8–13.5	20	Cubic	–	$>10^{12}$	[15]

[a] Ac = Acetate; $(CH_3COO)^-$.
[b] TU = Thiourea; $SC(NH_2)_2$.

A summary of optical/electrical properties and crystallinity of CBD-CdS films reported in the literature is shown in Table 1. As Table 1 indicates, two attempts [11,18] to study the effect of Cd sources on CdS thin film properties were reported, with two different Cd sources being used in each case. The objective of this work is to provide a comprehensive study on the effect of Cd sources on the physical properties of CBD-CdS thin films.

2. Experimental details

Each bath contained 100–120 ml of de-ionized water (resistivity ∼18 MΩ-cm) kept under stirring at 70 °C. Quartz substrates of 3.8 cm × 3.8 cm were used in the entire work. The cleaning steps of the substrate and the growth procedures are reported elsewhere [10]. With the help of Teflon holders, all substrates were kept vertically in the solutions. All substrates were held in the bath prior to the addition of any of the reagents. Single dip depositions (for 15 minutes) as well as multi-dip depositions (four successive depositions for 8–12 min each) were carried out. Single dip depositions were used solely to study the film thickness/growth rate dependence on Cd source. Multi-dip depositions were used to obtain thicker films for further characterizations.

Cadmium sulfate, acetate, iodide, and chloride (0.2 mmol each) were used as Cd precursors, while thiourea (0.4 mmol) was used as sulfur precursor. Ammonia was used as a complexing agent, similar to the work of Kitaev et al. [16]. To ensure a stable complex, we employed ammonium salt as NH_3 buffer. So, when $CdSO_4$ was used as Cd source, $(NH_4)_2SO_4$ was used as a buffer and when $CdCl_2$ was used as Cd source, NH_4Cl was used as a buffer and so forth. The anions from the cadmium and

ammonium salts are believed to play a role in the growth of CdS films. This role is suspected to be that of a complementary complexing agent. So, in addition to $Cd(NH_3)_4^{2+}$ complex in the solution, we have Cd–anion complex. The stability constants of these complementary Cd complexes as well as that of the $Cd(NH_3)_4^{2+}$ complex [23] are summarized in Table 2.

Each reagent was dissolved in 10–15 ml of de-ionized water before being added to the main solution. After the addition of all reagents, the final solution was ∼150 ml. The bath temperature was kept constant during the entire deposition process. Alpha-step 500 surface profilometer (Tencor) was used to determine the film thickness. 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. Specular reflectance measurements have been carried out at an angle of incidence of 7° in the wavelength range from 1200 to 350 nm.

The optical absorption coefficient α was calculated for each film using the equation:

$$I_t = I_o \exp(-\alpha t) \tag{1}$$

where t is the film thickness, I_t and I_o are the intensity of transmitted light and initial light, respectively.

The absorption coefficient α is related to the incident photon energy hν as:

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

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. The band gap E_g

Table 2
Stability constants of some Cd complexes [23]

$Cd[L]_n$	Stability constant (log scale)
$Cd[NH_3]_4^{2+}$	7
$Cd[SO_4]_3^{4-}$	<2
$Cd[CH_3COO]_2$	2.19
$Cd[Cl]_4^{2-}$	2.93
$Cd[I]_4^{2-}$	6.4

Table 3
Film thickness dependence on Cd source (single dip deposition, for 15 min, was carried out for each film)

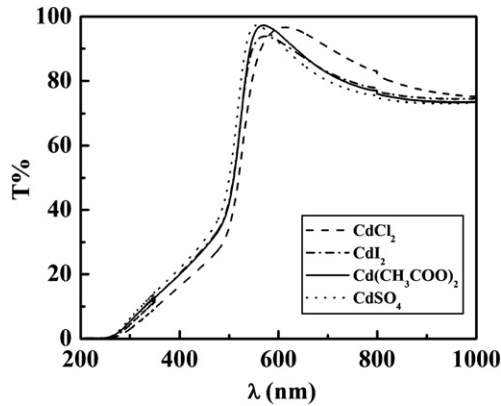| Cd source	Thickness (nm)
$CdSO_4$	95
$Cd(CH_3COO)_2$	90
$CdCl_2$	82.5
CdI_2	65

Fig. 1. Specular transmission spectra of CdS films grown using four different Cd sources; CdSO$_4$ (0.18 µm), Cd(CH$_3$COO)$_2$ (0.19 µm), CdCl$_2$ (0.20 µm), and CdI$_2$ (0.185 µm).

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.

Scanning Electron Microscopy (SEM) micrographs were obtained using JEOL 6400F SEM at an acceleration voltage of 10 kV. Rutherford Back Scattering (RBS) measurements were done using 2.25 MeV α-particles IONIX 1.7 MU Tandetron, with a surface barrier detector which has an energy resolution ≤ 15 keV (full width at half maximum—FWHM), positioned at a scattering angle of 165°. X-Ray Diffraction (XRD) was carrier

out using Rigaku D XRD unit (with 40 kV, 30 mA CuKα radiation, $\lambda=0.15406$ nm). 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^{-1}. Resistivity, mobility, and carrier concentration were evaluated by Hall effect measurements at room temperature in a Van der Pauw four-point probe configuration, using indium contacts, in an automated Hall effect unit (Quantum Technology Corp., Blaine WA, USA) with a magnetic induction of 0.75 T.

3. Results and discussion

3.1. Thickness dependence on Cd source

Table 3 shows the film thickness dependence on the Cd source used in the deposition process. The highest thickness obtained was in the case of CdSO$_4$, and the least thickness obtained was in the CdI$_2$ case. Apparently, among all other Cd salts, CdI$_2$ always results in a much thinner film. This observation was in agreement with what was reported by Kitaev et al. [16], and Ortega-Borges and Lincot [17]. However, in our work, CdSO$_4$, not CdCl$_2$, results in the highest film thickness.

This can be understood by considering the role played by the complementary Cd complexes in the deposition process. Table 2 shows that the Cd[I]$_4^{2-}$ complex has a much higher stability constant than Cd[Cl]$_4^{2-}$, Cd[CH$_3$COO]$_2$, or Cd[SO$_4$]$_3^{4-}$ complexes. This means much slower release of Cd ions and
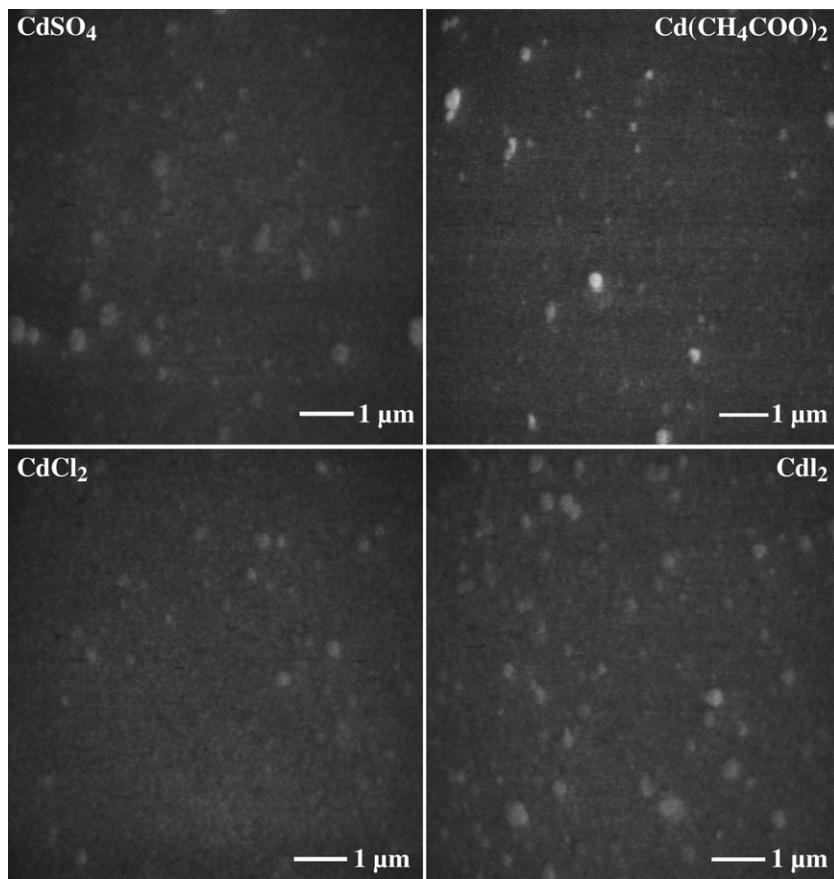

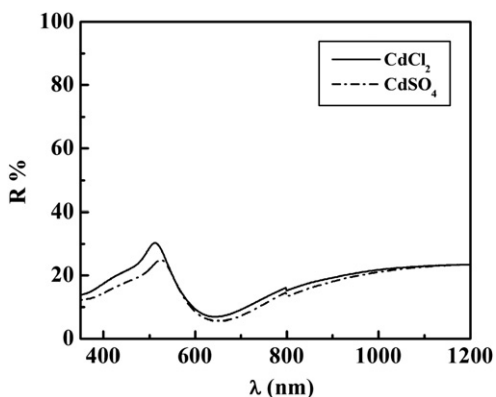Fig. 2. SEM micrograph of CdS films grown using four different Cd sources.

Fig. 3. Specular reflectance of CdCl$_2$-based film (0.20 μm) and CdSO$_4$-based film (0.18 μm).

Fig. 4. Optical band gap calculations of CdS films grown using four different Cd sources.

consequently a much thinner CdS film when CdI$_2$ was used. The same argument can be used to explain why the highest thickness was obtained when CdSO$_4$ was used. Actually, the order in which the stability constant decreased was exactly the same order the film thickness increased. In the Kitaev et al. [16] case, the Cl$^-$ concentration was too low to make the Cd[Cl]$_4^{2-}$ stable. Whereas in our case, the Cd[Cl]$_4^{2-}$ complex has a higher stability constant than the Cd[CH$_3$COO]$_2$, or the Cd[SO$_4$]$_3^{4-}$ complexes which caused the film thickness to be less than that of the Cd(CH$_3$COO)$_2$ or the CdSO$_4$-based CdS film. It should be noted that, comparing these stability constants to that of the Cd(NH$_3$)$_4^{2+}$ complex (Table 2), the role of the complementary Cd complexes in the growth process is very important.

3.2. Optical properties

Fig. 1 shows optical transmission spectra of all four films. All films have high transmission, with the transmission in the CdCl$_2$ case being better than that of the other three films. This was actually expected, since the SEM micrographs shown in Fig. 2, showed the CdCl$_2$-based film to be much smoother and more uniform than the other three films. The surface roughness, due to coverage by crystallite overgrowth, causes light scattering, which in turn lowers the transmission. As indicated in the captions of Fig. 1, there's no appreciable difference in film thickness for all four films. Fig. 3 shows specular reflectance for the two films with highest and lowest transmissions. Reflectance of CdCl$_2$-based film is higher than that of CdSO$_4$-based film. So, although no diffuse transmission/ reflectance measurements were carried out, we believe that the SEM micrographs as well as the reflectance measurements are sufficient to conclude that surface morphology is responsible for the higher transmission observed in the CdCl$_2$ case.

Another observation about these transmission spectra is that CdI$_2$ and Cd(CH$_3$COO)$_2$-based films share the same absorption edge. A red shift (towards longer wavelengths) in the CdCl$_2$-based film case and a blue shift in the case of the CdSO4-based film were observed. This reflected on their corresponding optical band gap, as shown in Fig. 4. The optical band gap of the CdSO$_4$-based film is the highest (2.36 eV) while the band gap of the CdCl$_2$-based film is the lowest (2.25 eV). The CdI$_2$ and Cd
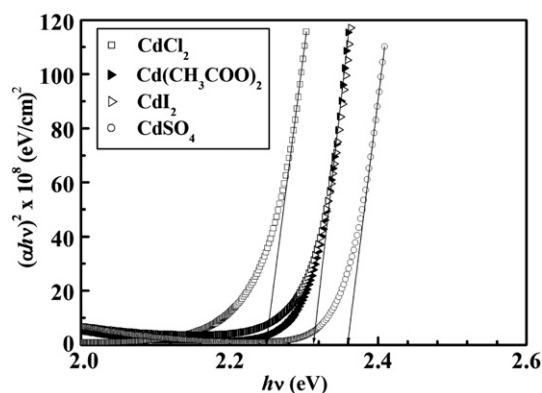
(CH$_3$COO)$_2$-based films have an intermediate band gap (2.31 eV). This band gap dependence on Cd source agrees with what Rami et al. [11] and Nakanishi and Ito [18] reported earlier.

3.3. Crystal structure

XRD patterns of the four films are shown in Fig. 5. Regardless of the Cd salt used, all films were cubic with a main (111) reflection and two weaker (220) and (311) peaks that confirmed the cubic nature of all films. A fourth peak was detected in the CdCl$_2$-based film case, which was found to be the (200) peak, which is also a characteristic peak of cubic CdS. A summary of XRD data for standard cubic CdS powder [24] and all four films is shown in Table 4. The observed relative intensities imply that all films are polycrystalline with preferred (111) orientation. However, when the relative intensities are carefully investigated, it's obvious that the degree of texture along the (111) orientation increases in the order: CdCl$_2$, CdI$_2$/ Cd(CH$_3$COO)$_2$, CdSO$_4$. As shown in Table 5, the relative
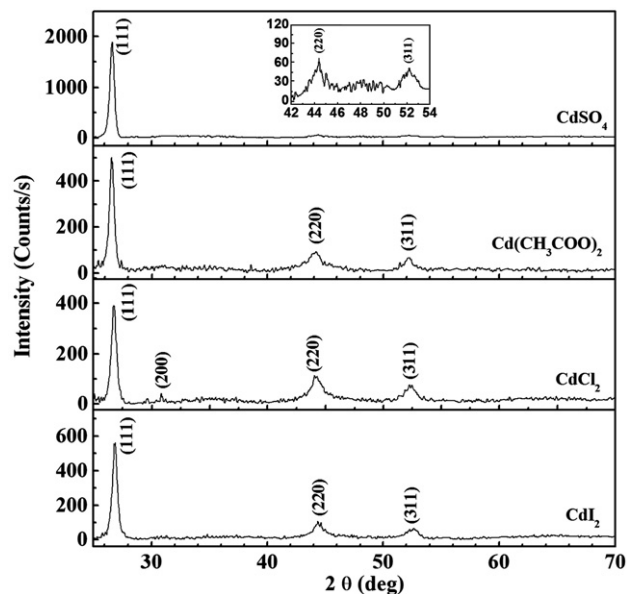

Fig. 5. XRD pattern of CdS films grown using four different Cd sources.

Table 4
A summary of XRD data for standard cubic CdS powder [24] and CdS films grown using four different Cd sources

Sample	2θ (deg.)	d (nm)	(hkl)	I/I_o (%)
Cubic (powder)	26.547	0.33550	(111)	100.0
	30.748	0.29055	(200)	21.6
	44.040	0.20545	(220)	46.7
	52.163	0.17521	(311)	33.2
	54.670	0.16775	(222)	4.5
	64.042	0.14528	(400)	5.8
$CdSO_4$-based film	26.640	0.33434	(111)	100.0
	44.435	0.20372	(220)	2.9
	52.280	0.17484	(311)	2.7
$Cd(CH_3COO)_2$-based film	26.580	0.33509	(111)	100.0
	44.180	0.20483	(220)	18.4
	52.240	0.17497	(311)	13.5
$CdCl_2$-based film	26.800	0.33239	(111)	100.0
	30.837	0.28973	(200)	9.3
	44.079	0.20528	(220)	28.9
	52.480	0.17422	(311)	19.4
CdI_2-based film	26.939	0.33070	(111)	100.0
	44.323	0.20421	(220)	16.4
	52.640	0.17373	(311)	11.8

intensities of both (220) and (311) peaks are closest to that of powder CdS when $CdCl_2$ is being used as Cd source. Both peaks are more suppressed when $Cd(CH_3COO)_2$ and CdI_2 are being used, and almost totally suppressed when $CdSO_4$ is being used where their relative intensities decrease to less than 3%. This may explain the optical band gap variation with Cd source. As shown in Table 5, as the (111) peak becomes more predominant and the other peaks get more suppressed, the band gap increases. That's why $CdCl_2$-based film has the least band gap (2.25 eV) and $CdSO_4$-based film has the highest band gap (2.36 eV) which is the closest, amongst all four films, to the band gap of single crystal CdS (2.42 eV) [25]. The other two films are expected to have the same band gap since relative intensities of both (220) and (311) peaks in $Cd(CH_3COO)_2$-based film are very close to those of CdI_2-based film. The intermediate values of these relative intensities may also explain their intermediate band gap. Such band gap dependence on film crystallinity has been observed for $CuInSe_2$ as well as $CuGaSe_2$ polycrystalline thin films; Chichibu et al. [26] found that $CuInSe_2$ films with a predominant (112) orientation and very

weak intensities from other diffraction peaks have a higher band gap than films with comparative intensities of (112) and (220) or (204) diffraction peaks. They attributed this band gap decrease to lattice defects in the latter films that may give rise to plasma screening of Coulomb interactions due to degradation of film quality. They reported similar band gap dependence on film crystallinity for $CuGaSe_2$ films.

The average crystallite size shown in Table 6 was calculated using the Debye–Scherrer formula [27]. The noticeable difference in grain size between the $CdSO_4$ film and the other films may be attributed to the fact that there are two different deposition processes in CBD that compete with each other [14]; cluster by cluster deposition and ion by ion deposition. Now, since using $CdSO_4$ resulted in a much faster growth rate than the other three films, this may indicate that the cluster by cluster deposition dominated the deposition process and consequently resulted in a much larger grain size. However, in the case of the other three films, ion by ion deposition dominated the deposition process and as a result a much smaller grain size and thinner films were obtained.

3.4. Stoichiometry

Using RBS measurements, the stoichiometry of all films were studied. Simulation using Rutherford Universal Manipulation Program (RUMP) [28] was implemented to find the best possible match to the RBS spectra. As shown in Fig. 6, the S:Cd ratio was found to be (1.00:1.00) in the case of CdI_2-based film as well as $CdCl_2$-based film. However, more cadmium was detected in the other two films. We found the S:Cd ratio to decrease to (1.00:1.06) when $Cd(CH_3COO)_2$ was used. This ratio decreased further to (1.00:1.09) when $CdSO_4$ was used. This is summarized in Table 7. These ratios appear to agree with the Cd-complex stability constants summarized in Table 2. Apparently, the smaller the stability constant of the complementary complex the more the Cd^{2+} ions in the growth solution that end up as excess Cd in the CdS film; whereas, when the stability constant is high the release of Cd^{2+} and S^{2-} is well controlled leading to a highly stoichiometric CdS film.

3.5. Hall effect measurements

Table 7 shows the Hall effect measurements conducted for the four films. They are in agreement with the RBS measurements. The carrier concentration decreases (and accordingly the resistivity increases) in the order $CdSO_4$, $Cd(CH_3COO)_2$, $CdCl_2$/CdI_2. According to the RBS results, the S:

Table 5
A summary of relative peak intensities and optical band gap for CdS films grown using four different Cd source

(hkl)	Cubic (powder)	$CdCl_2$-based film	$Cd(CH_3COO)_2$-based film	CdI_2-based film	$CdSO_4$-based film
	I/I_o (%)	I/I_o (%)	I/I_o (%)	I/I_o (%)	I/I_o (%)
(111)	100	100	100	100	100
(220)	46.7	28.9	18.4	16.4	2.9
(311)	33.2	19.4	13.5	11.8	2.7
Optical band gap (eV)		2.25	2.31	2.31	2.36

Table 6
Grain size dependence on Cd source

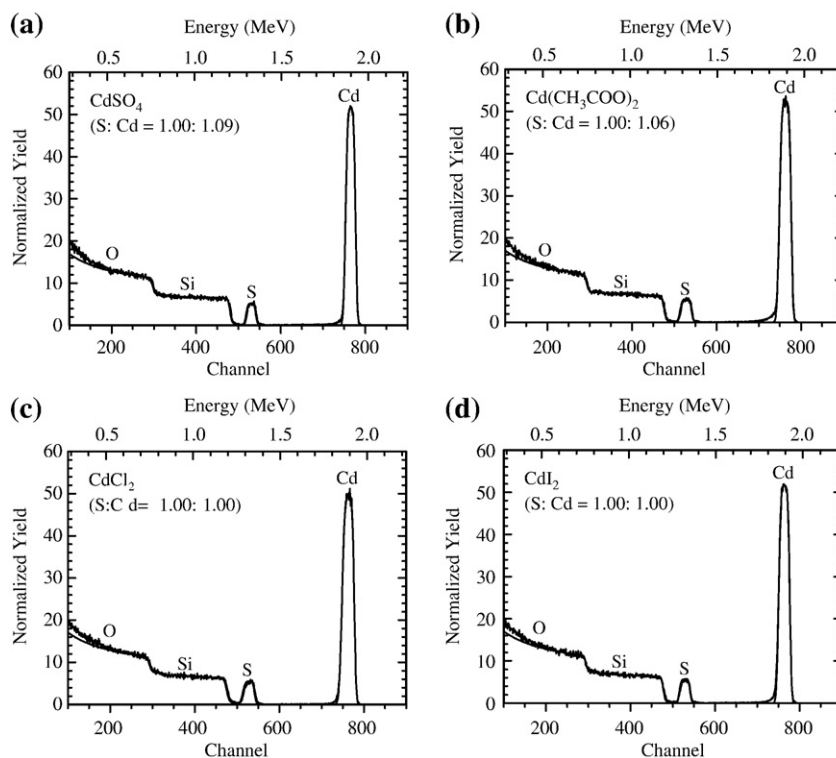| Cd source	Grain size (nm)
$CdSO_4$	145
CdI_2	13
$Cd(CH_3COO)_2$	14
$CdCl_2$	16

Fig. 6. RBS spectrum and RUMP simulation of CdS films grown using four different Cd sources.

Cd ratio decreases in the same order. We believe the excess content of Cd means that either interstitial Cd ions or sulfur vacancies exist in the film, acting as donors and resulting in an increase in the carrier concentration as well as a consequent decrease in the resistivity. The mobility measurements show the $Cd(CH_3COO)_2$, $CdCl_2/CdI_2$ based films to have very similar mobility. However, the $CdSO_4$ based film was found to have a mobility that's two times higher than the other three films. This can be understood by considering the grain size measurements shown in Table 6; the grain size of the $CdSO_4$ based film (145 nm) is much larger than that of the other three films (13–16 nm) which explains the higher mobility [29]. In the meantime, the grain size of the other three films is almost the same which may explain why these films have very close mobility values. The mobility values obtained in this work are in agreement with what has been reported earlier in the literature for polycrystalline CdS thin films [29,30].

4. Conclusion

A comprehensive study of the influence of Cd sources on electrical/optical properties as well as thickness, structure, surface morphology, and stoichiometry of chemical bath deposited CdS films is presented. Film thickness was found to decrease in the order $CdSO_4$, $Cd(CH_3COO)_2$, $CdCl_2$, CdI_2. However, the band gap was found to decrease in the order $CdSO_4$, $Cd(CH_3COO)_2/CdI_2$, $CdCl_2$. All films were found to be cubic, regardless of the Cd salt used. The grain size decreases in the order $CdSO_4$, $CdCl_2$, $Cd(CH_3COO)$, CdI_2. The RBS data showed that the usage of $CdCl_2$ and CdI_2 results in highly stoichiometirc films (S:Cd ratio=1:1). More Cd was detected when $CdSO_4$ and $Cd(CH_3COO)$ were used. The S:Cd ratio and carrier concentration were found to decrease in the order $CdSO_4$, $Cd(CH_3COO)_2$, $CdI_2/CdCl_2$. $CdCl_2$-based films were found to have a better transmission and much smoother surfaces than other films. Using $CdSO_4$ as Cd source leads to the highest growth rate, band gap, carrier concentration, and mobility.

Table 7
Hall effect and RBS measurements

Cd source	S:Cd ratio	Carrier concentration (cm^{-3})	Resistivity $(\Omega\text{-cm})$	Mobility $(cm^2/V\text{-}S)$
$CdSO_4$	1.00:1.09	1.68×10^{16}	8.01×10^1	4.64
$Cd(CH_3COO)_2$	1.00:1.06	8.83×10^{15}	3.38×10^2	2.09
$CdCl_2$	1.00:1.00	9.74×10^{14}	2.96×10^3	2.17
CdI_2	1.00:1.00	8.19×10^{14}	3.88×10^3	1.96

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