Investigation of aluminium and indium in situ doping of chemical bath deposited CdS thin films

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Abstract
Aluminum and indium in situ doping of CdS using chemical bath deposition (CBD) is investigated. The effects of Al and In-doping on optical properties as well as on electrical properties, crystal structure, chemistry and morphology of CdS films are studied. Al doping of CdS using CBD is shown to be successful where a resistivity as low as $4.6 \times 10^{-2} \text{\Omega cm}$ and a carrier density as high as $1.1 \times 10^{19} \text{cm}^{-3}$ were achieved. The bandgap of Al-doped films decreases to a minimum of $2.26 \text{eV}$, then slightly increases and finally saturates at $2.30 \text{eV}$ as the [Al]/[Cd] ratio in solution increases from 0.018 to 0.18. X-ray diffraction studies showed Al$^{3+}$ ions entering the lattice substitutionally at low concentration and interstitially at high concentration. Phase transition, due to annealing, and induced lattice damage, due to doping, were detected by micro-Raman spectroscopy. Film stoichiometry was found to be sensitive to Al concentration, while film morphology was unaffected by Al doping. Indium doping using CBD, however, was found to be highly unlikely due to the low solubility of indium sulfide. Instead, the formation of InS/In$_2$S$_3$ dominated the deposition process over CdS.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Chemical bath deposition (CBD) is known to be a simple, low temperature and inexpensive large-area deposition technique for group II–VI semiconductors such as CdS. It has been used in CdS thin films deposition since the 1960s [1, 2]. CdS films grown by CBD are known to be highly stoichiometric and exhibit a high dark resistance. A summary of dark resistances reported in the literature for several CBD-CdS thin films is shown in table 1. We have shown earlier [3] that with NH$_3$ as the complexing agent and thiourea as the sulfur source, using different Cd sources affects the stoichiometry as well as dark resistivity of CBD-CdS films. A direct relationship between sulfur deficiency and carrier concentration (CC)/resistivity in CdS films was established.

It was shown that using CdCl$_2$/CdI$_2$ as Cd sources results in highly stoichiometric films with an S : Cd ratio of 1.00 : 1.00, while using Cd(CH$_3$COO)$_2$ and CdSO$_4$ decreased that ratio to 1.00 : 1.06 and 1.00 : 1.09, respectively. Consequently, the dark resistivity of Cd(CH$_3$COO)$_2$ and CdSO$_4$-based CdS films was, respectively, 10 and 50 times smaller than that of CdCl$_2$/CdI$_2$-based CdS films. Yet, to be useful in solar cells as well as other optoelectronic applications, dark resistivity of CBD-CdS needs to be further reduced. In another work [4], we have shown that using nitrilotriacetic acid and N$_2$H$_4$ together as a complexing agent instead of NH$_3$ results in a S : Cd ratio of 1.00 : 1.08 instead of 1.00 : 1.00 for CdCl$_2$-based films, but this was at the expense of the growth rate as well as film quality due to domination of the homogenous reaction over the heterogeneous reaction in the deposition process.

One approach to reduce the dark resistivity of CBD-CdS is in situ doping. Over the past two decades, in situ doping of
CBD-CdS using Cu [14, 15], Li [16, 17], Na [18], Al [19, 20] and B [11, 21] has been reported. Ag doping of CBD-CdS was carried out using the ion exchange process [22, 23] and In-doped CdS films were grown by co-evaporation of CdS and indium [24, 25]. In this work, in situ doping of CBD-CdS using group III elements, namely, Al and In, is investigated. The objective of this work is to investigate the effectiveness of Al$_3^+$/In$_3^+$ doping through CBD. Transmittance and reflectance measurements of doped films were carried out to study the effect of Al/In doping on the optical properties and bandgap of CdS films. The resistivity, CC and mobility of doped films were acquired using Hall effect measurements. Film morphology was studied using scanning electron microscopy (SEM). Film chemistry and binding states were studied using x-ray photoelectron spectroscopy (XPS).

An Alpha-step 500 surface profilometer (Tencor) was used to determine the film thickness. Specular transmittance measurements were carried out at room temperature with unpolarized light at normal incidence in the wavelength range from 350 to 1200 nm using a Cary 500 (Varian) double beam UV/VIS spectrophotometer. Specular reflectance measurements have been carrier out at an angle of incidence of 7° in the same wavelength range. The optical absorption coefficient $\alpha$ was calculated for each film using the equation [26]

$$T = (1 - R)^2 \exp(-\alpha t), \quad (1)$$

where $T$ is the transmittance, $R$ is the reflectance and $t$ is the film thickness.

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

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

where $K$ is a constant, $E_b$ is the optical bandgap and $n$ is equal to 1 for a direct bandgap material such as CdS. The bandgap was determined for each film by plotting ($a h\nu$)$^2$ versus $h\nu$ and then extrapolating the straight line portion to the energy axis. XRD was carried out using Rigaku D XRD unit (with 40 kV, 30 mA CuK$\alpha$ radiation, $\lambda = 0.154.06$ nm). The sample was mounted at 2.5° and scanned from 25° to 55° in steps of 0.02° with a scan rate of 1.2° min$^{-1}$. Resistivity, mobility and carrier density were evaluated by Hall measurements at room temperature in a Van der Pauw four-point probe configuration, using indium contacts, in an automated Hall effect system (Ecopia HMS-3000, Bridge Technology, Chandler Heights AZ, USA) with a 0.55 T magnetic induction. Micro-Raman scattering was performed at room temperature with a Horiba Jobin Yvon LabRam IR system at a spatial resolution of 2 $\mu$m in a backscattering configuration. A 632.8 nm line of a helium–neon laser was used for off-resonance excitation with less than 4 mW power at the sample. The spectral resolution

### Table 1. A summary of the dark resistivity of some CBD-CdS films reported in the literature and the corresponding Cd source used.

<table>
<thead>
<tr>
<th>Cd source</th>
<th>Other reagents used in solution</th>
<th>$T_{\text{deposition}}$ (°C)</th>
<th>$\rho_{\text{dark}}$ (Ω cm)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. CdCl$_2$</td>
<td>NH$_4$OH/NH$_3$Cl/TU$^b$</td>
<td>80</td>
<td>$10^{6}$</td>
<td>[7]</td>
</tr>
<tr>
<td>2. CdCl$_2$</td>
<td>NH$_4$OH/NH$_3$Cl/TU$^b$</td>
<td>&gt;40</td>
<td>$10^{6}$</td>
<td>[9]</td>
</tr>
<tr>
<td>3. CdI$_2$</td>
<td>NH$_4$OH/NH$_3$I/TU$^b$</td>
<td>&gt;60</td>
<td>$10^{10}$</td>
<td>[9]</td>
</tr>
<tr>
<td>5. CdSO$_4$</td>
<td>NH$_4$OH/TU$^b$</td>
<td>70</td>
<td>$10^{8}$</td>
<td>[10]</td>
</tr>
<tr>
<td>6. CdCl$_2$</td>
<td>NH$_4$OH/NH$_3$Cl/TU$^b$</td>
<td>70</td>
<td>$10^{8}$</td>
<td>[3]</td>
</tr>
<tr>
<td>7. CdCl$_2$</td>
<td>NH$_4$OH/NH$_3$Ac/TU$^b$</td>
<td>10$^3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8. CdCl$_2$</td>
<td>NH$_4$OH/NH$_3$SO$_4$/TU$^b$</td>
<td>10$^3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9. CdCl$_2$</td>
<td>NH$_4$OH/NH$_3$Ac/TU$^b$</td>
<td>10$^3$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10. Cd(NO$_3$)$_2$</td>
<td>NH$_4$OH/NH$_3$Ac/TU$^b$</td>
<td>50–90</td>
<td>$10^{3}–8$</td>
<td>[11]</td>
</tr>
</tbody>
</table>

$^a$ Ac = Acetate; (CH$_3$COO)$^−$.

$^b$ TU = Thiourea; SC(NH$_2$)$_2$. 

CBD-CdS using Cu [14, 15], Li [16, 17], Na [18], Al [19, 20] and B [11, 21] has been reported. Ag doping of CBD-CdS was carried out using the ion exchange process [22, 23] and In-doped CdS films were grown by co-evaporation of CdS and indium [24, 25]. In this work, in situ doping of CBD-CdS using group III elements, namely, Al and In, is investigated. The objective of this work is to investigate the effectiveness of Al$_3^+$/In$_3^+$ doping through CBD. Transmittance and reflectance measurements of doped films were carried out to study the effect of Al/In doping on the optical properties and bandgap of CdS films. The resistivity, CC and mobility of doped films were acquired using Hall effect measurements. The crystal structure and crystal quality and phase transition were determined using x-ray diffraction (XRD) and micro-Raman spectroscopy. Film morphology was studied using scanning electron microscopy (SEM). Film chemistry and binding states were studied using x-ray photoelectron spectroscopy (XPS).

### 2. Experimental details

CdS films were prepared using stock solutions of CdSO$_4$ (0.038 M), (NH$_4$)$_2$SO$_4$ (0.076 M), NH$_3$OH (29.4%) and (NH$_2$)$_2$CS (0.076 M). Films were grown on 38 mm × 38 mm × 1 mm glass substrates (Schott Borofloat glass, supplied by S.I. Howard Glass Co., Inc.). Al/In doping was carried out by adding the appropriate amount from a 4 mM stock solution of Al$_2$(SO$_4$)$_3$/InCl$_3$ to the main solution. The deposition temperature was kept constant at 85°C. Details of the growth process have been previously reported [3]. Prior to the deposition of CdS films, glass substrates were cleaned by Liqui-Nox soap (supplied by Alconox, Inc.), then washed in de-ionized water, rinsed in acetone/methanol, washed again in de-ionized water, etched with dilute HCl for 2–3 min, etched with H$_2$O$_2$/H$_2$SO$_4$ (1:1 solution) for 5 min, etched in dilute HF for 1 min and then cleaned ultrasonically in de-ionized water for 5 min. After deposition, all films were annealed at 300°C in argon ambient for 1 h.
Figure 1. Specular transmittance and reflectance spectra of Al-doped CdS films grown at different [Al]/[Cd] ratios. The [Al]/[Cd] ratio in solution was varied from 0.018 to 0.18. It should be noted that a ratio of zero was assigned to the undoped film (purely CdS). All films exhibit a high transmittance that exceeds 80% in the visible region of the spectrum and exceeds 90% right before the absorption edge. The variation in transmittance with the [Al]/[Cd] ratio is likely attributed to variation in the film thickness. Table 2 shows that the thickness of doped films increases at first and then decreases. This may explain why the transmittance drops at first and then rises as the [Al]/[Cd] ratio increases. A red shift in the absorption edge towards a lower band gap is noticed in almost all doped films. The magnitude of the red shift was found to fluctuate as the [Al]/[Cd] ratio increases. Using transmittance and reflectance data, the absorption coefficient was calculated (using equation (1)) and was then used to determine the band gap, as shown in figure 2. As shown in figure 3, the bandgap of the doped films decreases to a minimum of 2.26 eV at a ratio of 0.018 and 0.036, then slightly increases and finally saturates at 2.30 eV as the [Al]/[Cd] ratio exceeds 0.10. The undoped film has a band gap of 2.41 eV which agrees well with the 2.42 eV band gap of single crystal CdS.

Table 2. Film thickness of Al-doped CdS films grown at different [Al]/[Cd] ratios (the 0.000 ratio is assigned to the undoped film).

<table>
<thead>
<tr>
<th>[Al]/[Cd] ratio</th>
<th>Film thickness (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>1100</td>
</tr>
<tr>
<td>0.018</td>
<td>1300</td>
</tr>
<tr>
<td>0.036</td>
<td>1500</td>
</tr>
<tr>
<td>0.054</td>
<td>1500</td>
</tr>
<tr>
<td>0.072</td>
<td>1200</td>
</tr>
<tr>
<td>0.108</td>
<td>1100</td>
</tr>
<tr>
<td>0.144</td>
<td>1000</td>
</tr>
<tr>
<td>0.180</td>
<td>1000</td>
</tr>
</tbody>
</table>

Figure 2. Optical bandgap calculations of Al-doped CdS films grown at different [Al]/[Cd] ratios. The [Al]/[Cd] ratio in solution was varied from 0.018 to 0.18. It should be noted that a ratio of zero was assigned to the undoped film (purely CdS). All films exhibit a high transmittance that exceeds 80% in the visible region of the spectrum and exceeds 90% right before the absorption edge. The variation in transmittance with the [Al]/[Cd] ratio is likely attributed to variation in the film thickness. Table 2 shows that the thickness of doped films increases at first and then decreases. This may explain why the transmittance drops at first and then rises as the [Al]/[Cd] ratio increases. A red shift in the absorption edge towards a lower band gap is noticed in almost all doped films. The magnitude of the red shift was found to fluctuate as the [Al]/[Cd] ratio increases. Using transmittance and reflectance data, the absorption coefficient was calculated (using equation (1)) and was then used to determine the band gap, as shown in figure 2. As shown in figure 3, the bandgap of the doped films decreases to a minimum of 2.26 eV at a ratio of 0.018 and 0.036, then slightly increases and finally saturates at 2.30 eV as the [Al]/[Cd] ratio exceeds 0.10. The undoped film has a band gap of 2.41 eV which agrees well with the 2.42 eV band gap of single crystal CdS.

Figure 3. Optical bandgap of Al-doped CdS films as a function of the [Al]/[Cd] ratio. The bandgap decreases to a minimum of 2.26 eV at a ratio of 0.018 and 0.036, then slightly increases and finally saturates at 2.30 eV as the [Al]/[Cd] ratio exceeds 0.10. The undoped film has a band gap of 2.41 eV which agrees well with the 2.42 eV band gap of single crystal CdS. CdS films are polycrystalline and cubic in nature, with a preferred orientation along the (1 1 1) direction. We have also shown that the degree of texture along the (1 1 1) orientation highly depends on the Cd source used. When CdSO4 is being used as the Cd source, which is the case in this work, the (2 2 0) and (3 1 1) peaks are almost totally suppressed and only
the (1 1 1) peak is detected. Now, keeping in mind that, at room temperature, cubic CdS is considered a metastable phase while hexagonal CdS is the stable phase, thermal annealing may cause a phase transition from the cubic phase to the hexagonal phase. The critical point for such a phase transition was reported to be 300°C [28], above which the hexagonal phase predominates over the cubic phase. Since all films were annealed at 300°C, it is difficult to determine if the peak shown in figure 4 is the (1 1 1) peak of the cubic phase or the (0 0 2) peak of the hexagonal phase which coincides with the (1 1 1) peak. We will show later in this work that there is some phase transition that has been detected by micro-Raman spectroscopy. In order to avoid confusion, we will refer to the peak detected as the (1 1 1) peak of cubic CdS. As shown in figure 4, no peaks of Al, AlS or Al2S3 were detected, which indicates that incorporation of Al3+ ions does not change the crystal structure of the CdS film. The average (1 1 1) interplanar distance $d_{111}$ was calculated using the formula $\lambda = 2d \sin \theta$, where $\lambda$ is the x-ray wavelength (1.5406 Å) and $\theta$ is the Bragg angle. As shown in figure 5, as the [Al]/[Cd] ratio increases, the spacing of the (1 1 1) lattice planes decreases below that of the undoped film until it reaches a minimum at a ratio of 0.055 and then it starts to increase as the [Al]/[Cd] ratio increases, and once that ratio exceeds 0.11, the $d_{111}$ value goes beyond that of the undoped CdS film. Now, since the ionic radius of Al3+ (0.50 Å) is smaller than that of Cd2+ (0.97 Å) [29], this suggests that at a low [Al]/[Cd] ratio, Al3+ ions replace Cd2+ ions in the lattice substitutionally which in turn results in a smaller $d_{111}$ value than that of the undoped CdS film. As this ratio increases beyond 0.055, Al3+ ions start to enter the lattice both substitutionally and interstitially which caused the $d_{111}$ values to increase again. As the [Al]/[Cd] ratio exceeds 0.11, most Al3+ ions incorporated in the lattice are in interstitial sites which caused $d_{111}$ values to exceed that of the undoped film. This will have an impact on the electrical properties of Al-doped films as Hall measurements will show later.

Figure 5 also shows the relative intensity of the (1 1 1) peak with respect to that of undoped film. As shown, all doped films have a relative intensity higher than one. It is worth noting that the way the relative intensity behaves as a function of the [Al]/[Cd] ratio is almost opposite to that of the $d_{111}$ values. This confirms our conclusion that Al3+ ions enter the lattice substitutionally at low concentration and interstitially at high concentration. The grain size shown in figure 6 was calculated using the formula $D = 0.9\lambda / \beta \cos \theta$, where $\beta$ is the full width at half maximum (FWHM) in radians. In agreement with the thickness measurements in table 2, the grain size increases with the [Al]/[Cd] ratio, and then as this ratio exceeds 0.055, the grain size decreases as the [Al]/[Cd] ratio increases. This can also explain the way the bandgap varies with the [Al]/[Cd] ratio. As suggested by Lokhande and Pawar [19] and later by Akintunde [20], incorporation of Al as well as sulfur deficiency in Al-doped films gives rise to donor levels...
in the bandgap of CdS. As the Al concentration increases which in turn increases the sulfur deficiency, the donor levels become degenerate and merge in the conduction band of CdS, causing the conduction band to extend into the bandgap which reduces the band gap. The reason the bandgap increases as the [Al]/[Cd] ratio goes beyond 0.055 may be attributed to the decrease in the grain size of the doped films (figure 6) which causes an increase in the lattice strain in the film. We have observed in a previous work [4] that such an increase in the lattice strain (due to decrease in the film thickness/grain size) increases the bandgap of CdS films.

Figure 7 shows the CC as a function of the [Al]/[Cd] ratio. The undoped film has a CC of about $4 \times 10^{16}$ cm$^{-3}$. The CC increases with the [Al]/[Cd] ratio until it reaches a maximum ($\sim 1.1 \times 10^{19}$ cm$^{-3}$) at a ratio of 0.036, and then decreases as the ratio exceeds 0.055 until it drops to $4.7 \times 10^{18}$ cm$^{-3}$ at a ratio of 0.18. The film resistivity as a function of the [Al]/[Cd] ratio is shown in figure 8. The dark resistivity drops from $1.03 \times 10^2 \ \Omega \ \text{cm}$ (undoped film) to a minimum of $4.6 \times 10^{-2} \ \Omega \ \text{cm}$ at a ratio of 0.036 and 0.055, after which it increases until it reaches $1.45 \times 10^{-1} \ \Omega \ \text{cm}$ at a ratio of 0.18. This agrees with the $d_{(111)}$ value variation with the [Al]/[Cd] ratio. As we pointed out earlier, at low [Al]/[Cd] ratios, Al$^{3+}$ ions replace the Cd$^{2+}$ ions in the lattice substitutionally, which increases the CC of the doped films and decreases the resistivity. However, at higher ratios, Al$^{3+}$ ions start to enter the lattice both substitutionally and interstitially. Interstitial Al$^{3+}$ ions will act as recombination centres decreasing the CC and increasing the resistivity. Such behaviour of CC as well as dark resistivity has been also reported by Lokhande and Pawar [19] and by Akintunde [20].

It should be noted that, although CC at the 0.055 ratio ($9.52 \times 10^{18}$ cm$^{-3}$) is less than that at the 0.036 ratio ($\sim 1.1 \times 10^{19}$ cm$^{-3}$), both films appear to have the same resistivity. This can be understood by considering the Hall mobility ($\mu$) values shown in figure 9. The Hall mobility at a ratio of 0.055 was 14.25 (cm$^2$ V$^{-1}$ S$^{-1}$) while the Hall mobility at a ratio of 0.036 was 12.33 (cm$^2$ V$^{-1}$ S$^{-1}$). This difference compensated for the CC difference and resulted in a similar resistivity value. In general, the Hall mobility values observed agree with what was reported earlier by Bertrán et al [24] and Hayashi et al [25]. Variation of $\mu$ with respect to the [Al]/[Cd] ratio agrees to some extent with the way grain size changes with respect to the [Al]/[Cd] ratio (figure 6).

Figure 10 shows micro-Raman spectra for all Al-doped films. All films show the same CdS characteristic peak at about 303 cm$^{-1}$. Another CdS characteristic peak, 2 longitudinal optical (LO) [38], is barely noticeable at about 600 cm$^{-1}$. A closer look at the main peak at 303 cm$^{-1}$ shows the peak being asymmetric, suggesting a superposition of more than one mode. Figure 11 shows the deconvolution of the 303 cm$^{-1}$ peak of the film grown at the [Al]/[Cd] ratio of 0.018, using the Gaussian fit from which the peak position and FWHM have been obtained. It should be noted that the Gaussian fit gave a better fit than the Lorentzian fit, which may be due to film defects and induced lattice damage because of Al doping, as will be discussed later. As shown in figure 11, that peak
can be deconvoluted into three different peaks: the highest at 302.8 cm$^{-1}$ with an FWHM of 12.8 cm$^{-1}$, the middle at 287.5 cm$^{-1}$ with an FWHM of 25.0 cm$^{-1}$ and the lowest peak at 258.3 cm$^{-1}$ with an FWHM of 30.0 cm$^{-1}$. The prominent peak at 302.8 cm$^{-1}$ is attributed to either the cubic $1\text{LO}$ phonon [36] or the hexagonal $A_1(\text{LO})/E_1(\text{LO})$ phonons [32]. The peak observed at 258.3 cm$^{-1}$ is the $E_2$ peak of hexagonal CdS [33, 35]. However, the peak observed at 287.5 cm$^{-1}$ is attributed to a shift in either the transverse optical (TO) peak of cubic CdS [36] or the $E_1(\text{TO})$ peak of hexagonal CdS [35]. This Raman shift results from a phase transition in the CdS film, from cubic to hexagonal, due to annealing at 300 °C. Zelaya-Angel et al [30] reported a similar shift for CdS films annealed at 350 °C, where they observed the $E_1(\text{TO})$ phonon at 276 cm$^{-1}$ instead of 240 cm$^{-1}$. According to their calculations, the Raman shift, due to phase transition in CdS, should be about 18% which causes the $E_1(\text{TO})$ peak to shift from 240 cm$^{-1}$ (original position in hexagonal CdS [35]) to 283 cm$^{-1}$. A similar shift in the TO peak of cubic CdS (originally at 246 cm$^{-1}$ [36]) will position this peak at about 290 cm$^{-1}$. Since the peak they observed for the annealed CdS film was at 276 cm$^{-1}$, they ruled out the TO phonon possibility and attributed this peak to a shift in the $E_2(\text{TO})$ peak of hexagonal CdS. In our work, however, this peak is observed at 287.5 cm$^{-1}$ rather than at 276 cm$^{-1}$, which may be attributed to the TO phonon of cubic CdS rather than the $E_1(\text{TO})$ peak of hexagonal CdS. No peaks were detected for the $A_1(\text{TO})$ phonon of hexagonal CdS. Table 3 lists some of the experimental and theoretical values reported for $A_1(\text{LO})$, $A_1(\text{TO})$, $E_1(\text{LO})$, $E_1(\text{TO})$ and $E_2$ phonons for hexagonal single crystal CdS as well as values of $1\text{LO}$, $2\text{LO}$, and TO phonons for cubic CdS.

Figure 12 shows an example of the effect of annealing on micro-Raman spectra of the CdS undoped film. As shown in figure 12(b), the $1\text{LO}$ peak observed at 303 cm$^{-1}$ for the as-grown undoped film is clearly symmetric. A Gaussian fit is shown in the inset of figure 12(b), according to which the peak has an FWHM of $\sim 16.6$ cm$^{-1}$. Figure 12(c) shows micro-Raman for the same undoped film after annealing; the peak is obviously asymmetric. Deconvolution of the peak using the Gaussian fit is shown in the inset of figure 12(c). It consists of three different peaks at 258.5, 288 and 302.5 cm$^{-1}$. This proves that the asymmetry in the main peak at $\sim 303$ cm$^{-1}$ is due to annealing, not Al doping. It was noticed that the FWHM of the peak at 302.5 cm$^{-1}$ of the annealed film is 12.2 cm$^{-1}$, which is much smaller than that of the as-grown film ($16.6$ cm$^{-1}$). This indicates an enhancement in film crystallinity due to annealing. The FWHM of the $1\text{LO}$ phonon of single crystal CdS was reported to be in the range 9–10 cm$^{-1}$ [31]. It is worth noting that the hump observed between 400 and 500 cm$^{-1}$ is due to fluorescence from the substrate, as shown in figure 12(a).

A similar deconvolution of the 303 cm$^{-1}$ peak was carried out for all Al-doped films. Figure 13 shows the position and FWHM of the $E_2$, TO and cubic $1\text{LO}$ or hexagonal $A_1(\text{LO})/E_1(\text{LO})$ peaks calculated from the Gaussian fit. Apparently, the position and FWHM of both $E_2$ and TO peaks are on average constant regardless of the $[\text{Al}] / [\text{Cd}]$ ratio used. The average position of the $E_2$ peak was found to be 258.3 cm$^{-1}$ (figure 13(a)) which agrees well with the 256 cm$^{-1}$ [33] and the 257 cm$^{-1}$ [35] values of $E_2$ that have been reported earlier (table 3). The average position of the middle peak (figure 13(b)) is 288 cm$^{-1}$ which confirms our conclusion that this peak is attributed to a shift in the TO peak of cubic CdS. However, as shown in figure 13(c), the position and FWHM of the cubic $1\text{LO}$ or the hexagonal $A_1(\text{LO})/E_1(\text{LO})$ peak are sensitive to the $[\text{Al}] / [\text{Cd}]$ ratio. As that ratio increases, the peak position and FWHM increase. The increase in FWHM is, however, more significant which implies an increase in the induced lattice damage as the $[\text{Al}] / [\text{Cd}]$ ratio increases.

Figure 14 shows XPS multiplex spectra for the undoped film and the Al-doped films grown at $[\text{Al}] / [\text{Cd}]$ ratios of 0.036 and 0.18. In all three cases, the binding energy of the S 2p peak (figure 14(a)) is 161.7 eV which is in the range characteristic of...
Table 3. A summary of E₁ (LO), E₁ (TO), A₁ (LO), A₁ (TO) and E₂ Raman peak positions of hexagonal CdS as well as 1LO, 2LO and TO Raman peak positions of cubic CdS reported in the literature.

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<tr>
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<th>Hexagonal CdS</th>
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<th></th>
<th></th>
<th>References</th>
<th>Cubic CdS</th>
<th>1LO</th>
<th>TO</th>
<th>2LO</th>
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<tr>
<td>E₁ (LO)</td>
<td>305</td>
<td>305</td>
<td>235</td>
<td>228</td>
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<td></td>
<td>305</td>
<td>246</td>
<td>610</td>
<td>[36]</td>
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<tr>
<td>A₁ (LO)</td>
<td>307</td>
<td>305</td>
<td>243</td>
<td>234</td>
<td>256</td>
<td></td>
<td>305</td>
<td>—</td>
<td>—</td>
<td>[37]</td>
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<tr>
<td>E₁ (TO)</td>
<td>306.9</td>
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<td>[38]</td>
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<td>A₁ (TO)</td>
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<td>[35]</td>
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Figure 12. Phase transition of undoped film due to annealing as detected by Raman spectroscopy. (a) Substrate, (b) as-grown undoped CdS film and (c) annealed undoped CdS film.

Figure 13. Peak position and FWHM as a function of the [Al]/[Cd] ratio. (a) E₂ peak of hexagonal CdS. (b) Shifted TO peak of cubic CdS. (c) Cubic 1LO or hexagonal A₁(LO)/E₁ (LO) peak.

Figure 14. XPS multiplex spectra of the undoped CdS film, Al-doped film grown at [Al]/[Cd] ratios of 0.036 and 0.18. (a) S 2p peak. (b) Cd 3d peak.

Sulfides. No peak shift was detected due to Al doping. Also, no sulfur oxides (166–171 eV) or elemental sulfur (164 eV) [40] are observed. The presence of two peaks arises from a spin–orbit splitting of 1.18 eV between the S 2p₁/₂ and the S 2p₃/₂ states. Similarly, the binding energy of the Cd 3d₅/₂ peak at 405.0 eV (figure 14(b)) was found to be the same for all three films. The binding energy of the Cd 3d₃/₂ peak was 411.7 eV, which agrees with the 6.74 eV energy splitting between Cd 3d₅/₂ and Cd 3d₃/₂ states [40]. Both values of binding energy for S 2p and Cd 3d peaks observed in all three films agree well.
with previously reported data on single crystal and thin film CdS [41, 42]. It is worth noting that the ratio of S 2p$_{3/2}$ signal intensity to that of the Cd 3d$_{5/2}$ signal was found to decrease as the [Al]/[Cd] ratio increases. It decreases in the order 0.154, 0.149 and 0.146 as the [Al]/[Cd] ratio increases in the order 0.000 (undoped film), 0.036 and 0.18, respectively. Clearly, Al doping increases the sulfur deficiency in doped films.

SEM images show that Al doping did not affect the morphology of the film. As shown in figure 15, both undoped and Al-doped films are smooth, continuous and uniform with some coverage by scattered crystallite overgrowth that appear to have the same density for both films. These are most probably aggregates due to colloidal particles formed in solution and then adsorbed on the film.

3.2. Investigation of indium doping

Due to the extremely low solubility product of In$_2$S$_3$ ($K_{sp} = 10^{-73.24}$) compared with that of CdS ($K_{sp} = 10^{-27.94}$) [43], only two [In]/[Cd] ratios, 0.009 and 0.018, were used. Once InCl$_3$ was added, the solution became turbid and a homogeneous reaction dominated the deposition process. In both cases, the substrate was kept in solution for less than 5 min to avoid deposition of porous, non-adhesive and poor quality layer due to the homogeneous reaction. Although the deposition process was repeated four times using a fresh solution each time, the film obtained in both cases was very thin (about 550 Å). Almost no film was deposited when a higher concentration of indium was used. This is due to the quick depletion of In$^{3+}$ and S$^{2-}$ ions in solution because of the homogeneous reaction that dominated the deposition process from the very beginning. Figure 16 shows transmittance and reflectance spectra of both films. The absorption edge observed for both films is not quite steep as in the case of Al-doped films, which may have to do with the small thickness as well as the inferior quality of both films. According to band gap calculations shown in figure 17, both films appear to have the band gap characteristic of indium sulfide rather than that of CdS. The band gap observed was 2.75 eV and 2.74 eV for films grown at [In]/[Cd] ratios of 0.009 and 0.018, respectively. This agrees well with the 2.75 eV bandgap of indium sulfide thin films reported by Lokhande et al [44] and Sanz et al [45].

As shown in figure 18, the XRD pattern of films grown at the [In]/[Cd] ratio of 0.018 is a mixture of cubic In$_2$S$_3$ (JCPDS 032-0456) [46] and Orthorhombic InS (JCPDS 019-0588) [47], with no peaks characteristic of cubic or hexagonal CdS being detected. In general, CBD of indium sulfide or cadmium sulfide takes place when the product of the ion concentration in the solution exceeds the solubility product, $K_{sp}$. Since $K_{sp}$ of indium sulfide is extremely low compared with that of CdS, the deposition of indium sulfide will dominate and no matter how small the concentration of indium is, it is highly unlikely, if not impossible, to incorporate indium in CdS using CBD. Certainly, our results prove that conclusion.

4. Conclusion

Aluminium in situ doping of CdS using CBD proves to be successful. A resistivity as low as $4.6 \times 10^{-2}$ $\Omega$ cm and a carrier density as high as $1.1 \times 10^{19}$ cm$^{-3}$ were achieved. The bandgap of doped films was found to decrease at first with the Al concentration and then slightly increases and finally saturates
at 2.30 eV. The minimum bandgap observed was 2.26 eV at [Al]/[Cd] ratios of 0.018. XRD measurements did not detect any new peaks due to Al doping indicating that incorporation of Al$^{3+}$ ions does not change the crystal structure of the CdS film. It also showed that at a low [Al]/[Cd] ratio, Al$^{3+}$ ions replace Cd$^{2+}$ ions in the lattice substitutionally, and as this ratio increases beyond 0.055, Al$^{3+}$ ions start to enter the lattice both substitutionally and interstitially, until that ratio exceeds 0.11 where most, if not all, Al$^{3+}$ ions incorporated in the lattice occupy interstitial sites. This explains the drop in carrier density and rise in resistivity once the [Al]/[Cd] ratio exceeds 0.055. Micro-Raman measurements show phase transition in all films, due to annealing, where modes of cubic and hexagonal phases were detected. An increase in the FWHM of cubic 1LO or hexagonal A$_1$(LO)/E$_1$(LO) peak with the [Al]/[Cd] ratio was observed, which implies an increase in the induced lattice damage as the [Al]/[Cd] ratio increases. XPS spectra showed that, however, Al doping did not cause any shift in the position of the S 2p and Cd 3d peaks; it increased the sulfur deficiency in doped films. SEM images showed that Al doping did not affect the morphology of the CdS film. Finally, we have shown that using CBD, it is highly unlikely, if not impossible, to incorporate indium in CdS. Unlike co-evaporation of CdS and indium [24, 25], CBD is not a suitable technique for growing In-doped CdS films.

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