Chemical Bath Deposition Of Group II-VI Semiconductor Thin Films For Solar Cells Applications

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CHEMICAL BATH DEPOSITION OF GROUP II-VI SEMICONDUCTOR THIN FILMS FOR SOLAR CELLS APPLICATIONS

by

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A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Physics in the College of Sciences at the University of Central Florida Orlando, Florida

Fall Term 2009

Major Professor: Lee Chow
ABSTRACT
Chemical bath deposition (CBD) 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 by a chemical reaction between dissolved precursors, with the help of a complexing agent. Among all techniques used to grow Group II-VI semiconductors, CBD has the advantage of being a simple, low temperature, and inexpensive large-area deposition technique. So far, its contribution in thin film solar cells industry has been mainly limited to growing n-type CdS and/or ZnS window layers for CdTe-based and CIGS-based solar cells.

In this work we first optimize the CBD process of CdS using nitrilotriacetic acid and hydrazine as complexing agents as an alternative to ammonia. We then study the effect of the cadmium precursor on the optical/electrical properties, as well as crystal structure, morphology, and composition of CBD-CdS films. A better understanding of the CBD process of CdS as a whole has been achieved and high quality CBD-CdS films have been obtained.

Next, we investigate in-situ doping of CBD-CdS with group III elements, such as B, Al, In, and Ga. The objective is to show that CBD is capable of not only growing CdS but also of doping it to reduce its resistivity and, as a result, facilitate its use in solar cells as well as other optoelectronic device fabrication. A four orders of magnitude drop of film resistivity has been achieved without a significant change in film bandgap, structure, or morphology.
Finally, we test the possibility of using CBD to grow transparent conducting oxide (TCO) films, such as Al-doped ZnO films and cadmium stannate films. First, we study CBD of ZnO and later *in-situ* doping of ZnO using Al. High quality ZnO thin films have been grown using CBD with the help of four different complexing agents. Post heat treatment in argon ambient helped reduce resistivity of CBD-ZnO undoped films to $\sim 10^{-1} \, \Omega\cdot\text{cm}$. *In-situ* doping of such films using Al shows promising results. Such films could be an alternative to indium tin oxide (ITO) layers that are commonly used as TCO layers for solar cells. Another approach is to use CBD to grow CdO and SnO$_2$ thin films, with the goal of obtaining Cd$_2$SnO$_4$ by later annealing of these two layers. Cadmium stannate is another TCO candidate that could replace ITO in the near future. We have succeeded in growing CBD-CdO thin films using three different complexing agents. Undoped CBD-CdO films with a resistivity as low as $1.01 \times 10^{-2} \, \Omega\cdot\text{cm}$ and a carrier density as high as $2.59 \times 10^{20} \, \text{cm}^{-3}$ have been obtained. SnO$_2$ films have been successfully grown using CBD. Fabrication of Cadmium stannate thin films using CBD is investigated.

In summary, our objective to expand the use of CBD beyond just growing CdS and ZnS, and to test the possibility of using it for *in-situ* doping of group II-VI semiconductors as well as TCO layers fabrication proved to be successful. We believe that this may have a significant impact on solar cells as well as other optoelectronic devices fabrication industry, due to the simplicity and the cost-effectiveness of CBD.
To my parents, my sister, and my brother for their endless support, encouragement, and unconditional love
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CHAPTER I: INTRODUCTION

1.1 Group II-VI Semiconductors

Group II-VI semiconductor compounds are formed from group II metals and group VI chalcogens of the periodic table. Among those semiconductors, compounds formed from elements of group IIB and group VI, such as ZnO, ZnS, ZnSe, ZnTe, CdO, CdS, CdSe, and CdTe have attracted a lot of attention for their applications in solar cells, light emitting diodes, semiconductor lasers, photodetectors, and other optoelectronic applications [1-8]. Therefore, we will be focusing our attention on group IIB-VI semiconductors only, but for simplicity we will be referring to them as group II-VI compounds. With the exception of mercury compounds, group II-VI semiconductors are direct bandgap materials with bandgap that ranges from 1.5 eV to 3.7 eV.

1.1.1 Crystal Structure

Table 1 shows the ground state electronic configuration (GSEC) of some group II and group VI elements. As shown, metals of group II have two $s^2$ electrons in the outer shell; while chalcogens of group VI have six $s^2p^4$ electrons. Group II-VI compounds of the form MX, where M denotes group II metal and X denotes group VI chalcogens, are typically characterized by the presence of four elongated electron clouds around each atom. These electron clouds are in the $sp^3$ configuration, which is due to the hybridization of the s- and p-orbitals [9]. This leads to a crystal lattice in which atoms M and X are tetrahedrally coordinated such that each atom is symmetrically surrounded by four
nearest neighbor atoms of the other element. Two possible structures can satisfy such arrangement of atoms; zincblende (cubic) and wurtzite (hexagonal) crystal structures [10].

<table>
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<th>GSEC</th>
<th>Group VI chalcogens</th>
<th>GSEC</th>
</tr>
</thead>
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<td>[Ar].3d¹⁰.4s²</td>
<td>O</td>
<td>[He].2s².2p⁴</td>
</tr>
<tr>
<td>Cd</td>
<td>[Kr].4d¹⁰.5s²</td>
<td>S</td>
<td>[Ne].3s².3p⁴</td>
</tr>
<tr>
<td>Hg</td>
<td>[Xe].4f¹⁴.5d¹⁰.6s²</td>
<td>Se</td>
<td>[Ar].3d¹⁰.4s².4p⁴</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>Te</td>
<td>[Kr].4d¹⁰.5s².5p⁴</td>
</tr>
</tbody>
</table>

Table 1
Ground state electronic configuration (GSEC) of some group II and group VI elements

Similar to the diamond structure, the zincblende structure (Fig. 1) may be viewed as two fcc structures displaced from each other by one quarter of a body diagonal [12]. However, in the zincblende structure, one of the fcc sub-lattices is formed by cations (group II metals) while the other sub-lattice is formed by anions (group VI chalcogens). Therefore, unlike diamond, the zincblende structure does not have inversion symmetry. The stacking sequence along the tetrahedral bonds is repeated every three anion-cation bilayers (ABCABC…..). The dimensions of the unit cell are defined in terms of the lattice constant \( a \). The coordination number is 4 for atoms of both elements. The space group is \( \overline{F}43m \).

Fig. 2 shows the wurtzite structure. It consists of two interpenetrating hexagonal close-packed lattices of lattice constants \( a \) and \( c \). These lattices are relatively displaced along the hexagonal axis \( c \) by the nearest neighbor distance \( d = (3/8) \ c [10] \). Ideally, the ratio of \( (c / a) \) should be \( (8/3)^{1/2} = 1.633 \ [13] \). However, most of the wurtzite compounds have slightly different \( (c / a) \) ratios [14] (Table 2).
Fig. 1 Zincblende structure of CdS [11]

Fig. 2 Wurtzite structure of ZnO [11]
This may be understood by considering the fact that the anion-cation bond length $d$ along the $c$-axis is slightly different than that along the other directions. As shown, the ratio $\gamma$ of the bond length $d$ to the other anion-cation distance is not unity.

Table 2
Crystal structure, lattice parameters $a$, $c$, $(c/a)$, bond length $d$, and bond ratio $\gamma$ of group II-VI semiconductors (all dimensions are in Å) [14]

<table>
<thead>
<tr>
<th>Group II-VI compound</th>
<th>Zinci blende</th>
<th>Wurtzite</th>
<th>$a$</th>
<th>$c$</th>
<th>$(c/a)$</th>
<th>$\gamma$</th>
<th>$d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>-</td>
<td>-</td>
<td>3.253</td>
<td>5.213</td>
<td>1.603</td>
<td>1.008</td>
<td>1.98</td>
</tr>
<tr>
<td>ZnS</td>
<td>5.406</td>
<td>2.341</td>
<td>3.811</td>
<td>6.235</td>
<td>1.636</td>
<td>-</td>
<td>2.335</td>
</tr>
<tr>
<td>ZnSe</td>
<td>5.668</td>
<td>2.454</td>
<td>4.003</td>
<td>6.540</td>
<td>1.634</td>
<td>-</td>
<td>2.453</td>
</tr>
<tr>
<td>ZnTe</td>
<td>6.103</td>
<td>2.643</td>
<td>4.310</td>
<td>7.090</td>
<td>1.645</td>
<td>-</td>
<td>2.646</td>
</tr>
<tr>
<td>CdS</td>
<td>5.835</td>
<td>2.327</td>
<td>4.137</td>
<td>6.714</td>
<td>1.623</td>
<td>1.005</td>
<td>2.528</td>
</tr>
<tr>
<td>CdSe</td>
<td>6.050</td>
<td>2.620</td>
<td>4.30</td>
<td>7.013</td>
<td>1.631</td>
<td>1.006</td>
<td>2.63</td>
</tr>
<tr>
<td>CdTe</td>
<td>6.478</td>
<td>2.805</td>
<td>4.572</td>
<td>7.484</td>
<td>1.637</td>
<td>-</td>
<td>2.802</td>
</tr>
<tr>
<td>HgS</td>
<td>5.872</td>
<td>2.543</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HgSe</td>
<td>6.085</td>
<td>2.635</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HgTe</td>
<td>6.460</td>
<td>2.797</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The stacking sequence is repeated every two bilayers ($ABAB....$). Again, the coordination number is 4 for atoms of both elements. The space group is $P\bar{6}$_3mc.

1.1.2 Chemical Binding

Group II-VI semiconductor compounds with the tetrahedral coordination with zincblende or wurtzite structure are formed when group II metals have sufficiently high ionization potentials and do not give up their electrons, but rather share them with neighboring chalcogens [9]. The stronger electronegativity of group VI chalcogens (Table 3) causes the electron clouds to shift from group II metals to group VI chalcogens. As a result, the binding is partly ionic and partly covalent.

This would be better understood by considering the effective charge of group II metals in pure ionic and covalent bonds. Pure ionic bonds are formed when the valence
electrons are detached from the metal $M$ and transferred to the chalcogens $X$. In this case, group II metal is fully ionized, with effective charge of “+2”. However, pure covalent bonds are formed upon equal distribution of valence electrons between the metal $M$ and the chalcogen $X$, with the center of the electron cloud located at the center of the inter-atomic distance $d_{MX}$.

Table 3
Some physical properties of group II-VI semiconductors [9]

<table>
<thead>
<tr>
<th>Group II-VI compound</th>
<th>$d_{MX}$ (Å)</th>
<th>Heat of atomization (Kcal/g-atom)</th>
<th>*$E_g$ (eV)</th>
<th>Melting point (°C)</th>
<th>Difference of electronegativity</th>
<th>Effective charge of metal atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnS</td>
<td>2.36</td>
<td>73.0</td>
<td>3.75</td>
<td>1830</td>
<td>0.9</td>
<td>0.268</td>
</tr>
<tr>
<td>ZnSe</td>
<td>2.45</td>
<td>66.0</td>
<td>2.72</td>
<td>1515</td>
<td>0.8</td>
<td>0.099</td>
</tr>
<tr>
<td>ZnTe</td>
<td>2.64</td>
<td>63.0</td>
<td>2.27</td>
<td>1295</td>
<td>0.5</td>
<td>0.066</td>
</tr>
<tr>
<td>CdS</td>
<td>2.52</td>
<td>57.0</td>
<td>2.42</td>
<td>1750</td>
<td>0.8</td>
<td>0.77</td>
</tr>
<tr>
<td>CdSe</td>
<td>2.62</td>
<td>52.0</td>
<td>1.75</td>
<td>1258</td>
<td>0.7</td>
<td>0.55</td>
</tr>
<tr>
<td>CdTe</td>
<td>2.79</td>
<td>48.0</td>
<td>1.51</td>
<td>1098</td>
<td>0.4</td>
<td>0.081</td>
</tr>
<tr>
<td>HgS</td>
<td>2.53</td>
<td>47.0</td>
<td>0.04</td>
<td>1450</td>
<td>0.6</td>
<td>-</td>
</tr>
<tr>
<td>HgSe</td>
<td>2.63</td>
<td>42.0</td>
<td>0.08</td>
<td>800</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>HgTe</td>
<td>2.80</td>
<td>37.0</td>
<td>0.15</td>
<td>670</td>
<td>0.2</td>
<td>-</td>
</tr>
</tbody>
</table>

* $E_g$ has been updated from the more recent literature

Consequently, the effective charge of the group II metal is “−2”. If this center is located at a distance $\frac{1}{4}d_{MX}$, the distribution of valence electrons may be described as $2e^-$ around the metal $M$ and $6e^-$ around the chalcogens $X$. The effective charges of the component atoms of the resultant compound $M^0X^0$ equal zero. This is the effective covalent bond between neutral atoms [10].

Table 3 indicates that the effective charge of the metal atoms is always positive but less than unity, which confirms that the chemical binding is partly ionic and partly covalent. It is worth noting that as the atomic number increases, the inter-atomic distance $d_{MX}$ increases. Consequently, the bond strength decreases which results in a decrease in
the heat of atomization, the optical bandgap, and the melting point. Fig. 3 shows the melting point of some II-VI semiconductor compounds as a function of the lattice constant \( a \). The solid line represents the least-squares fit with the relation [15]:

\[
T_m = 7159 - 957a
\]  

Table 3 also shows that such dependence on the atomic number is noticeable when the aforementioned properties are compared for different anions (\( S^{2-} \), \( Se^{2-} \), and \( Te^{2-} \)) within group II-VI compounds that have the same cation. The same is true when comparing compounds with the same anion and different cations (\( Zn^{2+} \), \( Cd^{2+} \), and \( Hg^{2+} \)). Meanwhile, considering compounds with common cation, the effective charge of the metal telluride is less than that of the metal selenide, which is less than that of the metal sulfides, indicating a decrease in the ionicity of bonds within each group when the atomic number of the chalcogen is increased.

### 1.1.3 Phonon Frequency

The phonon frequencies can be measured by using several techniques, such as Raman scattering, infrared reflectivity, and neutron scattering [15]. Table 4 summarizes the long-wavelength optical phonon frequencies for some group II-VI semiconductor compounds at \( T = 300 \) K.

### 1.1.4 Elastic Properties

Table 5 shows bulk modulus \( B \), Shear Modulus \( C_s \), linear compressibility \( C_o \), and microhardness \( H \) for some group II-VI semiconductor compounds at \( T = 300 \) K.
Fig. 3 Melting point $T_m$ versus lattice constant $a$ for some group II-VI semiconductor compounds
### Table 4

Long-wavelength optical phonon frequencies (cm\(^{-1}\)) for some group II-VI semiconductors at 300 K [15]

<table>
<thead>
<tr>
<th>Group II-VI compound</th>
<th>Zincblende (\hbar\omega_{LO}^*)</th>
<th>Wurtzite (\hbar\omega_{TO}^*)</th>
<th>(E_1) low</th>
<th>(A_1) (TO)</th>
<th>(E_1) (TO)</th>
<th>(E_2) high</th>
<th>(A_1) (LO)</th>
<th>(E_1) (LO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>-</td>
<td>-</td>
<td>100.0</td>
<td>380.0</td>
<td>410.0</td>
<td>439.0</td>
<td>576.0</td>
<td>587.0</td>
</tr>
<tr>
<td>ZnS</td>
<td>350.5</td>
<td>272.0</td>
<td>65.0</td>
<td>270.0</td>
<td>273.0</td>
<td>281.0</td>
<td>350.0</td>
<td>350.0</td>
</tr>
<tr>
<td>ZnSe</td>
<td>252.0</td>
<td>205.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ZnTe</td>
<td>210.0</td>
<td>181.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CdS</td>
<td>303.0</td>
<td>237.0</td>
<td>41.0</td>
<td>233.0</td>
<td>239.0</td>
<td>255.0</td>
<td>301.0</td>
<td>304.0</td>
</tr>
<tr>
<td>CdSe</td>
<td>211.0</td>
<td>169.0</td>
<td>34.0</td>
<td>166.0</td>
<td>170.0</td>
<td>-</td>
<td>210.0</td>
<td>211.0</td>
</tr>
<tr>
<td>CdTe</td>
<td>167.0</td>
<td>139.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HgS</td>
<td>224.0</td>
<td>177.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HgSe</td>
<td>174.0</td>
<td>132.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HgTe</td>
<td>135.0</td>
<td>116.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* \(\hbar\omega_{LO}^*\) = Longitudinal Optical & \(\hbar\omega_{TO}^*\) = Transverse Optical

### Table 5

Bulk modulus \(B\) (10\(^{11}\) dyn/cm\(^2\)), shear modulus \(C_s\) (10\(^{11}\) dyn/cm\(^2\)), linear compressibility \(C_v\) (10\(^{-13}\) cm\(^2\)/dyn), and microhardness \(H\) (GPa) for group II-VI semiconductors at 300 K [15]

<table>
<thead>
<tr>
<th>Group II-VI compound</th>
<th>Zincblende</th>
<th>Wurtzite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(B)</td>
<td>(C_s)</td>
</tr>
<tr>
<td>ZnO</td>
<td>7.71</td>
<td>1.870</td>
</tr>
<tr>
<td>ZnS</td>
<td>6.24</td>
<td>1.750</td>
</tr>
<tr>
<td>ZnSe</td>
<td>5.10</td>
<td>1.540</td>
</tr>
<tr>
<td>ZnTe</td>
<td>6.16</td>
<td>1.160</td>
</tr>
<tr>
<td>CdS</td>
<td>5.31</td>
<td>1.020</td>
</tr>
<tr>
<td>CdSe</td>
<td>4.24</td>
<td>0.830</td>
</tr>
<tr>
<td>CdTe</td>
<td>6.86</td>
<td>0.955</td>
</tr>
<tr>
<td>HgS</td>
<td>5.00</td>
<td>0.810</td>
</tr>
<tr>
<td>HgSe</td>
<td>4.23</td>
<td>0.820</td>
</tr>
</tbody>
</table>

* Along a direction \(\perp\) c-axis, ** Along a direction \(/\) c-axis

### 1.1.5 Thermal Properties

Many practical uses of semiconductors demand knowledge of their thermal properties over a wide range of temperatures [15]. Table 6 gives the values of some of the most essential thermal properties of group II-VI semiconductors, such as the specific heat at constant pressure \(C_p\), Debye temperature \(\theta_D\), thermal expansion coefficient \(\alpha_{th}\), and thermal conductivity \(K\).
Table 6
Specific heat $C_p$, Debye temperature $\theta_D$, thermal expansion coefficient $\alpha_{th}$, and thermal conductivity $K$ for group II-VI semiconductors at 300 K [15]

<table>
<thead>
<tr>
<th>Group II-VI compound</th>
<th>$C_p$ (J/g-K)</th>
<th>$\theta_D$ (K)</th>
<th>$\alpha_{th}$ ($10^{-6}$ K$^{-1}$)</th>
<th>$K$ (W/cm-K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>0.497</td>
<td>416</td>
<td>2.49*</td>
<td>0.540</td>
</tr>
<tr>
<td>ZnS</td>
<td>0.486</td>
<td>351</td>
<td>6.71</td>
<td>0.270</td>
</tr>
<tr>
<td>ZnSe</td>
<td>0.360</td>
<td>340</td>
<td>7.80</td>
<td>0.190</td>
</tr>
<tr>
<td>ZnTe</td>
<td>0.258</td>
<td>260</td>
<td>8.33</td>
<td>0.180</td>
</tr>
<tr>
<td>CdS</td>
<td>0.328</td>
<td>310</td>
<td>2.77*</td>
<td>0.200</td>
</tr>
<tr>
<td>CdSe</td>
<td>0.281</td>
<td>135</td>
<td>2.76*</td>
<td>0.090</td>
</tr>
<tr>
<td>CdTe</td>
<td>0.211</td>
<td>44</td>
<td>4.67</td>
<td>0.075</td>
</tr>
<tr>
<td>HgS</td>
<td>-</td>
<td>-</td>
<td>4.30</td>
<td>-</td>
</tr>
<tr>
<td>HgSe</td>
<td>0.355</td>
<td>242</td>
<td>1.41</td>
<td>0.001 - 0.035</td>
</tr>
<tr>
<td>HgTe</td>
<td>0.162</td>
<td>-</td>
<td>4.70</td>
<td>0.023</td>
</tr>
</tbody>
</table>

* Along the $c$-axis

1.1.6 Optical Properties

The bandgap dependence on temperature is mainly due to the thermal dilation of the lattice and the temperature dependent electron-phonon interaction [14]. The behavior of $E_g$ as a function of temperature $T$ can be described by the formula:

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{\beta + T}$$

Where $T$ is in degrees K, and $\alpha$ and $\beta$ are constants. At high temperatures ($T \gg \beta$), Eq. 2 reads:

$$E_g(T) = E_g(0) - \alpha T \quad \frac{dE_g}{dT} = -\alpha$$

Table 7 shows the temperature coefficient of bandgap energy $\alpha$ for some group II-VI semiconductors. It also lists the free exciton binding ($E_1$) and photoluminescence PL ($\lambda$) transition energies.

Table 8, however, lists the refractive index, the static and high-frequency dielectric constants, $\varepsilon_S$ and $\varepsilon_{\infty}$, for some cubic as well as hexagonal group II-VI semiconductors.
Table 7
Temperature coefficient of bandgap energy $\alpha$, free exciton binding ($E_1$) and photoluminescence PL ($X$) transition energies for group II-VI semiconductors [14]

<table>
<thead>
<tr>
<th>Group II-VI compound</th>
<th>$\alpha$ (meV/K)</th>
<th>$E_1$ (meV)</th>
<th>$X$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>-</td>
<td>59</td>
<td>3.376 - 3.378</td>
</tr>
<tr>
<td>ZnS</td>
<td>0.880</td>
<td>38.0</td>
<td>3.800 - 3.820</td>
</tr>
<tr>
<td>ZnSe</td>
<td>0.670</td>
<td>20.0</td>
<td>2.800 - 2.804</td>
</tr>
<tr>
<td>ZnTe</td>
<td>0.630</td>
<td>12.8</td>
<td>2.380 - 2.381</td>
</tr>
<tr>
<td>CdS</td>
<td>0.386</td>
<td>29.0</td>
<td>2.551 - 2.553</td>
</tr>
<tr>
<td>CdSe</td>
<td>0.370</td>
<td>15.0</td>
<td>1.824 - 1.827</td>
</tr>
<tr>
<td>CdTe</td>
<td>0.460</td>
<td>11.0</td>
<td>1.595 - 1.597</td>
</tr>
</tbody>
</table>

Table 8
Refractive indices, static and high-frequency dielectric constants, $\varepsilon_S$ and $\varepsilon_\infty$, of group II-VI semiconductors [15, 16]

<table>
<thead>
<tr>
<th>Group II-VI compound</th>
<th>$n$</th>
<th>Zincblende $\varepsilon_S$</th>
<th>Zincblende $\varepsilon_\infty$</th>
<th>Wurtzite $\varepsilon_S$</th>
<th>Wurtzite $\varepsilon_\infty$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>2.02</td>
<td>-</td>
<td>-</td>
<td>7.80</td>
<td>3.7</td>
</tr>
<tr>
<td>ZnS</td>
<td>2.40</td>
<td>8.3</td>
<td>5.10</td>
<td>8.10</td>
<td>5.4</td>
</tr>
<tr>
<td>ZnSe</td>
<td>2.89</td>
<td>8.9</td>
<td>5.90</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ZnTe</td>
<td>3.56</td>
<td>9.4</td>
<td>6.90</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CdS</td>
<td>2.50</td>
<td>9.8</td>
<td>5.40</td>
<td>10.20</td>
<td>5.4</td>
</tr>
<tr>
<td>CdSe</td>
<td>-</td>
<td>9.6</td>
<td>6.20</td>
<td>9.29</td>
<td>6.2</td>
</tr>
<tr>
<td>CdTe</td>
<td>2.75</td>
<td>10.4</td>
<td>7.10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HgS</td>
<td>-</td>
<td>18.2</td>
<td>11.36</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HgSe</td>
<td>-</td>
<td>26.0</td>
<td>7.50</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HgTe</td>
<td>3.70</td>
<td>21.0</td>
<td>7.00</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* $E \perp c$-axis

1.1.7 Electrical Properties

Table 9 gives the electron and hole mobility at 300 K as well as the electron and hole effective mass for some group II-VI semiconductors.
Table 9
Electron and hole mobility and effective mass for some group II-VI semiconductors at 300 K [16, 17]

<table>
<thead>
<tr>
<th>Group II-VI compound</th>
<th>Mobility (cm²/V-s)</th>
<th>Effective Mass (m*/m₀)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>e</td>
<td>h</td>
</tr>
<tr>
<td>ZnO</td>
<td>200</td>
<td>180</td>
</tr>
<tr>
<td>ZnS</td>
<td>165</td>
<td>5</td>
</tr>
<tr>
<td>ZnSe</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>ZnTe</td>
<td>-</td>
<td>7</td>
</tr>
<tr>
<td>CdS</td>
<td>340</td>
<td>50</td>
</tr>
<tr>
<td>CdSe</td>
<td>800</td>
<td>-</td>
</tr>
<tr>
<td>CdTe</td>
<td>1050</td>
<td>100</td>
</tr>
</tbody>
</table>
1.2 Chemical Bath Deposition

Chemical bath deposition (CBD) 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 by a chemical reaction between dissolved precursors, with the help of a complexing agent. CBD has been used in the deposition of semiconductor thin films for over forty years [18]. Among all techniques used to grow Group II-VI semiconductors, CBD has the advantage of being a simple, low temperature, and inexpensive large-area deposition technique. CBD is presently attracting considerable attention as it does not require sophisticated instrumentation like vacuum system and other expensive equipments. The starting chemicals are commonly available and inexpensive. Using CBD, a large number of substrates can be coated in a single run. Unlike electroplating, electrical conductivity of the substrate is not a necessary requirement. Any insoluble surface to which the solution has a free access will be a suitable substrate for deposition, which makes CBD suitable for coating surfaces of any morphology and geometry. The low temperature deposition avoids oxidation and corrosion of metallic substrates. Chemical deposition results in pin hole free, uniform and highly stoichiometric films since the basic building blocks are ions instead of atoms. The preparative parameters are easily controllable and better orientations and improved grain structure can be obtained [19]. CBD has been extensively used in growing group II-VI semiconductors, such as CdS [18, 20-47], CdSe [48-54], CdO [55-58], HgS [59-61], HgSe [54, 62, 63], ZnS [64-75], ZnSe [76-83], and ZnO [84-94].
The deposition medium for CBD of “MX” thin films (M$^{2+}$ is Group II metal while X$^{2-}$ is Group VI chalcogenide) consists of one or more salts of Group II metal ion M$^{2+}$ (Zn$^{2+}$, Cd$^{2+}$, or Hg$^{2+}$), a source for the chalcogenide X$^{2-}$ (O$^{2-}$, S$^{2-}$, or Se$^{2-}$), and usually a complexing agent, in aqueous solution. The metal precursors/salts are expected to have moderate to high solubility in water, e.g., chlorides, iodides, acetates, nitrates, or sulfates. Chalcogenide sources typically include thiourea, thiosulfate, or thioacetamide for S$^{2-}$ ions, and selenourea, selenosulfate, or N,N-dimethylselenourea for Se$^{2-}$ ions, while the dissociation of water itself provides oxygen in the form of OH$^{-}$ ions. The complexing agent provides ligands such as ammonia, ethanolamine, ethylenediamine, methylamine, dimethylamine, triethanolamine, hydrazine, tartrate, citrate, cyanide, etc.

Chemical bath deposition is believed to be based on the following steps [95]:

1) Equilibrium between the complexing agent and water;
2) Formation/dissociation of ionic metal-ligand complexes $[M(L)_{i}]^{2-i}k$,
   where $L^{k-}$ denotes one or more ligands;
3) Hydrolysis of the chalcogenide source;
4) Formation of the solid.

Most of the control of the CBD process resides in adjustment of the last three steps. Hydrolysis of the chalcogenide source (step 3) is critical because it provides the desired non-metal species that pull the metal cations out of solution to form the solid film. This step is highly sensitive to the solution’s pH and temperature. The formation of the solid MX thin film (step 4) begins when the rising concentration of X$^{2-}$ from step 3 causes the ionic product $[M^{2+}][X^{2-}]$ to exceed the solubility product. In practice, the central issue is whether the solid forms as a film or as particles dispersed in the liquid;
and in the case of film formation, whether deposition proceeds by ion-by-ion growth on
the substrate (heterogeneous reaction) or by adsorption and coagulation of colloids that
were formed in the solution (homogeneous reaction). The formation of the metal ion
complex (step 2) allows control over the rate of formation of solid metal hydroxides,
which competes with step 4, which would otherwise occur immediately in the normally
alkaline solutions. These steps together determine the composition, growth rate,
microstructure, and topography of the resulting thin films.

1.2.1 Chemical Bath Deposition of CdS

Among all group II-VI semiconductors, chemical bath deposition of CdS is the most
extensively investigated. Ammonium hydroxide is by far the most complexing agent that
has been used in growing CdS thin films using CBD. It provides amine ligand which,
when added to cadmium, forms cadmium tetraamine complex Cd(NH$_3$)$_4^{2+}$.

\[
\text{Cd}^{2+} + 4\text{NH}_3 \leftrightarrow \text{Cd(NH}_3)_4^{2+} \tag{4}
\]

The stability constant of cadmium tetraamine is [96]:

\[
\beta = \frac{[\text{Cd(NH}_3)_4^{2+}]}{[\text{Cd}^{2+}][\text{NH}_3]^4} = 10^{7.12} \tag{5}
\]

The formation of cadmium tetraamine complex in the solution ensures the slow release of
Cd$^{2+}$ ions so that Cd(OH)$_2$ will be formed at the solid liquid interface (substrate) and not
in the solution itself; Cd(OH)$_2$ nuclei at the substrate will act as nucleation centers for
CdS by adsorbing S$^{2-}$ ions, thereby converting Cd(OH)$_2$ into CdS. It is widely believed
that Cd(OH)$_2$ acts as a catalyst for decomposition of thiourea (the S$^{2-}$ source). As a
result, sulfide formation will occur preferentially at the surface of the hydroxide layer on
the substrate rather than nucleate separately in the solution [97]. Once nucleation of CdS has begun on the substrate, it becomes easier for the film to grow. The crystals will continue to grow until the homogenous reaction dominates over the heterogeneous reaction which will result in the depletion of the Cd\(^{2+}\) and S\(^{2-}\) ions in the solution. In principle, the growth kinetics of CdS using ammonia can be explained on the basis of the following equations:

\[
\text{Cd}^{2+} + 4\text{NH}_3 \leftrightarrow \text{Cd} (\text{NH}_3)_4^{2+}, \quad \beta = 10^{7.2} \tag{4}
\]

\[
\text{NH}_3 + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^{-}, \quad K_b = 1.8 \times 10^{-5} \tag{6}
\]

\[
\text{Cd}^{2+} + 2\text{OH}^- \leftrightarrow \text{Cd} (\text{OH})_2, \quad K_{sp} = 2.2 \times 10^{-14} \tag{7}
\]

\[
\text{Cd} (\text{OH})_2 + \text{S}^{2-} \leftrightarrow \text{CdS} + 2\text{OH}^- \tag{8}
\]

Where the dissociation constant \(K_b\) of the base \(\text{NH}_3\) is defined as:

\[
K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5} \tag{9}
\]

While the solubility product constant \(K_{sp}\) of \(\text{Cd} (\text{OH})_2\) is defined as:

\[
K_{sp} = [\text{Cd}^{2+}][\text{OH}^-]^2 = 2.2 \times 10^{-14} \tag{10}
\]

Now using the definition

\[
p[X] = -\log_{10} [X] \tag{11}
\]

As well as the equality

\[
\text{p}[\text{OH}^-] = 14 - \text{pH} \tag{12}
\]

Equation 10 then reads

\[
\text{pH} = 0.5 \text{p}[\text{Cd}^{2+}] + 7.17 \tag{13}
\]
As shown in Fig. 4, plotting Eq.13 as pH versus p[Cd$^{2+}$] will result in a straight line known as the hydroxide line, where Cd(OH)$_2$ is formed in solution only for pH values above that line.

Now, putting $[\text{NH}_4^+] = [\text{OH}^-]$, equation 9 reads

$$p[\text{NH}_3] = 23.24 - 2pH$$  \hspace{1cm} (14)

For $[\text{NH}_3] >> 4[\text{Cd-salt}]$, $[\text{Cd(NH}_3)_2^{2+}] \approx [\text{Cd-salt}]$. So, as suggested by Kaur et al. [28], for 0.1 M of cadmium salt, equation 5 reads

$$p[\text{Cd}^{2+}] = 8.12 - 4p[\text{NH}_3]$$  \hspace{1cm} (15)

Substituting equation 14 into 15, we obtain

$$pH = \frac{1}{8} p[\text{Cd}^{2+}] + 10.6$$  \hspace{1cm} (16)

Plotting Eq.16 as pH versus p[Cd$^{2+}$] will result in a straight line known as the complex line (Fig. 4), where the Cd(NH$_3$)$_4^{2+}$ complex is stable only for pH values below that line.

As shown, the whole diagram can be divided by a vertical line into two regions; I and II. In region I, the complex line lies above the hydroxide line implying that Cd(OH)$_2$ and Cd(NH$_3$)$_4^{2+}$ complex inevitably exist together in the solution. According to Kitaev et al. and Kaur et al. [18, 28], the true equilibrium of the Cd-NH$_3$ system in the solution lies in the highlighted regions A$_I$ and A$_{II}$. Working at other points in the diagram requires additional introduction of an acid or alkali to establish the hydroxide line, otherwise films grown are non-uniform, powdery, no-adhesive, and of poor quality. This shows that by applying thermodynamic methods, it is possible to determine the region of interrelated values of pH, p[NH$_3$], and p[Cd-salt] within which formation of Cd(OH)$_2$ is possible,
hence decomposition of thiourea with the liberation of $S^{2-}$ ions, and consequently formation of CdS film on the substrate. The same methodology could be employed in CBD of other group II-VI semiconductor compounds, which facilitates the experimental search for optimum deposition conditions considerably.
Fig. 4 Graphical solution of Eq. 13 (hydroxide line) and Eq. 16 (complex line) for CBD of Cd-NH$_3$ system
1.3 Research Objectives

Chemical bath deposition is simple yet powerful technique that makes a significant contribution in solar cells fabrication industry. So far, its contribution in thin film solar cells has been mainly limited to growing n-type CdS and/or ZnS window layers for CdTe-based and CIGS-based solar cells. Meanwhile, most CBD-CdS thin films for example are grown using only ammonia as a complexing agent. In addition, optimization of CBD is mainly limited to maximizing growth rate. The main objective of this dissertation is to demonstrate that CBD is a simple and inexpensive alternative to other sophisticated more expensive techniques that are currently used in growing group II-VI thin film semiconductors for solar cells applications. First, we investigate nitrilotriacetic acid (NTA) as well as NTA + hydrazine as alternative complexing agents for CBD-CdS and we try to test a new approach to optimize the CBD process of CdS, using two different Cd-salts. Furthermore, we study the effect of changing Cd precursors on the optical / electrical properties, crystal structure, as well as film thickness, stoichiometry, and morphology of CBD-CdS.

Second, since CBD-CdS films are in general highly resistive due to their stoichiometry, we investigate in-situ doping of these films with group III elements, such as B, Al, In, and Ga using CBD. The objective is to show that CBD is capable of not only growing CdS but also of doping CdS to reduce its resistivity to a tolerable level, which in turn will facilitate its use in solar cells as well as other optoelectronic device fabrication.
Finally, we test the possibility of using CBD to grow transparent conducting oxide (TCO) films, such as Al-doped ZnO films and cadmium stannate films. First, we study CBD of ZnO and later in-situ doping of ZnO using Al. The goal is to grow transparent ZnO films using CBD that, with the help of in-situ doping, will have a resistivity of the order of $10^{-3}$ $\Omega$-cm to $10^{-4}$ $\Omega$-cm. Such films could be an alternative to indium tin oxide (ITO) layers that are commonly used as TCO layers for solar cells. Another approach that we plan to test is using CBD to grow CdO and SnO$_2$ thin films, with the goal of obtaining Cd$_2$SnO$_4$ by later annealing of these two layers. Cadmium stannate is another TCO candidate that could replace ITO in the near future. In summary, our main objective is to expand the use of CBD beyond CdS and ZnS and to test the possibility of using it for in-situ doping of group II-VI semiconductors and for TCO layers fabrication. We believe that this may have a significant impact on solar cells as well as other optoelectronic devices fabrication industry, due to the simplicity and the cost-effectiveness of CBD.
CHAPTER II: A NEW APPROACH TOWARDS OPTIMIZATION OF CBD-CdS

2.1 Optimization of CBD-CdS Thin Films Using Nitrilotriacetic Acid as a Complexing Agent

2.1.1 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 (CuInSe₂), and/or Cu(In,Ga)Se₂ (CIGS). It has been widely used as a window material in high efficiency thin film solar cells based on CdTe or CIGS [98, 99]. CdS has also been used in other applications including electronic and optoelectronic devices [100-102]. In the past few decades, several techniques such as thermal evaporation [103], radio frequency sputtering [104], physical vapor deposition [105], pulsed laser evaporation [106], molecular beam epitaxy [107], electrodeposition [108], spray pyrolysis [109], metal organic chemical vapor deposition [110], successive ionic layer adsorption reaction [111], screen printing [112], close spaced vapor transport [113], and chemical bath deposition [18, 27-37] 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 [1, 2].
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 [18]. Several ligands have been utilized in the deposition of CdS, such as NH$_3$ [18, 27-29], triethanolamine [30], ethylenediamine [31], ethylenediaminetetraacetic acid [32], nitrilotriacetic acid (NTA) [33, 34], cyano-complex [35], citrato-complex [36], and more recently tartaric acid [37].

However, the usage of NTA was reported only few times in the literature. Gorer and Hodes [34] 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. [33], on the other hand, studied the dependence of the film thickness on the deposition time, the deposition temperature, and the pH of the 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$^{-}$ 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$_4$ and CdCl$_2$ 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$_2$ layer on one side. All measurements were carried out on films deposited on the SnO$_2$ layer side.

In addition, two sets of films were deposited on quartz, one set using CdSO$_4$ and the other using CdCl$_2$ 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$_2$ 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 backscattering spectroscopy (RBS), and X-ray diffraction (XRD) for both films deposited on quartz were carried out.

2.1.2 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 x 38 mm x 3 mm of SnO$_2$ 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 [27]. 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 minutes was carried out, except for the deposition
on quartz where two successive depositions for 8 minutes each, were executed. Three
different bath temperatures; 55 °C, 70 °C, and 85 °C were studied. Two different Cd
sources, CdSO₄ and CdCl₂ were used as Cd precursors, with only thiourea as sulfur
precursor. KOH (assay 45% w/w) was used as the OH⁻ 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 α was calculated for each film using the equation:

\[ I_t = I_o \exp(-\alpha t) \]  \hspace{1cm} (17)

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

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

\[ \alpha = \frac{K(h\nu - E_g)^{n/2}}{h\nu} \]  \hspace{1cm} (18)
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 over 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 MU Tandetron, with a surface barrier detector with energy resolution \( \leq 15 \) keV (full width at half maximum—FWHM), positioned at a scattering angle of 165º. 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 2.5º and scanned from 25º – 70º in steps of 0.02º with a scan rate of 1.2º min\(^{-1}\).

2.1.3 Results and Discussion

2.1.3.1 CdSO\(_4\) – Based CdS Films

2.1.3.1.1 Effect of Changing [NTA]/[Cd] Ratio

Fig. 5(a) shows the dependence of film thickness on [NTA]/[Cd] ratio, with [CdSO\(_4\)] = 0.2 mmol, [CS(NH\(_2\))\(_2\)] = 0.4 mmol, KOH = 1.5 ml, bath temperature = 70 ºC, and 30 minutes 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 [33, 34] that with NTA as a complexing agent, the CdS deposition mechanism is based on the formation of Cd(NTA)\(^-\) or Cd(NTA)\(^4-\) complex in solution. However, according to our findings we believe that this is not always the case. As shown
in Fig. 5(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)$_7^{-}$ and/or Cd(NTA)$_{10}^{-}$ 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 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)$_x^{-}$ 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 minutes 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.
Fig. 5 Film thickness/ $E_g$ dependence on (a) [NTA]/[Cd] ratio, (b) KOH concentration (Films were deposited on $\text{SnO}_2$ coated soda lime glass)
The stability constants $K_1$ and $K_2$ for Cd(NTA)$^-$ and Cd(NTA)$_2^{4-}$ complexes at $25^\circ$C are given by [114]:

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

(19)

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

(20)

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

The transmission spectra for all these films are shown in Fig. 6(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. 5(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 [115] 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. 5a) 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.
Fig. 6 Transmission spectra of films deposited at different (a) [NTA]/[Cd] ratios, (b) KOH concentration (Films were deposited on SnO₂ coated soda lime glass)
2.1.3.1.2 Effect of Changing KOH Concentrations

With $[\text{CdSO}_4] = 0.2 \text{ mmol}$, $[\text{CS(NH}_2)_2] = 0.4 \text{ mmol}$, $[\text{NTA}] = 0.8 \text{ mmol}$ ($([\text{NTA}]/[\text{Cd}] = 4.0)$, bath temperature = 70 °C, and 30 minutes deposition time, CdS films were grown at different KOH concentrations (from 0.5 ml to 5.0 ml). As shown in Fig. 5(b), the film thickness increases dramatically from almost zero (no deposition observed) at 0.5 ml KOH to ~ 900Å at 1.5 ml KOH, after which the film thickness decreases rapidly with KOH concentration. This, in fact, agrees with the observations of Němec et al. [33], where they studied the dependence of the film thickness on the pH of the final solution.

The transmission spectra of the grown films (Fig. 6b) 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. 5(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. 5(a).

2.1.3.1.3 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. Table 10 summarizes the details and results of the experiment. 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>
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<th>Sample #</th>
<th>CdSO$_4$ (mmol)</th>
<th>Thiourea (mmol)</th>
<th>KOH (ml)</th>
<th>NTA (mmol)</th>
<th>Temperature (ºC)</th>
<th>Thickness (Å)</th>
<th>$E_g$ (eV)</th>
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<td>0.6</td>
<td>85</td>
<td>250</td>
<td>2.23</td>
</tr>
<tr>
<td>30</td>
<td>0.12</td>
<td>0.65</td>
<td>1</td>
<td>0.6</td>
<td>85</td>
<td>650</td>
<td>2.25</td>
</tr>
<tr>
<td>31</td>
<td>0.12</td>
<td>0.26</td>
<td>1</td>
<td>1.0</td>
<td>85</td>
<td>200</td>
<td>2.2</td>
</tr>
</tbody>
</table>
2.1.3.2 CdCl₂ – Based CdS Films

2.1.3.2.1 Effect of Changing [NTA]/[Cd] Ratio

Fig. 7(a) shows the dependence of film thickness on [NTA]/[Cd] ratio, with [CdCl₂] = 0.2 mmol, [CS(NH₂)₂] = 0.4 mmol, KOH = 2.0 ml, bath temperature = 70°C, and 30 minutes 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⁻ 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. 8(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 E₉ of these films as shown in Fig. 7(a).

2.1.3.2.2 Effect of Changing KOH Concentrations

With [CdCl₂] = 0.2 mmol, [CS(NH₂)₂] = 0.4 mmol, [NTA] = 0.8 mmol ([NTA]/[Cd] = 4.0), bath temperature = 70°C, and 30 minutes 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 CdSO₄ – based films is observed (Fig. 7b), 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 E₉ calculated for all 9 films are shown in Fig. 8(b) and Fig. 7(b), respectively. E₉ was found to be minimal for KOH concentrations between 2.5 ml and 4.0 ml.
Fig. 7 Film thickness/ $E_g$ dependence on (a) [NTA]/[Cd] ratio, (b) KOH concentration (Films were deposited on SnO$_2$ coated soda lime glass)
Fig. 8 Transmission spectra of films deposited at different (a) [NTA]/[Cd] ratios, (b) KOH concentration (Films were deposited on SnO$_2$ coated soda lime glass)
2.1.3.2.3 Optimization of CdCl$_2$ – Based CdS Films

With the help of the results we obtained, a set of 14 more experiments were devised. Table 11 lists the details of the experiments, film thickness and bandgap of all 14 films. As shown, 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.

Table 11
Thickness and $E_g$ of optimized CdCl$_2$ – based CdS films

<table>
<thead>
<tr>
<th>Sample #</th>
<th>CdCl$_2$ (mmol)</th>
<th>Thiourea (mmol)</th>
<th>KOH (ml)</th>
<th>NTA (mmol)</th>
<th>Temperature ($^\circ$C)</th>
<th>Thickness (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>48</td>
<td>0.055</td>
<td>0.13</td>
<td>1.5</td>
<td>0.6</td>
<td>55</td>
<td>No Film</td>
</tr>
<tr>
<td>49</td>
<td>0.055</td>
<td>0.65</td>
<td>1.5</td>
<td>0.6</td>
<td>55</td>
<td>225</td>
</tr>
<tr>
<td>50</td>
<td>0.33</td>
<td>0.13</td>
<td>1.5</td>
<td>0.6</td>
<td>55</td>
<td>350</td>
</tr>
<tr>
<td>51</td>
<td>0.33</td>
<td>0.13</td>
<td>1.5</td>
<td>1.0</td>
<td>55</td>
<td>175</td>
</tr>
<tr>
<td>52</td>
<td>0.055</td>
<td>0.65</td>
<td>2.5</td>
<td>0.6</td>
<td>55</td>
<td>275</td>
</tr>
<tr>
<td>53</td>
<td>0.055</td>
<td>0.13</td>
<td>2.5</td>
<td>1.0</td>
<td>55</td>
<td>No Film</td>
</tr>
<tr>
<td>54</td>
<td>0.33</td>
<td>0.65</td>
<td>2.5</td>
<td>1.0</td>
<td>55</td>
<td>1200</td>
</tr>
<tr>
<td>55</td>
<td>0.055</td>
<td>0.13</td>
<td>1.5</td>
<td>1.0</td>
<td>85</td>
<td>No Film</td>
</tr>
<tr>
<td>56</td>
<td>0.055</td>
<td>0.65</td>
<td>1.5</td>
<td>1.0</td>
<td>85</td>
<td>275</td>
</tr>
<tr>
<td>57</td>
<td>0.33</td>
<td>0.65</td>
<td>1.5</td>
<td>0.6</td>
<td>85</td>
<td>250</td>
</tr>
<tr>
<td>58</td>
<td>0.33</td>
<td>0.65</td>
<td>1.5</td>
<td>1.0</td>
<td>85</td>
<td>1000</td>
</tr>
<tr>
<td>59</td>
<td>0.055</td>
<td>0.65</td>
<td>2.5</td>
<td>0.6</td>
<td>85</td>
<td>175</td>
</tr>
<tr>
<td>60</td>
<td>0.055</td>
<td>0.13</td>
<td>2.5</td>
<td>1.0</td>
<td>85</td>
<td>200</td>
</tr>
<tr>
<td>61</td>
<td>0.33</td>
<td>0.13</td>
<td>2.5</td>
<td>0.6</td>
<td>85</td>
<td>200</td>
</tr>
</tbody>
</table>

2.1.3.3 Deposition on Quartz

Using only NTA as a ligand, we tried to deposit two sets of CdS films on quartz, one using CdSO$_4$ and the other using CdCl$_2$. Unfortunately, in contrast to what was reported earlier by Gorer and Hodes [34] and Němec et al. [33], 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$_2$ side only with little or no deposition occurs on the glass side of the substrate. We believe that the SnO$_2$ layer acts as nucleation sites for the Cd$^{2+}$ and S$^{2-}$ ions resulting in formation of CdS film only on the SnO$_2$ side of the substrate.

However, when hydrazine monohydrate was added, adherent, specularly reflecting, high quality CdS films were obtained. Two successive depositions, for 8 minutes each, were carried out on 38 mm x 38 mm x 3 mm quartz substrates at 70 °C for both films. In the case of CdSO$_4$-based film, we had [CdSO$_4$] = 0.2 mmol, [CS(NH$_2$)$_2$] = 0.4 mmol, [NTA] = 0.4 mmol, KOH = 0.5 ml, and 2.0 ml of hydrazine monohydrate (assay 100%). Similarly, in the case of CdCl$_2$-based CdS film, the same conditions were used except for the Cd source, where 0.2 mmol of CdCl$_2$ was used instead of 0.2 mmol CdSO$_4$.

High quality films were obtained with thickness of 0.10 μm in the case of CdSO$_4$-based film, and 0.12 μm in the case of CdCl$_2$-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 with NTA also reduced the stability constant of the Cd complex formed in the solution achieving the hydroxide line where Cd(OH)$_2$ was adsorbed on the glass substrate and then CdS was formed by adsorption of thiourea on the Cd(OH)$_2$ followed by decomposition of Cd(OH)$_2$-thiourea complex to CdS [18]. 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. 9(a). The CdCl₂-based film shows similar transmission to the CdSO₄-based films, although it has a 20% higher thickness than that of the CdSO₄ one. This can be explained by considering the SEM micrographs (Fig. 10) for both films showing the CdCl₂-based film to have a much smoother surface than the CdSO₄-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 CdCl₂-based film, although thicker, shows similar transmission to the CdSO₄-based films. $E_g$ of both films was calculated and shown in Fig. 9(b). CdSO₄-based film has a relatively higher $E_g$ (2.32 eV) than that of CdCl₂-based film (2.30 eV).

XRD patterns of both films are shown in Fig. 11. Both films are cubic with a strong (111) reflection at $2\theta = 26.5^\circ$, and two 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 CdSO₄-based film, and about 172 nm in the case of the CdCl₂-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 [28, 34]. 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. [33].

RBS spectra of both films are shown in Fig. 12. It seems that in both cases, there’s more cadmium in the film than sulfur.
Fig. 9 Transmission spectra (a) and $E_g$ (b) of CdS films deposited on quartz using two different Cd sources.
Fig. 10 SEM micrographs of CdS films deposited on quartz using two different Cd sources

Fig. 11 XRD patterns of CdS films deposited on quartz using two different Cd sources
Fig. 12 RBS spectrum of CdS films deposited on quartz using two different Cd sources
The ratio of sulfur to cadmium was found to be higher in the CdCl₂-based film (S: Cd = 1.08 ± 0.01) than in the CdSO₄-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 Cd²⁺ ions in the growth solution end up as excess Cd in the CdS film. Table 12 summarizes some of the differences observed between both CdS films grown on quartz.

Table 12
A summary of properties of CdSO₄–based and CdCl₂–based CdS films deposited on quartz

<table>
<thead>
<tr>
<th>Film type</th>
<th>CdSO₄ – based CdS film</th>
<th>CdCl₂ – based CdS films</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness</td>
<td>0.10 μm</td>
<td>0.12 μm</td>
</tr>
<tr>
<td>Optical band gap</td>
<td>2.32 eV</td>
<td>2.30 eV</td>
</tr>
<tr>
<td>Crystal Structure</td>
<td>Cubic</td>
<td>Cubic</td>
</tr>
<tr>
<td>Grain Size</td>
<td>176 nm</td>
<td>172 nm</td>
</tr>
<tr>
<td>S: Cd Ratio</td>
<td>1.00: 1.05</td>
<td>1.00: 1.08</td>
</tr>
</tbody>
</table>

2.1.4 Conclusion

High quality CdS thin films were deposited onto SnO₂ 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)₁₀⁻ 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$_4$-based, and CdCl$_2$-based CdS films respectively. XRD showed that both films are cubic with grain size of about 176 nm for CdSO$_4$-based and 172 nm for CdCl$_2$-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$_2$-based film. Finally, SEM surface morphologies of both films showed that the CdCl$_2$-based film has a much smoother surface than the CdCl$_2$-based film resulting in higher transmission.
2.2 Characterization of CdS Thin Films Grown by Chemical Bath Deposition Using Four Different Cadmium Sources

2.2.1 Introduction

Chemical bath deposition 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 [18, 116]. CdS has been used as a window material in high efficiency thin film solar cells based on CdTe and Cu(In,Ga)Se₂ (CIGS) [98, 99]. It has also been used in other applications including electronic and optoelectronic devices [100]. 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 cells applications [1, 2].

Deposition of CdS using CBD is based on the slow release of Cd²⁺ ions and S²⁻ ions in an aqueous alkaline bath and the subsequent condensation of these ions on substrates suitably mounted in the bath. The slow release of Cd²⁺ 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 Cd²⁺ ions. The S²⁻ 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 [38, 39], cadmium acetate [27, 28, 30, 31, 40], cadmium iodide/nitrate [41-43, 117], and cadmium chloride [40, 43]. The effect of Cd source on the film properties has drawn attention for some time. Kitaev et al. [117] found that when CdCl₂ was used as Cd source, the CdS film thickness was higher than when Cd(CH₃COO)₂, CdSO₄, or Cd(NO₃)₂ was used. They also reported the least thickness when CdI₂ was
used. Similar results were obtained when Ortega-Borges and Lincot [42] studied the CdS growth rate dependence on the Cd salt. The latter, ranked the Cd salts, based on the least film thickness obtained to the highest, in the following order: CdI₂, CdSO₄, Cd(NO₃)₂, Cd(CH₃COO)₂, CdCl₂. However, other than film thickness, very few details were mentioned in both studies about the effect of Cd source on other film properties. Table 13 shows a summary of optical/electrical properties and crystallinity of some CBD-CdS films reported in the literature.

Table 13
A summary of optical/electrical properties and crystallinity of 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 (°C)</th>
<th>Crystal structure</th>
<th>Eₔ (eV)</th>
<th>ρdark (Ω-cm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. CdCl₂</td>
<td>NH₄OH / NH₄Cl / TUᵇ</td>
<td>80</td>
<td>Hexagonal</td>
<td>2.45</td>
<td>10⁶-⁷</td>
<td>[40]</td>
</tr>
<tr>
<td></td>
<td>CdAc₂ᵃ</td>
<td></td>
<td>Amorphous</td>
<td>2.50</td>
<td>10⁶-⁷</td>
<td></td>
</tr>
<tr>
<td>2. CdCl₂</td>
<td>NH₄OH / NH₄Cl / TU</td>
<td>&gt; 40</td>
<td>Cubic</td>
<td>2.45</td>
<td>10⁶-⁸</td>
<td>[43]</td>
</tr>
<tr>
<td></td>
<td>CdI₂</td>
<td>&gt; 60</td>
<td>Hexagonal</td>
<td>2.62</td>
<td>10⁸-¹⁰</td>
<td></td>
</tr>
<tr>
<td>3. CdSO₄</td>
<td>NH₄OH / TU</td>
<td>60-85</td>
<td>Hexagonal</td>
<td>2.45</td>
<td>10⁷</td>
<td>[38]</td>
</tr>
<tr>
<td>5. CdSO₄</td>
<td>NH₄OH / TU</td>
<td>70</td>
<td>-</td>
<td>2.47</td>
<td>10⁸</td>
<td>[44]</td>
</tr>
<tr>
<td>6. CdAc₂</td>
<td>NH₄OH / NH₄Ac / TU</td>
<td>85</td>
<td>-</td>
<td>2.39</td>
<td>10⁶-⁷</td>
<td>[27]</td>
</tr>
<tr>
<td>7. CdAc₂</td>
<td>NH₄OH / NH₄Ac / TU</td>
<td>50-90</td>
<td>Mixed</td>
<td>2.35</td>
<td>10⁶-⁶</td>
<td>[45]</td>
</tr>
<tr>
<td>8. CdAc₂</td>
<td>TEA + NH₄OH / TU</td>
<td>30-85</td>
<td>-</td>
<td>10⁹</td>
<td></td>
<td>[46]</td>
</tr>
<tr>
<td>9. CdAc₂</td>
<td>Na₃C₆H₅O₇ / NH₄OH / TU</td>
<td>50-90</td>
<td>-</td>
<td>2.58</td>
<td>10⁸</td>
<td>[47]</td>
</tr>
<tr>
<td>10. Cd(NO₃)₂</td>
<td>NH₄NO₃ / NaOH / TU</td>
<td>20</td>
<td>Cubic</td>
<td>-</td>
<td>&gt; 10¹²</td>
<td>[41]</td>
</tr>
</tbody>
</table>

ᵃ Ac = Acetate; (CH₃COO)⁻; ᵇ TU = Thiourea; SC(NH₂)₂

As shown, only two attempts [40, 43] to study the effect of Cd source 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 source on the physical properties of CBD-CdS thin films.
2.2.2 Experimental Details

Each bath contained 100-120 ml of de-ionized water (resistivity \( \sim 18 \text{ M}\Omega\text{-cm} \)) kept under stirring at 70°C. Quartz substrates of 3.8 cm x 3.8 cm were used in the entire work. Single dip depositions (for 15 minutes) as well as multi-dip depositions (four successive depositions for 8-12 minutes 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. [117]. To ensure a stable complex, we employed ammonium salt as NH\(_3\) buffer. So, when CdSO\(_4\) was used as Cd source, \((\text{NH}_4)_2\text{SO}_4\) was used as a buffer and when CdCl\(_2\) was used as Cd source, \text{NH}_4\text{Cl} 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.

### Table 14

<table>
<thead>
<tr>
<th>Cd[L](_n)</th>
<th>Stability constant (log scale)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd[NH(_3)](_4^{2+})</td>
<td>7</td>
</tr>
<tr>
<td>Cd[SO(_4)](_3^{-})</td>
<td>&lt; 2</td>
</tr>
<tr>
<td>Cd[CH(_3\text{COO})](_2)</td>
<td>2.19</td>
</tr>
<tr>
<td>Cd[Cl(_4^{-})]</td>
<td>2.93</td>
</tr>
<tr>
<td>Cd[I(_4^{-})]</td>
<td>6.4</td>
</tr>
</tbody>
</table>
Table 14 summarizes the stability constants of these complementary Cd complexes as well as that of the Cd(NH$_3$)$_4^{2+}$ complex [96]. 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 whole deposition process. 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. 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. Film thickness measurements, calculations of optical absorption coefficient $\alpha$ and optical band gap $E_g$ as well as specifications of SEM, RBS, and XRD are previously reported in sec. 2.1.2.

2.2.3 Results and Discussion

2.2.3.1 Thickness Dependence on Cd Source

Table 15 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. [117], and Ortega-Borges and Lincot [42]. However, in our work, CdSO$_4$, not CdCl$_2$, results in the highest film thickness.

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

<table>
<thead>
<tr>
<th>Cd source</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdSO$_4$</td>
<td>95</td>
</tr>
<tr>
<td>Cd(CH$_3$COO)$_2$</td>
<td>90</td>
</tr>
<tr>
<td>CdCl$_2$</td>
<td>82.5</td>
</tr>
<tr>
<td>CdI$_2$</td>
<td>65</td>
</tr>
</tbody>
</table>

This can be understood by considering the role played by the complementary Cd complexes in the deposition process. Table 14 shows that Cd[I]$_4^{2-}$ complex has 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 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 Kitaev et al. [117] case, the Cl$^-$ concentration was too low to make 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 14), the role of the complementary Cd complexes in the growth process is very important.
2.2.3.2 Optical Properties

Fig. 13 shows optical transmission spectra of all four films. All films have high transmission, with the transmission in the CdCl₂ case better than that of the other three films. This was actually expected, since the SEM micrographs shown in Fig. 14, showed the CdCl₂-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 lower the transmission. As indicated in the captions of Fig. 13, there’s no appreciable difference in film thickness for all four films. Fig. 15 shows specular reflectance for the two films with highest and lowest transmission. Reflectance of CdCl₂-based film is higher than that of CdSO₄-based film. So, although no diffuse transmission/reflectance measurements were carried out, we believe that SEM micrographs as well as reflectance measurements are sufficient to conclude that surface morphology is responsible for higher transmission observed in the CdCl₂ case. Another observation about these transmission spectra is that CdI₂ and Cd(CH₃COO)₂-based films share the same absorption edge. A red shift (towards longer wavelengths) in the CdCl₂-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. 16. The optical band gap of the CdSO₄-based film is the highest (2.36 eV) while the band gap of the CdCl₂-based film is the lowest (2.25 eV). The CdI₂ and Cd(CH₃COO)₂-based films have an intermediate band gap (2.31 eV). This band gap dependence on Cd source agrees with what Rami et al. [40] and Nakanishi and Ito [43] reported earlier.
Fig. 13 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)

Fig. 14 SEM micrograph of CdS films grown using four different Cd sources
Fig. 15 Specular reflectance of CdCl$_2$-based film (0.20 μm) and CdSO$_4$-based film (0.18 μm)

Fig. 16 Optical band gap calculations of CdS films grown using four different Cd sources
Fig. 17 XRD pattern of CdS films grown using four different Cd sources
2.2.3.3 Crystal Structure

XRD patterns of the four films are shown in Fig. 17. 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 CdCl₂-based film case, which was found to be the (200) peak, which is also a characteristic peak of cubic CdS. Table 16 shows a summary of XRD data for standard cubic CdS powder [118] and all four films. The observed relative intensities imply 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: CdCl₂, CdI₂/Cd(CH₃COO)₂, CdSO₄. The relative intensities of both (220) and (311) peaks are closest to that of powder CdS when CdCl₂ is being used as Cd source (Table 17). Both peaks are more suppressed when Cd(CH₃COO)₂ and CdI₂ are being used, and almost totally suppressed when CdSO₄ is being used where their relative intensities decrease to less than 3%. This may explain the optical band gap variation with Cd source. Table 17 shows that as the (111) peak becomes more predominant and the other peaks get more suppressed, the band gap increases.

That’s why CdCl₂-based film has the least band gap (2.25 eV) and CdSO₄-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) [17]. The other two films are expected to have the same band gap since relative intensities of both (220) and (311) peaks in
Cd(CH$_3$COO)$_2$-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.

Table 16
A summary of XRD data for standard cubic CdS powder [118] and CdS films grown using four different Cd sources

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\theta$ (deg.)</th>
<th>d (nm)</th>
<th>(hkl)</th>
<th>I/I$_0$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic (powder)</td>
<td>26.547</td>
<td>0.33550</td>
<td>(1 1 1)</td>
<td>100.0</td>
</tr>
<tr>
<td></td>
<td>30.748</td>
<td>0.29055</td>
<td>(2 0 0)</td>
<td>21.6</td>
</tr>
<tr>
<td></td>
<td>44.040</td>
<td>0.20545</td>
<td>(2 2 0)</td>
<td>46.7</td>
</tr>
<tr>
<td></td>
<td>52.163</td>
<td>0.17521</td>
<td>(3 1 1)</td>
<td>33.2</td>
</tr>
<tr>
<td></td>
<td>54.670</td>
<td>0.16775</td>
<td>(2 2 2)</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>64.042</td>
<td>0.14528</td>
<td>(4 0 0)</td>
<td>5.8</td>
</tr>
<tr>
<td>CdSO$_4$-based film</td>
<td>26.640</td>
<td>0.33434</td>
<td>(1 1 1)</td>
<td>100.0</td>
</tr>
<tr>
<td></td>
<td>44.435</td>
<td>0.20372</td>
<td>(2 2 0)</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td>52.280</td>
<td>0.17484</td>
<td>(3 1 1)</td>
<td>2.7</td>
</tr>
<tr>
<td>Cd(CH$_3$COO)$_2$-based film</td>
<td>26.580</td>
<td>0.33509</td>
<td>(1 1 1)</td>
<td>100.0</td>
</tr>
<tr>
<td></td>
<td>44.180</td>
<td>0.20483</td>
<td>(2 2 0)</td>
<td>18.4</td>
</tr>
<tr>
<td></td>
<td>52.240</td>
<td>0.17497</td>
<td>(3 1 1)</td>
<td>13.5</td>
</tr>
<tr>
<td>CdCl$_2$-based film</td>
<td>26.800</td>
<td>0.33239</td>
<td>(1 1 1)</td>
<td>100.0</td>
</tr>
<tr>
<td></td>
<td>30.837</td>
<td>0.28973</td>
<td>(2 0 0)</td>
<td>9.3</td>
</tr>
<tr>
<td></td>
<td>44.079</td>
<td>0.20528</td>
<td>(2 2 0)</td>
<td>28.9</td>
</tr>
<tr>
<td></td>
<td>52.480</td>
<td>0.17422</td>
<td>(3 1 1)</td>
<td>19.4</td>
</tr>
<tr>
<td>CdI$_2$-based film</td>
<td>26.939</td>
<td>0.33070</td>
<td>(1 1 1)</td>
<td>100.0</td>
</tr>
<tr>
<td></td>
<td>44.323</td>
<td>0.20421</td>
<td>(2 2 0)</td>
<td>16.4</td>
</tr>
<tr>
<td></td>
<td>52.640</td>
<td>0.17373</td>
<td>(3 1 1)</td>
<td>11.8</td>
</tr>
</tbody>
</table>

Table 17
A summary of relative peak intensities and optical band gap for CdS films grown using four different Cd sources

<table>
<thead>
<tr>
<th>(hkl)</th>
<th>Cubic (powder)</th>
<th>CdCl$_2$-based film</th>
<th>Cd(CH$_3$COO)$_2$-based film</th>
<th>CdI$_2$-based film</th>
<th>CdSO$_4$-based film</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I/I$_0$ (%)</td>
<td>I/I$_0$ (%)</td>
<td>I/I$_0$ (%)</td>
<td>I/I$_0$ (%)</td>
<td>I/I$_0$ (%)</td>
</tr>
<tr>
<td>(111)</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>(220)</td>
<td>46.7</td>
<td>28.9</td>
<td>18.4</td>
<td>16.4</td>
<td>2.9</td>
</tr>
<tr>
<td>(311)</td>
<td>33.2</td>
<td>19.4</td>
<td>13.5</td>
<td>11.8</td>
<td>2.7</td>
</tr>
<tr>
<td>Optical band gap (eV)</td>
<td>2.25</td>
<td>2.31</td>
<td>2.31</td>
<td>2.31</td>
<td>2.36</td>
</tr>
</tbody>
</table>

Such band gap dependence on film crystallinity has been observed for CuInSe$_2$ as well as CuGaSe$_2$ polycrystalline thin films; Chichibu et al. [119] 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 CuGaSe₂ films.

The average crystallite size (Table 18) was calculated using the Debye-Scherrer formula [120]. The noticeable difference in grain size between the CdSO₄ film and the other films may be attributed to the fact that there’re two different deposition processes in CBD that compete with each other [28]; cluster by cluster deposition and ion by ion deposition.

<table>
<thead>
<tr>
<th>Cd source</th>
<th>Grain size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdSO₄</td>
<td>145</td>
</tr>
<tr>
<td>CdI₂</td>
<td>13</td>
</tr>
<tr>
<td>Cd(CH₃COO)₂</td>
<td>14</td>
</tr>
<tr>
<td>CdCl₂</td>
<td>16</td>
</tr>
</tbody>
</table>

Now, since using CdSO₄ 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.
2.2.3.4 Stoichiometry

Using RBS measurements, the stoichiometry of all films were studied. Simulation using Rutherford universal manipulation program (RUMP) [121] was implemented to find the best possible match to the RBS spectra. As shown in Fig. 18, the S: Cd ratio was found to be (1.00: 1.00 ± 0.01) in the case of CdI₂-based film as well as CdCl₂-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 ± 0.01) when Cd(CH₃COO)₂ was used.

This ratio decreased further to (1.00: 1.09 ± 0.01) when CdSO₄ was used. These ratios appear to agree with the Cd-complex stability constants (Table 14). Apparently, the smaller the stability constant of the complementary complex the more the Cd²⁺ 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 Cd²⁺ and S²⁻ is well controlled leading to a highly stoichiometric CdS film.

2.2.3.5 Hall Effect Measurements

Table 19 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 CdSO₄, Cd(CH₃COO)₂, CdCl₂/CdI₂. According to the RBS results, the S: 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 and act as donors and result in an increase in the carrier concentration and a consequent decrease in the resistivity.
Fig. 18 RBS spectrum and RUMP simulation of CdS films grown using four different Cd sources
Table 19
Hall effect and RBS measurements

<table>
<thead>
<tr>
<th>Cd source</th>
<th>S: Cd ratio</th>
<th>Carrier concentration (cm$^{-3}$)</th>
<th>Resistivity ($\Omega$-cm)</th>
<th>Mobility (cm$^2$/V-S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdSO$_4$</td>
<td>1.00: 1.09</td>
<td>$1.68 \times 10^{16}$</td>
<td>$8.01 \times 10^{1}$</td>
<td>4.64</td>
</tr>
<tr>
<td>Cd(CH$_3$COO)$_2$</td>
<td>1.00: 1.06</td>
<td>$8.83 \times 10^{15}$</td>
<td>$3.38 \times 10^{2}$</td>
<td>2.09</td>
</tr>
<tr>
<td>CdCl$_2$</td>
<td>1.00: 1.00</td>
<td>$9.74 \times 10^{14}$</td>
<td>$2.96 \times 10^{3}$</td>
<td>2.17</td>
</tr>
<tr>
<td>CdI$_2$</td>
<td>1.00: 1.00</td>
<td>$8.19 \times 10^{14}$</td>
<td>$3.88 \times 10^{3}$</td>
<td>1.96</td>
</tr>
</tbody>
</table>

The mobility measurements show the Cd(CH$_3$COO)$_2$, 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 (Table 18); 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 [122]. 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 [122, 123].

2.2.4 Conclusion

A comprehensive study of the influence of the Cd source 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$_3$COO)$_2$, CdCl$_2$, CdI$_2$. However, the band gap was found to decrease in the order CdSO$_4$, Cd(CH$_3$COO)$_2$/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$_3$COO)$_2$, CdI$_2$. The RBS data showed that the usage of CdCl$_2$ and CdI$_2$ results in
highly stoichiometric films (S: Cd ratio = 1:1). More Cd was detected when CdSO$_4$ and Cd(CH$_3$COO)$_2$ were used. The S: Cd ratio and carrier concentration were found to decrease in the order CdSO$_4$, Cd(CH$_3$COO)$_2$, 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.
CHAPTER III: IN–SITU DOPING OF CBD–CdS USING GROUP III ELEMENTS

3.1 Investigation of Aluminum and Indium In-situ Doping of Chemical Bath Deposited CdS Thin Films

3.1.1 Introduction

Chemical bath deposition 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 [18, 116]. CdS films grown by CBD are known to be highly stoichiometric and exhibit a high dark resistance. Table 20 summarizes the dark resistances reported in the literature for several CBD-CdS thin films. We have shown earlier [21] that with NH$_3$ as complexing agent and thiourea as 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/resistivity in CdS films was established. It was shown that using CdCl$_2$/CdI$_2$ as Cd sources results in highly stoichiometric films with 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 [20], 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.

Table 20
A summary of 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{\textsubscript{deposition}} (\textdegree C)</th>
<th>(\rho\text{\textsubscript{dark}}) ((\Omega\text{-cm}))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. CdCl\textsubscript{2}</td>
<td>NH\textsubscript{4}OH / NH\textsubscript{4}Cl / TU\textsuperscript{b}</td>
<td>80</td>
<td>(10^6)</td>
<td>[40]</td>
</tr>
<tr>
<td>CdAc\textsubscript{2}\textsuperscript{a}</td>
<td></td>
<td></td>
<td>(10^6)</td>
<td></td>
</tr>
<tr>
<td>2. CdCl\textsubscript{2}</td>
<td>NH\textsubscript{4}OH / NH\textsubscript{4}Cl / TU</td>
<td>&gt; 40</td>
<td>(10^6)</td>
<td>[43]</td>
</tr>
<tr>
<td>CdI\textsubscript{2}</td>
<td>NH\textsubscript{4}OH / NH\textsubscript{4}I / TU</td>
<td>&gt; 60</td>
<td>(10^6)</td>
<td></td>
</tr>
<tr>
<td>3. CdSO\textsubscript{4}</td>
<td>NH\textsubscript{4}OH / TU</td>
<td>60 - 85</td>
<td>(10^7)</td>
<td>[38]</td>
</tr>
<tr>
<td>4. CdSO\textsubscript{4}</td>
<td>NH\textsubscript{4}OH / N\textsubscript{2}H\textsubscript{4} / TU</td>
<td>60</td>
<td>(10^{10})</td>
<td>[39]</td>
</tr>
<tr>
<td>5. CdSO\textsubscript{4}</td>
<td>NH\textsubscript{4}OH / TU</td>
<td>70</td>
<td>(10^8)</td>
<td>[44]</td>
</tr>
<tr>
<td>6. CdCl\textsubscript{2}</td>
<td>NH\textsubscript{4}OH / NH\textsubscript{4}Cl / TU</td>
<td>70</td>
<td>(10^3)</td>
<td>[21]</td>
</tr>
<tr>
<td>CdI\textsubscript{2}</td>
<td>NH\textsubscript{4}OH / NH\textsubscript{4}I / TU</td>
<td></td>
<td>(10^3)</td>
<td></td>
</tr>
<tr>
<td>CdAc\textsubscript{2}</td>
<td>NH\textsubscript{4}OH / NH\textsubscript{4}Ac / TU</td>
<td></td>
<td>(10^2)</td>
<td></td>
</tr>
<tr>
<td>CdSO\textsubscript{4}</td>
<td>NH\textsubscript{4}OH / (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} / TU</td>
<td></td>
<td>(10^1)</td>
<td></td>
</tr>
<tr>
<td>7. CdAc\textsubscript{2}</td>
<td>NH\textsubscript{4}OH / NH\textsubscript{4}Ac / TU</td>
<td>50 - 90</td>
<td>(10^4)</td>
<td>[45]</td>
</tr>
<tr>
<td>8. CdAc\textsubscript{2}</td>
<td>TEA + NH\textsubscript{4}OH / TU</td>
<td>30 - 85</td>
<td>(10^8)</td>
<td>[46]</td>
</tr>
<tr>
<td>9. CdAc\textsubscript{2}</td>
<td>Na\textsubscript{3}C\textsubscript{6}H\textsubscript{5}O\textsubscript{7} / NH\textsubscript{4}OH / TU</td>
<td>50 - 90</td>
<td>(10^8)</td>
<td>[47]</td>
</tr>
<tr>
<td>10. Cd(NO\textsubscript{3})\textsubscript{2}</td>
<td>NH\textsubscript{4}NO\textsubscript{3} / NaOH / TU</td>
<td>20</td>
<td>(&gt; 10^{12})</td>
<td>[41]</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Ac = Acetate; (CH\textsubscript{3}COO)\textsuperscript{-}
\textsuperscript{b} TU = Thiourea; SC(N\textsubscript{2}H\textsubscript{2})

One approach to reduce the dark resistivity of CBD-CdS is \textit{in-situ} doping. Over the past two decades, \textit{in-situ} doping of CBD-CdS using Cu [124, 125], Li [126, 127], Na [128], Al [129, 130], and B [45, 131] has been reported. Ag-doping of CBD-CdS was carried out using ion exchange process [132, 133], and In-doped CdS films were grown by co-evaporation of CdS and Indium [134, 135]. In this work, \textit{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\textsuperscript{3+}/In\textsuperscript{3+} doping through chemical bath deposition. 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.
Resistivity, carrier concentration, and mobility of doped films were acquired using Hall effect measurements. Crystal structure as well as crystal quality and phase transition were determined using X-ray diffraction and Micro-Raman spectroscopy. Film morphology was studied using Scanning Electron Microscopy. Film chemistry and binding states were studied using X-ray photoelectron spectroscopy (XPS).

3.1.2 Experimental Details

CdS films were prepared using stock solutions of CdSO₄ (0.038 M), (NH₄)₂SO₄ (0.076 M), NH₄OH (29.4 %), and (NH₂)₂CS (0.076 M). Films were grown on 38 mm x 38 mm x 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 Al₂(SO₄)₃/InCl₃ to the main solution. The deposition temperature was kept constant at 85 ºC. Details of the growth process have been previously reported [21]. 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 minutes, etched with H₂O₂: H₂SO₄ (1:1 solution) for 5 minutes, etched in dilute HF for 1 minute, and then cleaned ultrasonically in de-ionized water for 5 minutes. After deposition, all films were annealed at 300 ºC in Argon ambient for 1 hour.

Specular transmittance and reflectance measurements were carried out at room temperature in the wavelength range from 350 to 1200 nm. The optical absorption coefficient α was calculated for each film using the equation [16]:

\[ T = (1 - R)^2 \exp(-\alpha t) \]  
(21)
where $T$ is transmittance, $R$ is reflectance, and $t$ is film thickness.

XRD was carried out from $25^\circ$-$55^\circ$ in steps of $0.02^\circ$ with a scan rate of $1.2^\circ \text{ min}^{-1}$. Hall measurements were acquired at room temperature using an automated Hall effect system (Ecopia HMS-3000, Bridge Technology, Chandler Heights AZ, USA) with a $0.55 \ T$ magnetic induction. Further details of Hall measurements are reported in sec. 2.2.2. Micro-Raman scattering was performed at room temperature with a Horiba Jobin Yvon LabRam IR system at a spatial resolution of $2 \mu \text{m}$ in a backscattering configuration. A $632.8 \text{ nm}$ line of a Helium Neon laser was used for off-resonance excitation with less than $4 \text{mW}$ power at the sample. The spectral resolution was $2 \text{ cm}^{-1}$, and the instrument was calibrated to the same accuracy using a naphthalene standard. XPS was performed on a Physical Electronics PHI 5400 ESCA using unmonochromated Mg K$\alpha$ radiation at $1253.6 \text{ eV}$. Each of the XPS spectra was acquired from 30 repeated sweeps. Spectra were corrected from charging effects by referencing the adventitious C 1s peak to $284.6 \text{ eV}$. Film thickness measurements, calculations of the optical band gap $E_g$ as well as specifications of spectrophotometer, SEM, and XRD are previously reported in sec. 2.1.2.

3.1.3 Results and Discussion

3.1.3.1 Investigation of Aluminum Doping

Fig. 19 shows optical transmittance and reflectance spectra of all Al-doped films grown at different $[\text{Al}] / [\text{Cd}]$ ratios. The $[\text{Al}] / [\text{Cd}]$ ratio in solution was varied from 0.018 to 0.18. It should be noted that a ratio of zero was assigned to 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.
Fig. 19 Specular transmittance and reflectance spectra of Al-doped CdS films grown at different [Al] / [Cd] ratios (R denotes [Al] / [Cd] ratio & R = 0.000 refers to undoped film)

Fig. 20 Optical bandgap calculations of Al-doped CdS films grown at different [Al] / [Cd] ratios (R denotes [Al] / [Cd] ratio & R = 0.000 refers to undoped film)
Table 21
Film Thickness of Al-doped CdS films grown at different [Al] / [Cd] ratio (0.000 ratio is assigned to 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>

The variation in transmittance with [Al] / [Cd] ratio is likely attributed to variation in film thickness. Table 21 shows that thickness of doped films increases at first and then decreases. This may explain why transmittance drops at first and then rises as [Al] / [Cd] ratio increases. A red shift in the absorption edge towards lower band gap is noticed in almost all doped films. The magnitude of the red shift was found to fluctuate as [Al] / [Cd] ratio increases. Using transmittance and reflectance data, the absorption coefficient $\alpha$ was calculated (using Eq. 21) and was then used to determine the band gap, as shown in Fig. 20. As shown in Fig. 21, the bandgap of 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. Undoped film has a band gap of 2.41 eV which agrees well with the 2.42 eV band gap of single crystal CdS [17].

XRD patterns of Al-doped films as well as undoped film are shown in Fig. 22. We have shown earlier [21] that as-grown CdS films are polycrystalline and cubic in nature, with a preferred orientation along the (111) direction. We have also shown that the degree of texture along the (111) orientation highly depends on the Cd source used.
Fig. 21 Optical bandgap of Al-doped CdS films as a function of [Al] / [Cd] ratio

Fig. 22 XRD pattern of Al-doped CdS films grown at different [Al] / [Cd] ratios (R denotes [Al] / [Cd] ratio & R = 0.000 refers to undoped film)
When CdSO₄ is being used as the Cd source, which is the case in this work, the (220) and (311) peaks are almost totally suppressed and only the (111) 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 cubic phase to hexagonal phase. The critical point for such phase transition was reported to be 300 °C [136], above which hexagonal phase predominates over cubic phase. Since all films were annealed at 300 °C, it is difficult to determine if the peak shown in Fig. 22 is the (111) peak of the cubic phase or the (002) peak of the hexagonal phase which coincides with the (111) 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 (111) peak of cubic CdS.

As shown in Fig. 22, 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 (111) 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 Fig. 23, as \([\text{Al}] / [\text{Cd}]\) ratio increases, the spacing of the (111) lattice planes decreases below that of undoped film until it reaches a minimum at a ratio of 0.055 and then it starts to increase as the \([\text{Al}] / [\text{Cd}]\) ratio increases, and once that ratio exceeds 0.11, the \(d_{(111)}\) value goes beyond that of undoped CdS film. Now, since the ionic radius of Al³⁺ (0.50 Å) is smaller than that of Cd²⁺ (0.97 Å) [137], this suggests that at low \([\text{Al}] / [\text{Cd}]\) ratio, Al³⁺ ions replace Cd²⁺ ions in the lattice substitutionally which in turn results in smaller \(d_{(111)}\) value than that of undoped CdS film.
Fig. 23 Average (111) interplanar distance $d_{(111)}$ and relative intensity $I / I_0$ of the (111) peak with respect to that of undoped film as a function of [Al] / [Cd] ratio.

Fig. 24 Grain size dependence on [Al] / [Cd] ratio.
As this ratio increases beyond 0.055, Al$^{3+}$ ions start to enter the lattice both substitutionally and interstitially which caused the $d_{(111)}$ values to increase again. As the $[\text{Al}] / [\text{Cd}]$ ratio exceeds 0.11, most Al$^{3+}$ ions incorporated in the lattice are in interstitial sites which caused $d_{(111)}$ values to exceed that of undoped film. This will have an impact on the electrical properties of Al-doped films as Hall measurements will show later. Fig. 23 also shows the relative intensity of the (111) 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 $[\text{Al}] / [\text{Cd}]$ ratio is almost opposite to that of $d_{(111)}$ values. This confirms our conclusion that Al$^{3+}$ ions enter the lattice substitutionally at low concentration, and interstitially at high concentration. The grain size shown in Fig. 24 was calculated using the formula $D = \frac{0.9 \lambda}{\beta \cos \theta}$, where $\beta$ is the full width at half maximum (FWHM) in radians. In agreement with the thickness measurements (Table 21), the grain size increases with the $[\text{Al}] / [\text{Cd}]$ ratio, and then as this ratio exceeds 0.055, the grain size decreases as $[\text{Al}] / [\text{Cd}]$ ratio increases.

This can also explain the way the bandgap varies with $[\text{Al}] / [\text{Cd}]$ ratio. As suggested by Lokhande and Pawar [129] and later by Akintunde [130], incorporation of Al as well as sulfur deficiency in Al-doped films gives rise to donor levels in the bandgap of CdS. As Al concentration increases which in turn increases 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 $[\text{Al}] / [\text{Cd}]$ ratio goes beyond 0.055 may be attributed to decrease in grain size of doped films (Fig. 24) which causes an increase in lattice strain in the film.
We have observed in a previous work [20] that such increase in lattice strain (due to decrease in film thickness/grain size) increases the bandgap of CdS films.

Fig. 25 shows the carrier concentration (C.C.) as a function of [Al] / [Cd] ratio. The undoped film has a C.C. of about 4 x 10^{16} cm^{-3}. The C.C. increases with [Al] / [Cd] ratio until it reaches a maximum (~ 1.1 x 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 x 10^{18} cm^{-3} at a ratio of 0.18. The film resistivity as a function of [Al] / [Cd] ratio is shown in Fig. 26. The dark resistivity drops from 1.03 x 10^{2} \ \Omega \cdot \text{cm} \ (\text{undoped film}) \ to \ a \ minimum \ of \ 4.6 \times 10^{-2} \ \Omega \cdot \text{cm} \ at \ a \ ratio \ of \ 0.036 \ and \ 0.055, \ after \ which \ it \ increases \ until \ it \ reaches \ 1.45 \times 10^{-1} \ \Omega \cdot \text{cm} \ at \ a \ ratio \ of \ 0.18. \ This \ agrees \ with \ the \ d_{(111)} \ values \ variation \ with \ [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 \ C.C. \ 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 \ centers \ decreasing \ the \ C.C. \ and \ increasing \ the \ resistivity. \ Such \ behavior \ of \ C.C. \ as \ well \ as \ dark \ resistivity \ has \ been \ also \ reported \ by \ Lokhande \ and \ Pawar [129] \ and \ by \ Akintunde [130]. \ It \ should \ be \ noted \ that, \ although \ C.C. \ at \ 0.055 \ ratio \ (9.52 \times 10^{18} \ \text{cm}^{-3}) \ is \ less \ than \ that \ at \ 0.036 \ ratio \ (~ 1.1 \times 10^{19} \ \text{cm}^{-3}), \ both \ films \ appear \ to \ have \ the \ same \ resistivity. \ This \ can \ be \ understood \ by \ considering \ the \ Hall \ mobility (\mu) \ values \ shown \ in \ Fig. 27. \ The \ Hall \ mobility \ at \ a \ ratio \ of \ 0.055 \ was \ 14.25 \ (\text{cm}^{2}/\text{V-S}) \ while \ the \ Hall \ mobility \ at \ a \ ratio \ of \ 0.036 \ was \ 12.33 \ (\text{cm}^{2}/\text{V-S}). \ This \ difference \ compensated \ for \ the \ C.C. \ 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. [134] \ and \ Hayashi \ et \ al. [135].
Fig. 25 Carrier concentration dependence on [Al] / [Cd] ratio

Fig. 26 Dark resistivity as a function of [Al] / [Cd] ratio
Fig. 27 Variation of Hall mobility with [Al] / [Cd] ratio

Fig. 28 Raman spectra of Al-doped films grown at different [Al] / [Cd] ratio (R denotes [Al] /[Cd] ratio)
Fig. 29 Deconvolution of the 303 cm\(^{-1}\) Raman peak of film grown at [Al] / [Cd] ratio of 0.018 into three peaks using Gaussian fit

![Deconvolution of the 303 cm\(^{-1}\) Raman peak of film grown at [Al] / [Cd] ratio of 0.018 into three peaks using Gaussian fit](image)

Fig. 30 Phase transition of undoped film due to annealing as detected by Raman; (a) Substrate, (b) As-grown undoped CdS film, and (c) Annealed undoped CdS film

![Phase transition of undoped film due to annealing as detected by Raman](image)
Variation of $\mu$ with respect to [Al] / [Cd] ratio agrees to some extent with the way grain size changes with respect to [Al] / [Cd] ratio (Fig. 24). Fig. 28 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; 2LO (Longitudinal Optical) [146] 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. Fig. 29 shows the deconvolution of the 303 cm$^{-1}$ peak of film grown at [Al] / [Cd] ratio of 0.018, using Gaussian fit from which peak position and FWHM have been obtained. It should be noted that Gaussian fit gave better fit than 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 Fig. 29, that peak can be deconvoluted into three different peaks; the highest at 302.8 cm$^{-1}$ with a FWHM of 12.8 cm$^{-1}$, the middle at 287.5 cm$^{-1}$ with a FWHM of 25.0 cm$^{-1}$, and the lowest peak at 258.3 cm$^{-1}$ with a FWHM of 30.0 cm$^{-1}$. The prominent peak at 302.8 cm$^{-1}$ is attributed to either the cubic 1LO phonon [144] or the hexagonal $A_1$(LO) / $E_1$(LO) phonons [140]. The peak observed at 258.3 cm$^{-1}$ is the $E_2$ peak of hexagonal CdS [141, 143]. However, the peak observed at 287.5 cm$^{-1}$ is attributed to a shift in either the TO (Transverse Optical) peak of cubic CdS [144] or the $E_1$(TO) peak of hexagonal CdS [143]. This Raman shift results from a phase transition in CdS film, from cubic to hexagonal, due to annealing at 300 °C. Zelaya-Angel et al. [138] reported similar shift for CdS films annealed at 350 °C, where they observed the $E_1$(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 $E_1$(TO) peak to shift from 240 cm$^{-1}$ (original position in hexagonal CdS [143]) to 283 cm$^{-1}$. A similar
shift in the TO peak of cubic CdS (originally at 246 cm\(^{-1}\) [144]) will position this peak at about 290 cm\(^{-1}\). Since the peak they observed for 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\(_1\)(TO) peak of hexagonal CdS. In our work, however, this peak is observed at 287.5 cm\(^{-1}\) rather than 276 cm\(^{-1}\), which may be attributed to the TO phonon of cubic CdS rather than the E\(_1\)(TO) peak of hexagonal CdS. No peaks were detected for the A\(_1\)(TO) phonon of hexagonal CdS. Table 22 lists some of the experimental and theoretical values reported for A\(_1\)(LO), A\(_1\)(TO), E\(_1\)(LO), E\(_1\)(TO), and E\(_2\) phonons for hexagonal single crystal CdS as well as values of 1LO, 2LO, and TO phonons for cubic CdS.

Table 22
A summary of E\(_1\)(LO), E\(_1\)(TO), A\(_1\)(LO), A\(_1\)(TO), and E\(_2\) Raman peaks position of hexagonal CdS as well as 1LO, 2LO, and TO Raman peaks position of cubic CdS reported in the literature

<table>
<thead>
<tr>
<th>Hexagonal CdS</th>
<th>Cubic CdS</th>
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<tbody>
<tr>
<td>E(_1)(LO)</td>
<td>A(_1)(LO)</td>
</tr>
<tr>
<td>305</td>
<td>305</td>
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<tr>
<td>307</td>
<td>305</td>
</tr>
<tr>
<td>306.9</td>
<td>303.6</td>
</tr>
<tr>
<td>308</td>
<td>298</td>
</tr>
</tbody>
</table>

Fig. 30 shows an example of the effect of annealing on Micro-Raman spectra of CdS undoped film. As shown in Fig. 30 (b), the 1LO peak observed at 303 cm\(^{-1}\) for as-grown undoped film is clearly symmetric. A Gaussian fit is shown in the inset of Fig. 30 (b), according to which the peak has a FWHM of \(~16.6\) cm\(^{-1}\). Fig. 30 (c) shows Micro-Raman for the same undoped film after annealing; the peak is obviously asymmetric. Deconvolution of the peak using Gaussian fit is shown in the inset of Fig. 30 (c). It consists of three different peaks at 258.5 cm\(^{-1}\), 288 cm\(^{-1}\), and 302.5 cm\(^{-1}\). This proves that
the asymmetry in the main peak at ~303 cm\(^{-1}\) is due to annealing not Al-doping. It was noticed that 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 as-grown film (16.6 cm\(^{-1}\)). This indicates an enhancement in film crystallinity due to annealing. FWHM of the 1LO phonon of single crystal CdS was reported to be in the range of 9-10 cm\(^{-1}\) [139]. It is worth noting that the hump observed between 400 cm\(^{-1}\) and 500 cm\(^{-1}\) is due to fluorescence from the substrate, as shown in Fig. 30 (a). Similar deconvolution of the 303 cm\(^{-1}\) peak was carried out for all Al-doped films. Fig. 31 shows the position and FWHM of the E\(_2\), TO, and cubic 1LO or hexagonal A\(_1\)(LO) / E\(_1\)(LO) peaks calculated from the Gaussian fit. Apparently, the position and FWHM of both E\(_2\) and TO peaks are on the average constant regardless of the [Al] / [Cd] ratio used. The average position of the E\(_2\) peak was found to be 258.3 cm\(^{-1}\) (Fig. 31 a) which agrees well with the 256 cm\(^{-1}\) [141] and the 257 cm\(^{-1}\) [143] value of E\(_2\) that has been reported earlier (Table 22). The average position of the middle peak (Fig. 31 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 Fig. 31 (c), the position and FWHM of the cubic 1LO or hexagonal A\(_1\)(LO) / E\(_1\)(LO) peak are sensitive to the [Al] / [Cd] ratio. As that ratio increases, peak position and FWHM increase. The increase in FWHM is, however, more significant which implies an increase in induced lattice damage as [Al] / [Cd] ratio increases.

Fig. 32 shows XPS multiplex spectra for undoped film, and Al-doped films grown at [Al] / [Cd] ratio of 0.036 and 0.18. In all three cases, binding energy of the S 2p peak (Fig. 32 a) is 161.7 eV which is in the range characteristic of sulfides. No peak shift was detected due to Al-doping.
Fig. 31 Peak position and FWHM as a function of [Al] / [Cd] ratio; (a) $E_2$ peak of hexagonal CdS, (b) Shifted TO peak of cubic CdS, and (c) Cubic $1LO$ or hexagonal $A_1(LO)$ / $E_1(LO)$ peak
Fig. 32 XPS multiplex spectra of undoped CdS film, Al-doped film grown at [Al] / [Cd] ratio of 0.036 and 0.18; (a) S 2p peak, and (b) Cd 3d peak.
Also, no sulfur oxides (166-171 eV) or elemental sulfur (164 eV) [148] are observed. The presence of two peaks arises from a spin orbit splitting of 1.18 eV between the S 2p\textsubscript{1/2} and the S 2p\textsubscript{3/2} states. Similarly, the binding energy of the Cd 3d\textsubscript{5/2} peak at 405.0 eV (Fig. 32 b) was found to be the same for all three films. The binding energy of the Cd 3d\textsubscript{3/2} peak was 411.7 eV, which agrees with the 6.74 eV energy splitting between Cd 3d\textsubscript{5/2} and Cd 3d\textsubscript{3/2} states [148]. Both values of binding energy for the S 2p and Cd 3d peaks observed in all three films agree well with previously reported data on single crystal and thin film CdS [149, 150]. It is worth noting that the ratio of S 2p\textsubscript{3/2} signal intensity to that of Cd 3d\textsubscript{5/2} signal was found to decrease as [Al] / [Cd] ratio increases. It decreases in the order: 0.154, 0.149, and 0.146 as [Al] / [Cd] ratio increases in the order 0.000 (undoped film), 0.036, and 0.18 respectively. Clearly, Al-doping increases sulfur deficiency in doped films.

SEM images show that Al-doping did not affect the morphology of the film. As shown in Fig. 33, 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.

### 3.1.3.2 Investigation of Indium Doping

Due to the extremely low solubility product of In\textsubscript{2}S\textsubscript{3} (K\textsubscript{sp} = 10^{-73.24}) compared to that of CdS (K\textsubscript{sp} = 10^{-27.94}) [96], only two [In] / [Cd] ratios; 0.009 and 0.018 were used. Once InCl\textsubscript{3} was added, solution became turbid and homogeneous reaction dominated the deposition process.
Fig. 33 SEM micrographs of (a) CdS undoped film, and (b) Al-doped film grown at [Al] / [Cd] ratio of 0.036

Fig. 34 Specular transmittance and reflectance spectra of films grown at [In] / [Cd] ratios of 0.009 and 0.018
Fig. 35 Optical bandgap calculations of films grown at [In] / [Cd] ratios of 0.009 and 0.018

Fig. 36 XRD pattern of film grown at [In] / [Cd] ratio of 0.018
In both cases, substrate was kept in solution for less than five minutes to avoid deposition of porous, non-adhesive, and poor quality layer due to homogeneous reaction. Although deposition process was repeated four times using fresh solution each time, film obtained in both cases was very thin (about 550 Å). Almost no film was deposited when 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.

Fig. 34 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 Fig. 35, 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] ratio 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. [151] and Sanz et al. [152]. As shown in Fig. 36, the XRD pattern of film grown at [In] / [Cd] ratio of 0.018 is a mixture of cubic In$_2$S$_3$ (JCPDS 032-0456) [153] and Orthorhombic InS (JCPDS 019-0588) [154], 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 ion concentration in the solution exceeds the solubility product, $K_{sp}$. Since, $K_{sp}$ of indium sulfide is extremely low compared to 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.
3.1.4 Conclusion

Aluminum *in-situ* doping of CdS using CBD proves to be successful. A resistivity as low as 4.6 x 10\(^{-2}\) Ω-cm and a carrier density as high as 1.1 x 10\(^{19}\) cm\(^{-3}\) were achieved. The bandgap of doped films was found to decrease at first with 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 and 0.036. 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 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 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 [Al] / [Cd] ratio was observed, which implies an increase in induced lattice damage as [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 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 [134, 135], CBD is not a suitable technique for growing In-doped CdS films.
3.2 Boron *In-Situ* Doping of Chemical Bath Deposited CdS Thin Films

3.2.1 Introduction

Due to its wide band gap (2.42 eV), photoconductivity, and high electron affinity, CdS has been widely used as a window material in high efficiency thin film solar cells based on CdTe and Cu(In,Ga)Se$_2$ [1, 2]. Chemical bath deposition is one of the most commonly used techniques to grow CdS thin films [20, 21]. It’s known to be a simple, low temperature, and inexpensive large-area deposition technique for group II-VI semiconductors such as CdS. CdS films grown by CBD are known to be highly stoichiometric and exhibit a high dark resistance. A dark resistivity as high as $10^8$ Ω-cm [44], $10^9$ Ω-cm [46], and $10^{10}$ Ω-cm [39] has been reported earlier for CBD-CdS. In a previous work [21], we have established a direct relationship between Cd precursors used in the deposition of CBD-CdS and film resistivity. Film resistivity was found to vary from $3.88 \times 10^3$ Ω-cm to $8.01 \times 10^1$ Ω-cm, depending on Cd precursor used and film stoichiometry. Although a resistivity of $8.01 \times 10^1$ Ω-cm is considerably small for CBD-CdS, a lower resistivity is needed for solar cells and other optoelectronic applications.

One approach to reduce dark resistivity of CBD-CdS is *in-situ* doping. Over the past two decades, *in-situ* doping of CBD-CdS using Al [22, 129, 130], Cu [124, 125], Li [126, 127], and Na [128] has been reported. In this work, the effectiveness of B$^{3+}$ doping through chemical bath deposition is investigated. Transmittance and reflectance measurements of doped films were carried out to study the effect of B-doping on the optical properties and bandgap of CdS films. Resistivity, carrier concentration, and Hall mobility of doped films were acquired using Hall effect measurements. Crystal structure
as well as crystal quality and phase transition were determined using X-ray diffraction, transmission electron microscopy (TEM), and micro-Raman spectroscopy. Film morphology was studied using scanning electron microscopy. Film chemistry and binding states were studied using X-ray photoelectron spectroscopy.

3.2.2 Experimental Details

CdS films were prepared using stock solutions of CdSO₄ (0.038 M), (NH₄)₂SO₄ (0.076 M), NH₄OH (29.4 %), and (NH₂)₂CS (0.076 M). Films were grown on 38 mm x 38 mm x 1 mm glass substrates (Schott Borofloat glass, supplied by S.I. Howard Glass Co., Inc.). Boron doping was carried out by adding boric acid (H₃BO₃) as dopant source to the main solution. The deposition temperature was kept constant at 85 °C. After deposition, all films were annealed at 300 °C in argon ambient for 1 hour. Details of the growth process have been previously reported [21]. The cleaning steps of the substrate are reported elsewhere [22]. Details of the specular transmittance/reflectance measurements, bandgap calculations, Hall effect measurements, XRD, SEM, XPS, and micro-Raman measurements are mentioned in sec. 3.1.2. Transmission electron microscopy was performed using a Tecnai F30 TEM at an acceleration voltage of 300 kV. Cross sections of the B-doped CdS film were prepared with FEI 200 focused ion beam system.

3.2.3 Results and Discussion

Fig. 37 shows optical transmittance and reflectance spectra of all B-doped films grown at different [B] / [Cd] ratios. The [B] / [Cd] ratio in solution was varied from 8.5 x 10⁻³ to 0.1. Adding higher concentration of (H₃BO₃) resulted in a homogeneous reaction that quickly dominated the deposition process and affected the quality of doped-CdS films.
(films were porous, non-adherent, and powdery like). It should be noted that a ratio of zero was assigned to undoped film (purely CdS).

As shown, all films exhibit a high transmittance that exceeds 80% in the visible region of the spectrum and exceeds 90% right before the absorption edge. A red shift in the absorption edge towards lower bandgap is noticed in all doped films. This red shift was found to increase as $[B] / [Cd]$ ratio increases. Using transmittance and reflectance data, the absorption coefficient $\alpha$ was calculated and was then used to determine the band gap, as shown in Fig. 38. Fig. 39 shows the bandgap dependence on $[B] / [Cd]$ ratio. B-doped films’ bandgap decreases as $[B] / [Cd]$ ratio increases. 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 [17]. Such drop in bandgap due to Boron doping is similar to what we’ve reported earlier for Al-doped CdS films [22]. We believe that the incorporation of $B^{3+}$ ions as well as sulfur deficiency in B-doped CdS films gives rise to donor levels in the bandgap of CdS. As $B^{3+}$ 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 and therefore reducing the bandgap.

XRD patterns of B-doped films and undoped CdS film are shown in Fig. 40. Only one peak is detected which is either the (111) peak of cubic (zincblende) CdS or the (0002) peak of hexagonal (wurtzite) CdS. Cubic CdS is a metastable phase while hexagonal CdS is the stable phase at room temperature. Thermal annealing typically causes a phase transition from cubic phase to hexagonal phase. The critical point for such phase transition is believed to be 300 °C [136].
Fig. 37 Specular transmittance and reflectance spectra of B-doped CdS films grown at different $\frac{[B]}{[Cd]}$ ratio, $R$ ($R = 0.0$ is assigned to the undoped film)

Fig. 38 Optical bandgap calculations of B-doped CdS films grown at different $\frac{[B]}{[Cd]}$ ratio, $R$
Fig. 39 Optical bandgap of B-doped CdS films as a function of [B] / [Cd] ratio

Fig. 40 XRD pattern of B-doped CdS films grown at different [B] / [Cd] ratio, R
Since all films were annealed at 300 °C and no other hexagonal / cubic peaks are being detected, it is impossible to determine which phase is dominating. As shown in Fig. 40, no peaks of B, BS, or B₂S₃ were detected, which indicates that incorporation of B³⁺ ions doesn’t affect the crystal structure of the CdS film. The average (111)ₑₓₜₖₐₜ / (0002)ₑₓₜₖₐₜ interplanar distance d(111) / d(0002) 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 Fig. 41; when the [B] / [Cd] ratio increases, the spacing of the (111) / (0002) lattice planes decreases further below that of the undoped film. Since the ionic radius of B³⁺ (0.20 Å) is smaller than that of Cd²⁺ (0.97 Å) [137], this suggests that B³⁺ ions replace the Cd²⁺ ions in the lattice substitutionally which in turn results in smaller d-values than for undoped CdS films. There’s always the possibility that some of the B³⁺ ions enter the lattice interstitially, but since the d-value continues to decrease as [B] / [Cd] ratio increases, it’s more likely that the majority of B³⁺ ions are replacing Cd²⁺ ions substitutionally.

High-resolution TEM of CdS film grown at [B] / [Cd] ratio of 5.1 x 10⁻² reveals a wurtzite structure with frequent stacking faults. The stacking sequence of the (0002) planes is not perfectly ABAB..., and is often interspersed with ABC stacking sequences which are characteristic of the zincblende structure. The wurtzite structure is however dominating, as shown in Fig. 42, where the edge of the B-doped CdS layer is shown with the crystal lattice imaged along the a-axis of the hexagonal lattice. A high density of defects like stacking faults and partial dislocations is observed. The TEM diffraction pattern shown in Fig. 43 was taken from a small area of the CdS layer with only a few grains.
Fig. 41 Average (111) / (0002) interplanar distance $d_{(111)} / d_{(0002)}$ as a function of $[B] / [Cd]$ ratio

Fig. 42 High-resolution TEM of film grown at a $[B] / [Cd]$ ratio of $5.1 \times 10^{-2}$
Fig. 43 TEM diffraction pattern of film grown at a [B] / [Cd] ratio of 5.1 x 10^{-2}

Fig. 44 Carrier concentration (C.C.) dependence on [B] / [Cd] ratio
Instead of diffraction rings, the spot pattern shows distinct 0002 diffraction spots of the wurtzite structure. However, the high stacking faults density is responsible for streaks in the diffraction pattern instead of sharp $\overline{1}100$ and $\overline{1}102$ reflections. These streaks indicate that the stacking sequence of the wurtzite structure is imperfect.

Fig. 44 shows the carrier concentration (C.C.) as a function of $[B] / [Cd]$ ratio. The undoped film has a C.C. of about $4 \times 10^{16}$ cm$^{-3}$. The C.C. increases as $[B] / [Cd]$ ratio increases, until it reaches $1.91 \times 10^{19}$ cm$^{-3}$ at a ratio of 0.1. The film dark resistivity as a function of $[B] / [Cd]$ ratio is shown in Fig. 45. The resistivity of the undoped film is about $1.03 \times 10^2$ Ω-cm. As shown, the resistivity of boron doped films gradually decreases as $[B] / [Cd]$ ratio increases. The lowest resistivity obtained was $1.7 \times 10^{-2}$ Ω-cm at a ratio of 0.1. This gradual increase of C.C. and decrease of resistivity as $[B] / [Cd]$ ratio increases agree with our conclusion from XRD data that the majority of $B^{3+}$ ions are replacing $Cd^{2+}$ ions substitutionally rather than interstitially. The Hall mobility values shown in Fig. 46 are consistent with these reported earlier for Al-doped CdS films [22].

Fig. 47 shows Micro-Raman spectra for all B-doped films. All films have the same CdS characteristic peak at about 303 cm$^{-1}$. Another CdS characteristic peak 2LO (Longitudinal Optical) is barely noticeable at about 600 cm$^{-1}$. As shown, the peak at 303 cm$^{-1}$ is asymmetric suggesting a superposition of more than one mode. Fig. 48 shows the deconvolution of the 303 cm$^{-1}$ peak of film grown at $[B] / [Cd]$ ratio of $5.1 \times 10^{-2}$, using Gaussian fit from which peak position and FWHM have been obtained. Similar to what we have observed in Al-doped films [22], this peak consists of a superposition of three different peaks; the cubic 1LO [144] or hexagonal $A_1(LO)$ / $E_1(LO)$ peak [140] at 303 cm$^{-1}$ with a FWHM of 13.5 cm$^{-1}$, the shifted TO (Transverse Optical) peak of cubic CdS
at 288.3 cm\(^{-1}\) with a FWHM of 25.5 cm\(^{-1}\), and the E\(_2\) peak of hexagonal CdS at 259 cm\(^{-1}\) with a FWHM of 30.5 cm\(^{-1}\). The Raman shift in the TO peak (originally at 246 cm\(^{-1}\) [144]) is due to a phase transition in CdS film, from cubic to hexagonal, because of the annealing at 300 °C. So, unlike XRD, TEM and Micro-Raman detect the phase transition in CdS due to annealing. We have shown earlier [22] that this phase transition is attributed to annealing rather than doping. Similar deconvolution of the 303 cm\(^{-1}\) peak was carried out for all B-doped films. Fig. 49 shows position and FWHM of the E\(_2\), TO, and cubic 1LO or hexagonal A\(_1\)(LO) / E\(_1\)(LO) peaks calculated from the Gaussian fit. Apparently, the position and FWHM of both E\(_2\) and TO peaks are on the average constant regardless of the [B] / [Cd] ratio used. The average position of the E\(_2\) peak was found to be 258 cm\(^{-1}\) (Fig. 49 a) which agrees well with the 256 cm\(^{-1}\) [141] and the 257 cm\(^{-1}\) [143] value of E\(_2\) mode that has been reported earlier. The average position of the TO peak (Fig. 49 b) is 288 cm\(^{-1}\) which agrees with what we’ve reported earlier for Al-doped films [22]. However, as shown in Fig. 49 (c), the FWHM of the cubic 1LO or hexagonal A\(_1\)(LO) / E\(_1\)(LO) peak is sensitive to the [B] / [Cd] ratio. As the ratio increases, the FWHM increases from 12.2 cm\(^{-1}\) for undoped CdS to 14.3 cm\(^{-1}\) for film grown at [B] / [Cd] ratio of 0.1. Such increase in FWHM implies an increase in induced lattice defects due to B-doping. It’s worth noting that the FWHM of the 1LO phonon of single crystal CdS was reported to be in the range of 9 - 10 cm\(^{-1}\) [139]. This agrees with the TEM observations of high defect densities (stacking faults and partial dislocations).
Fig. 45 Dark resistivity as a function of $[B] / [Cd]$ ratio

Fig. 46 Variation of Hall mobility ($\mu$) with $[B] / [Cd]$ ratio
Fig. 47 Raman spectra of B-doped films grown at different [B] / [Cd] ratio, R

Fig. 48 Deconvolution of the 303 cm\(^{-1}\) Raman peak of film grown at [B] / [Cd] ratio of 5.1 x 10\(^{-2}\) into three peaks using Gaussian fitting
Fig. 49 Peak position and FWHM as a function of [B] / [Cd] ratio; (a) $E_2$ peak of hexagonal CdS, (b) Shifted TO peak of cubic CdS, and (c) Cubic 1LO or hexagonal $A_1$(LO) / $E_1$(LO) peak.

Fig. 50 XPS multiplex spectra of undoped CdS film, and B-doped film grown at [B] / [Cd] ratio of $1.7 \times 10^{-2}$; (a) S 2p peak, and (b) Cd 3d peak.
Fig. 51 SEM micrographs of (a) CdS undoped film, and (b) B-doped film grown at [B] / [Cd] ratio of $1.7 \times 10^{-2}$. 
No peak shift was detected due to B-doping. Also, no sulfur oxides (166-171 eV) or elemental sulfur (164 eV) [148] are observed. The presence of two peaks arises from a spin orbit splitting of 1.18 eV between the S 2p$_{1/2}$ and the S 2p$_{3/2}$ states. Similarly, the binding energy of the Cd 3d$_{5/2}$ peak at 405.0 eV (Fig. 50 b) was found to be the same for both films. The binding energy of the Cd 3d$_{3/2}$ peak was 411.7 eV, which agrees with the well-known energy splitting of 6.74 eV between Cd 3d$_{5/2}$ and Cd 3d$_{3/2}$ states [148]. Both values of binding energy for S 2p and Cd 3d peaks observed in both films agree well with previously reported data on single crystalline and thin-film CdS [149, 150].

SEM images show that B-doping didn’t affect the morphology of the CdS film. As shown in Fig. 51, both undoped and B-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 the formation of colloidal particles in solution which are later adsorbed on the film.

3.2.4 Conclusion

Boron in-situ doping of CdS using CBD proves to be successful. A resistivity as low as $1.7 \times 10^{-2}$ Ω-cm and a carrier density as high as $1.91 \times 10^{19}$ cm$^{-3}$ were achieved. The bandgap of doped films was found to decrease slightly as the [B] / [Cd] ratio increases. The minimum bandgap observed was 2.25 eV at a [B] / [Cd] ratio of 0.1. XRD measurements did not reveal any new peaks due to B-doping indicating that the incorporation of B$^{3+}$ ions does not change the crystal structure of the CdS film. It also revealed that B$^{3+}$ ions are more likely replacing Cd$^{2+}$ ions in the lattice substitutionally. Micro-Raman measurements show a phase transition in all films, due to annealing, where
peaks related to cubic and hexagonal phases were detected. An increase in the FWHM of cubic 1LO or hexagonal A$_1$(LO) / E$_1$(LO) peak with [B] / [Cd] ratio is observed, which implies an increase in induced lattice defects as [B] / [Cd] ratio increases. A high density of defects like stacking faults and partial dislocations is observed by TEM. XPS spectra give a clear indication that B-doping does not affect the chemistry of the CdS film. SEM images show that B-doping does not affect the morphology of the CdS film.
3.3 Characterization of Gallium-Doped CdS Thin Films Grown by Chemical Bath Deposition

3.3.1 Introduction

*In-situ* doping with group III elements has been widely used to decrease the dark resistivity of CdS thin films grown by chemical bath deposition [45, 131]. The need to such doping is attributed to the fact that CBD-CdS thin films are highly stoichiometric [20, 21]. Accordingly, the dark resistivity of CdS films grown by CBD is so high that, in some cases, it was reported to be in the order of $10^8$ - $10^{10}$ Ω-cm [39, 44, 46]. *In-situ* doping using group III elements such as aluminum, indium, boron, and gallium, is the most suitable approach to tackle this problem where the need for post-deposition treatments, such as ion-implantation, is being eliminated.

In a previous work [22], we have shown that CBD is a suitable technique for aluminum *in-situ* doping of CdS. We have also shown that due to extremely low solubility product of indium sulfide ($K_{sp} = 10^{-73.24}$) compared to that of Cadmium Sulfide ($K_{sp} = 10^{-27.94}$) [96], it is highly unlikely, if not impossible, to incorporate indium in CdS, using CBD. In another work [24], we have investigated boron *in-situ* doping of CdS using CBD, and proved it to be successful. We have found that, regardless of boron concentration used, $B^{3+}$ ions tend to replace $Cd^{2+}$ ions in the lattice substitutionally. However, $Al^{3+}$ ions tend to enter the lattice substitutionally at low concentration, and interstitially at high concentration. In both cases, a dark resistivity in the order of $10^2$ Ω-cm and a carrier density as high as ~ $10^{19}$ cm$^{-3}$ were achieved. The effect of Al-doping as well as B-doping on the optical properties and bandgap of CdS films was investigated. In both cases, bandgap of doped films was found to be always less than that of undoped
film. X-ray diffraction did not detect any Al or B peaks in doped films indicating that incorporation of Al$^{3+}$ or B$^{3+}$ ions does not affect the crystal structure of CdS film. Phase transition, due to annealing, as well as induced lattice defects, due to doping, were detected in both cases by Micro-Raman spectroscopy. An increase in sulfur deficiency due to doping was detected by X-ray photoelectron spectroscopy. However, scanning electron microscopy micrographs showed morphology of films unaffected by Al or B-doping.

In extension to this work, Gallium in-situ doping of CdS using chemical bath deposition is being reported. The same investigation methodology used in Al / B-doping work [22, 24] is being implemented here as well. The objective of this work is mainly to provide a comparison between Ga-doping of CdS and Al / B-doping. Therefore, in addition to using the same characterization techniques, the [dopant] / [Cd] ratio used in this work was exactly the same as that used earlier in B-doping [24]. Similarly, transmittance and reflectance measurements of doped films were carried out to study the effect of Ga-doping on the optical properties and bandgap of CdS films. Resistivity, carrier concentration, and mobility of doped films were acquired using Hall effect measurements. Crystal structure as well as crystal quality and phase transition were determined using XRD and Micro-Raman spectroscopy. Film morphology was studied using SEM, while film chemistry and binding states were studied using XPS.

### 3.3.2 Experimental Details

CdS films were prepared using stock solutions of CdSO$_4$ (0.038 M), (NH$_4$)$_2$SO$_4$ (0.076 M), NH$_4$OH (29.4 %), and (NH$_2$)$_2$CS (0.076 M). Films were grown on 38 mm x 38 mm
x 1 mm glass substrates (Schott Borofloat glass, supplied by S.I. Howard Glass Co., Inc.). Gallium doping was carried out by adding the appropriate amount from a 4 mM stock solution of Ga(NO$_3$)$_3$ to the main solution. The deposition temperature was kept constant at 85 °C. After deposition, all films were annealed at 300 °C in argon ambient for 1 hour. Details of the growth process have been previously reported [21]. The cleaning steps of the substrate are reported elsewhere [22].

Details of the specular transmittance/reflectance measurements, bandgap calculations, Hall effect measurements, XRD, SEM, XPS, and Micro-Raman measurements are mentioned in sec. 3.1.2.

3.3.3 Results and Discussion

Fig. 52 shows optical transmittance and reflectance spectra of all Ga-doped films grown at different [Ga] / [Cd] ratios. The [Ga] / [Cd] ratio in solution was varied from 8.5 x 10$^{-3}$ to 0.1. Adding higher concentration of Ga(NO$_3$)$_3$ resulted in a homogeneous reaction that quickly dominated the deposition process and affected the quality of doped-CdS films. It should be noted that a ratio of zero was assigned to undoped film (purely CdS). As shown, all films exhibit a high transmittance that exceeds 80% in the visible region of the spectrum and exceeds 90% right before the absorption edge. A red shift in the absorption edge towards lower band gap is noticed in all doped films. The magnitude of the red shift was found to fluctuate as [Ga] / [Cd] ratio increases. Using transmittance and reflectance data, the absorption coefficient $\alpha$ was calculated and was then used to determine the bandgap, as shown in Fig. 53. Fig. 54 shows the bandgap dependence on [Ga] / [Cd] ratio.
Fig. 52 Specular transmittance and reflectance spectra of Ga-doped CdS films grown at different [Ga] / [Cd] ratios (R denotes [Ga] / [Cd] ratio & R = 0.0 refers to undoped film)

Fig. 53 Optical bandgap calculations of Ga-doped CdS films grown at different [Ga] / [Cd] ratios (R denotes [Ga] / [Cd] ratio & R = 0.0 refers to undoped film)
Fig. 54 Optical bandgap of Ga-doped CdS films as a function of [Ga] / [Cd] ratio

Fig. 55 XRD pattern of Ga-doped CdS films grown at different [Ga] / [Cd] ratios (R denotes [Ga] / [Cd] ratio & R = 0.0 refers to undoped film)
The bandgap of doped films decreases to a minimum of 2.26 eV at a ratio of 0.017, then increases and finally saturates at 2.32 eV as the [Al] / [Cd] ratio exceeds 0.06. Undoped film has a bandgap of 2.41 eV which agrees well with the 2.42 eV bandgap of single crystal CdS [17]. This is very similar to what we have observed earlier for Al-doped CdS films [22]. It has been suggested by Lokhande and Pawar [129] that, in the case of Al-doped CdS films, incorporation of Al$^{3+}$ ions 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 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. Similar argument can be used to explain the decrease in bandgap of Ga-doped CdS thin films. The later increase in bandgap for [Ga] / [Cd] ratio higher than 0.04 may be attributed to an increase in lattice strain due to decrease in grain size of doped films grown at [Ga] / [Cd] ratio higher than 0.04, as will be shown later. We have shown, in a previous work [20], the bandgap of CdS films to be sensitive to film thickness and lattice strain. Considering the fact that the bandgap of GaS is 3.05 eV and that of Ga$_2$S$_3$ is 3.42 eV [155], this rules out any formation of ternary compounds, such as Cd$_x$Ga$_{1-x}$S.

XRD patterns of Ga-doped films and undoped CdS film are shown in Fig. 55. Only one peak is detected which is either the (111) peak of cubic CdS or the (002) peak of hexagonal CdS. As explained earlier, Cubic CdS is a metastable phase while hexagonal CdS is the stable phase at room temperature. Thermal annealing typically causes a phase transition from cubic phase to hexagonal phase. The critical point for such phase transition is believed to be 300 °C [136], above which hexagonal phase
predominates over cubic phase. Since no other peaks are detected, it is difficult to
determine if the peak shown in Fig. 55 is the (111) peak of the cubic phase or the (002)
peak of the hexagonal phase which coincides with the (111) peak. In order to avoid
confusion, we will refer to the peak detected as the (111) peak of cubic CdS. As shown
in Fig. 55, no peaks of Ga, GaS, or Ga$_2$S$_3$ were detected, which indicates that
incorporation of Ga$^{3+}$ ions does not affect the crystal structure of CdS film. This also
confirms our conclusion from bandgap calculations of Ga-doped films.

The average (111) 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 Fig. 56, as the [Ga] / [Cd] ratio increases, the spacing of the (111) lattice planes
decreases below that of undoped film until it reaches a minimum at a ratio of 0.034 and
then it starts to increase as [Ga] / [Cd] ratio increases, and once that ratio exceeds 0.06,
the $d_{(111)}$ value goes beyond that of undoped CdS film. Now, since the ionic radius of
Ga$^{3+}$ (0.62 Å) is smaller than that of Cd$^{2+}$ (0.97 Å) [137], this suggests that at low [Ga] /
[Cd] ratio, Ga$^{3+}$ ions replace Cd$^{2+}$ ions in the lattice substitutionally which in turn results
in smaller $d_{(111)}$ value than that of undoped CdS film. As this ratio increases beyond
0.034, Ga$^{3+}$ ions start to enter the lattice both substitutionally and interstitially which
caused the $d_{(111)}$ values to increase again. As [Ga] / [Cd] ratio exceeds 0.06, most Ga$^{3+}$
ions incorporated in the lattice are in interstitial sites which caused $d_{(111)}$ values to exceed
that of undoped film. This will have an impact on the electrical properties of Ga-doped
films as Hall measurements will show later.

The grain size shown in Fig. 57 was calculated using the formula $D = 0.9 \frac{\lambda}{\beta \cos \theta}$, where $\beta$ is the full width at half maximum (FWHM) in radians.
Fig. 56 Average (111) interplanar distance $d_{(111)}$ as a function of [Ga] / [Cd] ratio

Fig. 57 Grain size dependence on [Ga] / [Cd] ratio
As shown, the grain size increases with the [Ga] / [Cd] ratio, and then as this ratio exceeds 0.034, the grain size decreases as that ratio increases. This decrease in grain size may have caused lattice strain that resulted in the increase observed in the band gap of doped films grown at [Ga] / [Cd] ratio higher than 0.04, as we mentioned earlier.

Fig. 58 shows the carrier concentration (C.C.) as a function of [Ga] / [Cd] ratio. The undoped film has a C.C. of about 4 x 10^{16} cm^{-3}. The C.C. increases with [Ga] / [Cd] ratio until it reaches a maximum (\sim 2.96 x 10^{19} cm^{-3}) at a ratio of 0.034, and then decreases as the ratio exceeds 0.04. The film resistivity as a function of [Ga] / [Cd] ratio is shown in Fig. 59. The dark resistivity drops from 1.03 x 10^{2} \Omega\text{-cm} (undoped film) to a minimum of 1.2 x 10^{-2} \Omega\text{-cm} at a ratio of 0.034, after which it starts to increase as [Ga] / [Cd] ratio increases. This agrees with the d_{(111)} values variation with [Ga] / [Cd] ratio. As we pointed out earlier, at low [Ga] / [Cd] ratios, Ga^{3+} ions replace the Cd^{2+} ions in the lattice substitutionally, which increases the C.C. of the doped films and decreases the resistivity. However, at higher ratios, Ga^{3+} ions start to enter the lattice both substitutionally and interstitially. Interstitial Ga^{3+} ions will act as recombination centers decreasing the C.C. and increasing the resistivity. Such behavior of C.C. as well as dark resistivity has been also reported by Lokhande and Pawar [129] and by Akintunde [130], for Al-doped CdS films. The Hall mobility (\mu) values shown in Fig. 60 are consistent with what we reported earlier for Al-doped and B-doped CdS films [22, 24]. Variation of \mu with respect to [Ga] / [Cd] ratio agrees with the way grain size changes with respect to [Ga] / [Cd] ratio (Fig. 57). Fig. 61 shows Micro-Raman spectra for all Ga-doped films. All films show the same CdS characteristic peak at about 303 cm\textsuperscript{-1}. Another CdS characteristic peak; 2LO (Longitudinal Optical) is barely noticeable at about 600 cm\textsuperscript{-1}.
Fig. 58 Carrier concentration dependence on [Ga] / [Cd] ratio

Fig. 59 Dark resistivity as a function of [Ga] / [Cd] ratio
Fig. 60 Variation of Hall mobility with [Ga] / [Cd] ratio

Fig. 61 Raman spectra of Ga-doped films grown at different [Ga] / [Cd] ratio (R denotes [Ga] / [Cd] ratio)
As shown, the peak at 303 cm\(^{-1}\) is asymmetric; suggesting a superposition of more than one mode. Fig. 62 shows the deconvolution of the 303 cm\(^{-1}\) peak of film grown at [Ga] / [Cd] ratio of 6.8 x 10\(^{-2}\), using Gaussian fit from which peak position and FWHM have been obtained. Similar to what we have observed in Al-doped and B-doped films [22, 24], this peak consists of a superposition of three different peaks; the cubic 1LO [144] or hexagonal A\(_{1}LO\) / E\(_{1}LO\) peak [140] at 303.2 cm\(^{-1}\) with a FWHM of 13.3 cm\(^{-1}\), the shifted TO (Transverse Optical) peak of cubic CdS at 288 cm\(^{-1}\) with a FWHM of 24.8 cm\(^{-1}\), and the E\(_{2}\) peak of hexagonal CdS at 260.5 cm\(^{-1}\) with a FWHM of 30.3 cm\(^{-1}\). This Raman shift in the TO peak (originally at 246 cm\(^{-1}\) [144]) is due to a phase transition in CdS film, from cubic to hexagonal, because of the annealing at 300 °C [22]. So, unlike XRD, Micro-Raman detects a phase transition in CdS due to annealing. We have shown earlier that this phase transition is attributed to annealing rather than doping [22].

Similar deconvolution of the 303 cm\(^{-1}\) peak was carried out for all Ga-doped films. Fig. 63 shows position and FWHM of the E\(_{2}\), TO, and cubic 1LO or hexagonal A\(_{1}LO\) / E\(_{1}LO\) peaks calculated from the Gaussian fit, as a function of [Ga] / [Cd] ratio. Apparently, the position and FWHM of both the E\(_{2}\) and TO peaks are on the average constant regardless of the [Ga] / [Cd] ratio used. The average position of the E\(_{2}\) peak was found to be 260 cm\(^{-1}\) (Fig. 63 a) which is slightly higher than what we observed for Al-doped (258.3 cm\(^{-1}\)) and B-doped (258 cm\(^{-1}\)) films [22, 24], but still agrees with the 256 cm\(^{-1}\) [141] and the 257 cm\(^{-1}\) [143] value of E\(_{2}\) mode that has been reported earlier. The average position of the TO peak (Fig. 63 b) is 288 cm\(^{-1}\) which is the same Raman shift observed for both Al-doped and B-doped CdS thin films [22, 24].
Fig. 62 Deconvolution of the 303 cm\(^{-1}\) Raman peak of film grown at [Ga] / [Cd] ratio of 6.8 \(\times\) 10\(^{-2}\) into three peaks using Gaussian fit.

Fig. 63 Peak position and FWHM as a function of [Ga] / [Cd] ratio; (a) \(E_2\) peak of hexagonal CdS, (b) Shifted TO peak of cubic CdS, (c) Cubic 1LO or hexagonal \(A_1(LO) / E_1(LO)\) peak.
However, as shown in Fig. 63 (c), the position and FWHM of the cubic 1LO or hexagonal $A_1$(LO) / $E_1$(LO) peak are sensitive to [Ga] / [Cd] ratio. As the ratio increases, peak position and FWHM increase. The increase in FWHM is, however, more significant which implies an increase in induced lattice defects as [Ga] / [Cd] ratio increases. As shown, FWHM increases from 12.2 cm$^{-1}$ for undoped CdS to 13.7 cm$^{-1}$ for film grown at [Ga] / [Cd] ratio of 0.1. It is worth noting that FWHM of the 1LO phonon of single crystal CdS was reported to be in the range of 9-10 cm$^{-1}$ [139].

Fig. 64 shows XPS multiplex spectra for undoped film, and Ga-doped film grown at [Ga] / [Cd] ratio of 5.1 x 10$^{-2}$. In both cases, binding energy of the S 2p peak (Fig. 64 a) is 161.7 eV which is in the range characteristic of sulfides. No peak shift was detected due to Ga-doping. Also, no sulfur oxides (166-171 eV) or elemental sulfur (164 eV) [148] are observed. The presence of two peaks arises from a spin orbit splitting of 1.18 eV between the S 2p$_{1/2}$ and the S 2p$_{3/2}$ states. Similarly, the binding energy of the Cd 3d$_{5/2}$ peak at 405.0 eV (Fig. 64 b) was found to be the same for both films. The binding energy of the Cd 3d$_{3/2}$ peak was 411.7 eV, which agrees with the well-known energy splitting of 6.74 eV between Cd 3d$_{5/2}$ and Cd 3d$_{3/2}$ states [148]. Both values of binding energy for S 2p and Cd 3d peaks observed in both films agree well with previously reported data on single crystal and thin film CdS [149, 150]. It is worth noting that the ratio of S 2p$_{3/2}$ signal intensity to that of Cd 3d$_{5/2}$ signal was 0.154 for undoped film and became 0.151 for Ga-doped film. Such drop in ratio is similar to what we observed for Al-doped films [22], where it decreased in the order: 0.154, 0.149, and 0.146 as [Al] / [Cd] ratio increased in the order 0.000 (undoped film), 0.036, and 0.18 respectively.
Fig. 64 XPS multiplex spectra of undoped CdS film, and Ga-doped film grown at [Ga]/[Cd] ratio of $5.1 \times 10^{-2}$; (a) S 2p peak, (b) Cd 3d peak

Fig. 65 SEM micrographs of (a) CdS undoped film, (b) Ga-doped film grown at [Ga]/[Cd] ratio of $1.7 \times 10^{-2}$
This shows that, similar to Al-doping, Ga-doping increases sulfur deficiency in doped films. SEM images show that Ga-doping did not have a significant effect on the morphology of CdS film. As shown in Fig. 65, both undoped and Ga-doped films are smooth, continuous, and uniform with some coverage by scattered crystallite overgrowth that appear to have slightly higher density for Ga-doped film. These are most probably aggregates due to colloidal particles formed in solution and then adsorbed on the film.

### 3.3.4 Conclusion

Gallium in-situ doping of CdS using CBD proves to be successful. A resistivity as low as $1.2 \times 10^{-2} \ \Omega \cdot \text{cm}$ and a carrier density as high as $2.96 \times 10^{19} \ \text{cm}^{-3}$ have been achieved. The bandgap of doped films was found to decrease at first with Ga concentration and then saturates at 2.32 eV. The minimum bandgap observed was 2.26 eV at $[\text{Ga}] / [\text{Cd}]$ ratios of 0.017. XRD measurements did not detect any new peaks due to Ga-doping indicating that incorporation of Ga$^{3+}$ ions does not change the crystal structure of the CdS film. It also showed that at low $[\text{Ga}] / [\text{Cd}]$ ratio, Ga$^{3+}$ ions replace Cd$^{2+}$ ions in the lattice substitutionally, and as this ratio increases beyond 0.034, Ga$^{3+}$ ions start to enter the lattice both substitutionally and interstitially, until that ratio exceeds 0.06 where most, if not all, Ga$^{3+}$ ions incorporated in the lattice occupy interstitial sites. This explains the drop in carrier density and rise in resistivity once the $[\text{Ga}] / [\text{Cd}]$ ratio exceeds 0.034.

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 $A_1(\text{LO}) / E_1(\text{LO})$ peak with $[\text{Ga}] / [\text{Cd}]$ ratio was observed, which implies an increase in induced lattice defects as $[\text{Ga}] / [\text{Cd}]$ ratio increases. XPS
spectra showed that, however Ga-doping did not cause any shift in the position of the S 2p and Cd 3d peaks, it increased sulfur deficiency in doped films. SEM images showed that Ga-doping did not affect the morphology of the CdS film.
CHAPTER VI: CHEMICAL BATH DEPOSITION OF TRANSPARENT CONDUCTING OXIDES

4.1 Investigation of Chemical Bath Deposition of ZnO Thin Films Using Six Different Complexing Agents

4.1.1 Introduction

Chemical bath deposition is known to be a simple, low temperature, and inexpensive large-area deposition technique. It has been widely used in the deposition of groups II-VI semiconductors thin films, such as CdS [20, 21], CdSe [156, 157], CdO [56, 158], ZnS [75, 159], ZnSe [81, 160], and ZnO [85-92, 161, 162]. Several complexing agents have been employed in CBD of ZnO thin films. Saeed and O’Brien [85] reported deposition of good-quality ZnO thin films using ethylenediamine (EDA) at pH value of 10.5 – 11. Films grown at pH 10 or less were powdery, spotted and non-uniform and can be easily removed by abrasion with a tissue. The starting bath pH of 9.0 - 9.1 was raised to 10.0 – 11.0 by the addition of NaOH. The band gap values of the ZnO films grown were found to be 3.15 eV [85, 86]. Ortega-López and Morales-Acevedo [161] reported CBD of ZnO using NH₄OH and H₂O₂ (30 %) at pH value of 10.5 – 11.2. They found that using H₂O₂ is essential for obtaining polycrystalline ZnO. All films grown in the absence of hydrogen peroxide were amorphous for any deposition temperature and they continued to be amorphous after annealing. The grown films before and after annealing showed a band gap of 4.2 eV and 3.3 eV, respectively. In another work [87], they have added NH₄Cl as a buffer and reported a slower deposition rate. The band gap values of as-grown and annealed films were 4.2 eV and 3.25 eV, respectively.
Ennaoui et al. [88], however, reported CBD as well as successive ionic layer adsorption and reaction of ZnO using NH₄OH only. Mikami et al. [162] investigated both EDA and NH₄OH as complexing agents for CBD of ZnO and concluded that the growth of ZnO is unstable for the perturbation of EDA concentration. They reported that films grown with EDA showed a quite poor adhesion and uniformity, while films grown with ammonia showed a good adhesion and uniformity. They considered Zn(OH)₂ as the ZnO precursor in their work, and showed numerically that in the case of ammonia, the concentration of Zn(OH)₂ is almost constant in a wide range of ammonia concentration. However, in the case of EDA, the concentration of Zn(OH)₂ is strongly dependent on the EDA concentration in solution. The ZnO film was reported to have a band gap of 3.4 eV and a resistivity of 10⁹ Ω-cm. Drici et al. [90] grew adherent but non-specular ZnO films using EDA at a fixed pH value of 11.0, with the help of NaOH. They reported a resistivity of the order of 10⁴ Ω-cm, measured with a two point electrodes longitudinal structure with an electrode gap of 2 mm.

Ouerfelli et al. [91] reported a five orders of magnitude drop in resistivity of CBD-ZnO films annealed under vacuum compared to those annealed in air. All ZnO films were grown using EDA at a fixed pH value of 11.0, with the help of NaOH. Peiró et al. [92] reported growing nanostructured ZnO thin films using zinc nitrate/zinc acetate as Zn-precursor and urea/ hexamethylenetetramine as complexing agents. They have shown that microwave activated CBD-ZnO films are crystalline and no additional heat treatment/annealing is necessary. In this work, chemical bath deposition of ZnO thin films using six different complexing agents, namely ammonia, hydrazine (N₂H₄), ethanolamine (EA) C₂H₇NO, methylamine (MA) CH₃NH₂, triethanolamine (TEA)
C₆H₁₅NO₃, and dimethylamine (DMA) C₂H₇N, is investigated. ZnSO₄ is used as zinc source and H₂O₂ is used as an oxidation agent. Transmittance, reflectance measurements and band gap calculations are carried out for as-grown films as well as annealed films. Resistivity, carrier density, and Hall mobility of annealed films are acquired using Hall effect measurements. Crystal structure as well as crystal quality are determined using X-ray diffraction, transmission electron microscopy, Fourier transform infrared spectroscopy (FTIR), and micro-Raman spectroscopy. Film morphology, composition, and binding energy are studied using scanning electron microscopy, Rutherford backscattering spectroscopy, and X-ray photoelectron spectroscopy, respectively.

4.1.2 Experimental Details

ZnO films were prepared using aqueous solutions of ZnSO₄ (0.014 M), H₂O₂ (34%), and NH₄OH (29.4 %). Each bath contained 100-120 ml of de-ionized water (resistivity ~ 18.2 MΩ·cm) that was kept under stirring at 85 °C. In addition to ammonia, five more complexing agents were used; N₂H₄, EA, MA, TEA, and DMA. To ensure stable Zn[NH₃]₂⁺ complex in the main solution, ammonia was added whenever one of these five complexing agents is being used. It was noticed that adding ammonia is necessary to dissolve the Zn(OH)₂ formed upon mixing the Zn-source and any of the five aforementioned complexing agents. ZnSO₄ and the desired complexing agent were mixed at room temperature before being added to the main solution. Appropriate amounts of hydrogen peroxide were then added to the main solution. Films were grown on 38 mm x 38 mm x 1 mm glass substrates (Schott Borofloat glass). With the help of a Teflon holder, the glass substrate was kept vertically in the solution. All substrates were
held in the bath prior to the addition of any of the reagents. To ensure deposition of high-quality, adhesive, and specularly reflecting films, the substrate was removed from the solution when the solution becomes turbid and the homogeneous reaction starts to take place. The cleaning steps of the substrate are reported elsewhere [22].

The FTIR micro-analysis was carried out at room temperature using contact ATR optimized objective that covers a range of wavenumbers from 650 cm\(^{-1}\) to 4000 cm\(^{-1}\). Details of the specular transmittance/reflectance measurements, bandgap calculations, Hall effect measurements, XRD, SEM, XPS, and Micro-Raman measurements are mentioned in sec. 3.1.2. Details of the TEM measurements are reported in sec. 3.2.2. Details of the RBS measurements can be found in sec. 2.1.2.

**4.1.3 Results and Discussion**

Fig. 66 shows the optical transmittance of as-grown films for all six complexing agents. As shown, five of these films exhibit a sharp absorption edge around 280 nm – 290 nm and a high transmittance that exceeds 80% in the visible region. The films grown using DMA, however, were of poor quality. It was noticed that when using DMA, the homogeneous reaction quickly dominated over the heterogeneous reaction and all films grown were whitish, non-uniform, and extremely thin (less than 500 Å). Such poor quality is responsible for the absence of a clear absorption edge and the low transmittance observed in the case of DMA-based films. As a result, these films were discarded from any further characterizations. Films grown using other five ligands were adhesive, transparent, uniform, and specularly reflecting with a thickness in the range of 0.2 µm - 0.7 µm.
Fig. 66 Specular transmittance of as-grown ZnO films deposited using six different complexing agents
To ensure full conversion to ZnO, as-grown films were annealed at 400 °C in air for one hour. It was noticed that the quality of EA-based films deteriorated upon annealing and these films lost their integrity and became flakes-like. Annealing at lower temperatures, such as 200 °C and 300 °C in air as well as in argon ambient had the same effect on all EA-based films. Apparently, there is too much stress in EA-based films that resulted in a high density of cracks as shown in Fig. 67 (a). Post heat treatments induced further stress in the films which in turn caused the films to lose their integrity and thus become flakes-like, as observed under optical microscope. Films grown using ammonia, N₂H₄, MA and TEA maintained the same quality after annealing. SEM micrographs of as-grown as well as annealed MA-based film are shown in Fig. 67 (b) & (c). As shown, other than an increase in grain size after annealing, film quality remains almost the same. Further characterizations are therefore limited to films grown using ammonia, N₂H₄, MA and TEA only.

Fig. 68 shows the optical transmittance and reflectance of ZnO films annealed at 400 °C in air. All films maintain their quality after annealing and show a better transmission that exceeds 90 % right before the absorption edge. The absorption edge of annealed films is sharper than that of as-grown films. This indicates an enhancement in film crystallinity after annealing. The absorption edge observed is around 375 nm – 380 nm. Table 23 summarizes the band gap of as-grown films as well as annealed films. Fig. 69 shows the typical red shift observed after annealing for ZnO films grown using N₂H₄. The band gap values calculated for as-grown films agree with what has been reported earlier for Zn(OH)₂ / ZnO₂ [87, 161], while the band gap values calculated for annealed films agree well with the 3.3 eV band gap of single crystalline ZnO [17].
Fig. 67 SEM micrographs of (a) as-grown EA-based film, (b) as-grown MA-based film, and (c) annealed MA-based film
Fig. 68 Specular transmittance and reflectance of NH$_3$, N$_2$H$_4$, MA and TEA-based annealed films

Fig. 69 Optical band gap calculations of as-grown and annealed N$_2$H$_4$-based film
According to the XRD pattern shown in Fig. 70 (a), TEA-based as-grown films are polycrystalline and mainly consist of cubic zinc peroxide with a preferential orientation along the [200] direction. Other phases of hexagonal ZnO as well as traces of elemental zinc have been detected. No diffraction peaks of Zn(OH)$_2$ have been observed. Similar XRD patterns of ZnO$_2$ have been reported by Ortega-López et al. [87], Han et al. [163], Hsu C and Wu [164]. We believe that using hydrogen peroxide as an oxidation agent resulted in the formation of ZnO$_2$ instead of Zn(OH)$_2$. This agrees with results reported earlier in the literature [87, 163-167]. Fig. 70 (b) shows the XRD pattern of the same film after annealing at 400 °C in air for one hour. As shown, only diffraction peaks of hexagonal ZnO have been detected. Annealed films are polycrystalline with preferred orientation along the [101] direction with no cubic phases of ZnO$_2$ been detected. Table 24 shows a summary of XRD data for standard cubic ZnO$_2$, hexagonal ZnO, and elemental zinc as well as XRD data of as-grown and annealed films.

Micro-Raman spectra of MA-based as-grown and annealed films are shown in Fig. 71. The peak observed at 840 cm$^{-1}$ for as-grown film is attributed to ZnO$_2$ and has been reported earlier by Uekawa et al. [165] and Sun et al. [166]. Uekawa et al. [165] assigned this peak to the stretching band of the O-O bond of the peroxo ion (O$_2^{2-}$).

<table>
<thead>
<tr>
<th>Complexing agent</th>
<th>Optical band gap (eV)</th>
</tr>
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<tr>
<td></td>
<td>As-grown film</td>
</tr>
<tr>
<td>NH$_3$</td>
<td>4.35</td>
</tr>
<tr>
<td>N$_2$H$_4$</td>
<td>4.29</td>
</tr>
<tr>
<td>TEA</td>
<td>4.38</td>
</tr>
<tr>
<td>MA</td>
<td>4.27</td>
</tr>
<tr>
<td>EA</td>
<td>4.30</td>
</tr>
<tr>
<td>DMA</td>
<td>3.75</td>
</tr>
</tbody>
</table>

Table 23
A summary of the optical band gap of as-grown and annealed ZnO films
Fig. 70 XRD pattern of (a) as-grown TEA-based film and (b) annealed TEA-based film

Fig. 71 Raman spectra of as-grown and annealed MA-based film
Table 24
A summary of XRD data for standard cubic ZnO₂, hexagonal ZnO, elemental Zn, and as-
grown and annealed TEA-based film

<table>
<thead>
<tr>
<th>Sample</th>
<th>2θ (deg.)</th>
<th>d (nm)</th>
<th>I/I₀ (%)</th>
<th>(hkl)</th>
<th>Sample</th>
<th>2θ (deg.)</th>
<th>d (nm)</th>
<th>I/I₀ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO₂ (*C)</td>
<td>31.794</td>
<td>0.28123</td>
<td>65.5</td>
<td>(1 1 1)</td>
<td>As-grown</td>
<td>31.786</td>
<td>0.28129</td>
<td>10.6</td>
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<tr>
<td></td>
<td>36.876</td>
<td>0.24355</td>
<td>100.0</td>
<td>(2 0 0)</td>
<td></td>
<td>36.950</td>
<td>0.24308</td>
<td>100.0</td>
</tr>
<tr>
<td>Zn (*H)</td>
<td>43.220</td>
<td>0.20915</td>
<td>100.0</td>
<td>(1 0 1)</td>
<td></td>
<td>43.147</td>
<td>0.20950</td>
<td>7.1</td>
</tr>
<tr>
<td>ZnO (†H)</td>
<td>47.535</td>
<td>0.19113</td>
<td>21.1</td>
<td>(1 0 2)</td>
<td></td>
<td>47.547</td>
<td>0.19108</td>
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<tr>
<td>ZnO₂ (*C)</td>
<td>53.139</td>
<td>0.17222</td>
<td>44.1</td>
<td>(2 2 0)</td>
<td></td>
<td>53.142</td>
<td>0.17221</td>
<td>7.5</td>
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<tr>
<td></td>
<td>63.268</td>
<td>0.14687</td>
<td>21.1</td>
<td>(3 1 1)</td>
<td></td>
<td>63.350</td>
<td>0.14669</td>
<td>6.7</td>
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<tr>
<td>ZnO (†H)</td>
<td>31.766</td>
<td>0.28147</td>
<td>56.5</td>
<td>(1 0 0)</td>
<td>Annealed</td>
<td>31.761</td>
<td>0.28151</td>
<td>89.2</td>
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<tr>
<td></td>
<td>34.419</td>
<td>0.26036</td>
<td>41.5</td>
<td>(0 0 2)</td>
<td></td>
<td>34.437</td>
<td>0.26022</td>
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<td>0.24761</td>
<td>100.0</td>
<td>(1 0 1)</td>
<td></td>
<td>36.379</td>
<td>0.24676</td>
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<tr>
<td></td>
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<td>0.19113</td>
<td>21.1</td>
<td>(1 0 2)</td>
<td></td>
<td>47.459</td>
<td>0.19141</td>
<td>26.1</td>
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<tr>
<td></td>
<td>56.590</td>
<td>0.16251</td>
<td>30.5</td>
<td>(1 1 0)</td>
<td></td>
<td>56.638</td>
<td>0.16238</td>
<td>39.3</td>
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<tr>
<td></td>
<td>62.851</td>
<td>0.14774</td>
<td>26.8</td>
<td>(1 0 3)</td>
<td></td>
<td>62.739</td>
<td>0.14798</td>
<td>15.0</td>
</tr>
<tr>
<td></td>
<td>67.941</td>
<td>0.13786</td>
<td>21.7</td>
<td>(1 1 2)</td>
<td></td>
<td>68.041</td>
<td>0.13768</td>
<td>21.1</td>
</tr>
</tbody>
</table>

*C = Cubic [168], *H = Hexagonal [169], †H = Hexagonal [170]

After annealing, the peak at 840 cm⁻¹ disappeared and only one peak at 437.2 cm⁻¹
was observed, which is the characteristic peak of the non-polar Raman active E₂-high
mode of ZnO [171, 172]. A Lorentzian fit of the peaks at 840 cm⁻¹ and 437.2 cm⁻¹
showed a FWHM of 58.7 cm⁻¹ and 7.8 cm⁻¹, respectively. The observed reduction in
FWHM after annealing indicates an enhancement in film crystallinity as is suggested by
the SEM and the transmittance measurements reported earlier (Fig. 67 & Fig. 68). It
should be noted that the baseline noise in the micro-Raman spectra is estimated to be
about 6% of the peak height. As a result, bearing in mind that the relative intensity of the
(102) peak of ZnO to that of the (200) peak of ZnO₂ in the as-grown film is about 7.9 %
(Table 24), it is not surprising that no vibration modes of ZnO were observed for the as-
grown films. Such low percentage of the hexagonal phase of ZnO in the as-grown film
compared to that of the cubic phase of ZnO₂ may be the reason for not detecting any vibration modes of ZnO in the as-grown films.

Fig. 72 shows the RBS spectra of N₂H₄-based film annealed at 400°C in air for one hour. Simulation using Rutherford Universal Manipulation Program (RUMP) [121] was implemented to obtain the best possible match to the raw RBS spectra. As shown, the Zn: O ratio obtained for the annealed film was (1.00: 1.25 ± 0.01). Since ZnO films are inherently n-type in nature which is due to either oxygen deficiency in the film or zinc ions existing in interstitial positions, a ratio of Zn: O less than unity was unexpected. RBS carried out on films grown using MA as well as NH₃ that are annealed under the same conditions (not shown in this work), also detected more oxygen content than zinc in both films. Because of their high resistivity, we were not able to perform Hall measurements on films annealed at 400 °C.

Although both XRD and micro-Raman spectroscopy are suggesting that as-grown films are mainly zinc peroxide, FTIR absorption spectroscopy of MA-based as-grown film, as shown in Fig. 73, detects a broadband around 3300 cm⁻¹ which is assigned to the O-H stretching mode of the hydroxyl group. This suggests that as-grown films may consist of a mixture of zinc peroxide and zinc hydroxide. Peaks detected between 2840 cm⁻¹ and 2930 cm⁻¹ are due to the C-H stretching vibration mode, which corresponds to the CH₃ group of Methylamine. Similar observation has been reported earlier by Ortega-López and Morales-Acevedo [161], where they detected a broad absorption band with a peak at 3354 cm⁻¹ related to the longitudinal stretching mode (3380 cm⁻¹) of the OH group. Xiong et al. [173] observed the same stretching mode at 3500 cm⁻¹ for ZnO nanoparticles grown via plasma synthesis.
Fig. 72 RBS spectrum and RUMP simulation of annealed N$_2$H$_4$-based film

ZnO - N$_2$H$_4$
(Zn: O = 1.00: 1.25)

Fig. 73 FTIR absorbance spectrum of as-grown MA-based film

As-grown Film

O-H stretch
C-H stretch

Fig. 73 FTIR absorbance spectrum of as-grown MA-based film
Fig. 74 (a) XPS multiplex spectra of O 1s of as-grown and annealed TEA-based film, (b) XPS multiplex spectra of Zn 2p₃/₂ of as-grown and annealed TEA-based film, and (c) deconvolution of the O 1s peak of annealed TEA-based film
Fig. 74 (a) shows the XPS multiplex spectra of the O 1s peak for as-grown as well as annealed TEA-based film. The binding energy of the O 1s peak of as-grown film is located at 532.0 eV. According to Dupin et al. [174], binding energies of the O 1s peak in the range of 527.7 eV to 530.6 eV are characteristics of O$^{2-}$ oxides, and binding energies in the range of 530.6 eV to 531.1 eV are characteristics of oxygen species integrated in the material as OH$^-$ or O$_2^-$, while binding energies in the range of 531.1 eV to 532.0 eV are due to low coordinated oxygen ions that could be described as “O$^-$” species. However, it should be noted that binding energies as high as 532.8 eV and 533.6 eV have been reported earlier for peroxides and hydro-peroxides at polymer surfaces [175].

Therefore, considering the findings of the XRD and micro-Raman (Fig. 70 & Fig. 71), we believe that the binding energy observed in this work at 532.0 eV is attributed to zinc peroxide. A shift of about 2.0 eV was observed for the O 1s peak of annealed film. Fig. 74 (b) shows the XPS multiplex of the Zn 2p$_{3/2}$ peak. The binding energy of the Zn 2p$_{3/2}$ of the as-grown film was observed at 1022.2 eV, while the binding energy associated with the Zn 2p$_{3/2}$ peak of the annealed film is 1021.8 eV, which indicates a small shift of 0.4 eV after annealing. Both values are within the range of binding energy characteristics of ZnO [148].

Since the O 1s peak of annealed film is asymmetric, a deconvolution of this peak was carried out, as shown in Fig. 74 (c). As shown, deconvolution of the O 1s peak of annealed ZnO film renders two doublets with the main doublet located at 530.0 eV, and the smaller one located at 531.8 eV. The contribution observed at 530.0 eV is a
characteristic of O\(^{2-}\) oxides [148, 174], while the contribution at 531.8 eV is due to either peroxide or “O\(^{-}\)” species. This explains the excess oxygen content in the ZnO film after annealing at 400 °C that was detected by RBS (Fig. 72). Since it is widely believed that zinc peroxide completely decomposes into zinc oxide at annealing temperatures higher than 200 °C [163-165], we believe that the contribution at 531.8 eV is mainly due to low coordinated “O\(^{-}\)” species, as suggested by Dupin et al. [174]. The presence of such low coordinated “O\(^{-}\)” species in the film could be attributed to the chemisorption of oxygen at the grain boundaries during the CBD process [19, 176].

High resolution transmission electron microscopy (HRTEM) of NH\(_3\)-based ZnO film that was annealed at 400 °C in air is shown in Fig. 75 (a). As shown, the ZnO layer is about 0.2 µm and the average grain size is about 10 nm. Only small variations in film thickness are observed, which are in the range of the 10 nm average grain diameter. Occasional cracks due to annealing are found at the surface of the film, which typically extend about half way into the ZnO layer.

The electron diffraction pattern observed (Inset of Fig. 75 (a)) confirms that the ZnO film is polycrystalline with a hexagonal crystal lattice. The Fourier-filtered HRTEM image in Fig. 75 (b) shows the crystal structure of the individual ZnO grains and their size.

As mentioned earlier, films annealed at 400 °C were highly resistive and, as a result, performing Hall measurements on such films was not possible. Therefore, films used for Hall measurements were further annealed at 500 °C in argon ambient for one hour.
Fig. 75 (a) HRTEM and TEM diffraction pattern (inset) of annealed NH$_3$-based ZnO film, and (b) Fourier-filtered HRTEM of annealed NH$_3$-based ZnO film (low boundary is glass substrate)
Table 25 shows the carrier density, resistivity, and Hall mobility of undoped films grown using ammonia, N$_2$H$_4$, MA and TEA. Table 25 also shows the Hall measurements carried out for Al-doped TEA-based ZnO film grown at [Al] / [Zn] ratio of ~ 0.008. As shown, all films show high carrier density and low resistivity for CBD undoped ZnO films. A carrier density as high as 2.24 x 10$^{19}$ cm$^{-3}$ and a resistivity as low as 6.48 x 10$^{-1}$ Ω-cm were obtained for undoped films. Resistivity of Al-doped film, however, was one order of magnitude less than the smallest resistivity achieved for undoped films. This may be a good indication that future in-situ doping of CBD-ZnO films using group III elements, such as aluminum, boron, indium, or gallium may reduce the resistivity further to achieve a transparent conducting CBD-ZnO thin films.

### 4.1.4 Conclusion

CBD of ZnO thin films using six different complexing agents is investigated. Four of these six ligands proved to be successful where high quality; adherent, uniform, transparent, and specularly reflecting ZnO films were obtained. As-grown films were mainly ZnO$_2$ with a band gap around 4.3 eV. Films annealed at 400 °C were ZnO with a band gap around 3.3 eV. XRD and micro-Raman revealed that as-grown film mainly consists of cubic ZnO$_2$ that was transformed into hexagonal ZnO after annealing. FTIR
of as-grown film, however, showed a broad absorption band around 3300 cm\(^{-1}\), which is
assigned to the O-H stretching mode of the hydroxyl group suggesting that as-grown film
may consist of a mixture of ZnO\(_2\) and Zn(OH)\(_2\). RBS detected excess oxygen content in
ZnO films after annealing. XPS spectra were found to be consistent with the RBS
observations of annealed films. HRTEM showed small variations in film thickness; in
the range of the 10 nm average grain diameter. Occasional cracks, due to annealing, are
found at the surface of the film, which typically extend about half way into the ZnO
layer. The electron diffraction pattern observed confirms only a slight texture of the
crystal lattice with respect to the substrate. A carrier density as high as 2.24 x 10\(^{19}\) cm\(^{-3}\)
and a resistivity as low as 6.48 x10\(^{-1}\) Ω-cm were obtained for annealed ZnO films. One
of the challenges we have faced in this work is the strong alkalinity of our solutions that
prevented us from growing thicker ZnO films using multi-dip deposition; any attempt to
dip the original film in a fresh solution to grow another layer of ZnO resulted in
immediate etching of the original layer and a subsequent deposition of a non-uniform and
a porous new ZnO layer with inferior quality. Therefore, in this work, we were limited to
one single deposition with a film thickness that ranged from 0.2 µm to 0.7 µm. Another
challenge was the occasional cracks that appear in ZnO films after annealing, as was
revealed by SEM and TEM of annealed MA-based and NH\(_3\)-based ZnO films (Fig. 67 (a)
& Fig. 75 (a), respectively). This, in turn, has a dramatic effect on film Hall mobility, as
shown (Table 25). One more challenge we faced is the unexpected excess oxygen
content in ZnO films after annealing which resulted in a Zn: O ratio less than unity. As a
result, films annealed at 400 °C in air were highly resistive and further annealing at 500
°C in argon ambient was necessary for Hall measurements to be attainable. We believe
that more careful post-heat treatments as well as in-situ doping of such CBD-ZnO films using group III elements, such as aluminum, boron, indium, or gallium may reduce the resistivity further where a transparent conducting CBD-ZnO is achievable.
4.2 Investigation of Chemical Bath Deposition of CdO Thin Films Using Three Different Complexing Agents

4.2.1 Introduction

Chemical bath deposition (CBD) is the analog in liquid phase of the well-known chemical vapor deposition technique in the vapor phase. Among all techniques used to grow group II-VI semiconductors, CBD has the advantage of being a simple, low temperature, and inexpensive large-area deposition technique. It has been employed in the deposition of semiconductor thin films for over forty years [18]. CBD has been extensively used in growing Group II-VI semiconductors, such as CdS [18, 20-24], CdSe [48-51], HgS [60, 61], HgSe [62, 63], ZnS [64-67], ZnSe [76-79], and ZnO [84-88].

CdO thin films reported in the literature have been obtained mainly by dc magnetron reactive sputtering [177], metal organic chemical vapor deposition [178, 179], vacuum evaporation [180], electrochemical deposition [181], pulsed laser deposition [182], electron beam evaporation [183], spray pyrolysis [184], sol-gel [185], RF magnetron sputtering [186], and successive ionic layer adsorption and reaction [187]. However, only few attempts to grow CdO thin films using CBD have been reported [55-58], where only ammonia has been used as complexing agent.

In this work, we report CBD of CdO using three different complexing agents, namely ammonia, ethanolamine (EA), and methylamine (MA). Transmittance, reflectance measurements and band gap calculations are carried out for as-grown films as well as annealed films. Resistivity, carrier density, and Hall mobility of annealed films are acquired using Hall effect measurements. Crystal structure as well as crystal quality are determined using X-ray diffraction, transmission electron microscopy, and Fourier
transform infrared spectroscopy. Film morphology, composition, and binding energy are studied using scanning electron microscopy, Rutherford backscattering spectroscopy, and X-ray photoelectron spectroscopy, respectively.

4.2.2 Experimental Details

CdO films were prepared using aqueous solutions of CdSO₄ (0.038 M), (NH₄)₂SO₄ (0.076 M), H₂O₂ (34%), and NH₄OH (29.4 %). Each bath contained 100-120 ml of de-ionized water (resistivity ~ 18.2 MΩ·cm) that was kept under stirring at 85 °C. In addition to ammonia, two other complexing agents were used; EA and MA. To ensure stable Cd[NH₃]₂⁺⁺ complex in the main solution, ammonia was added whenever EA or MA is being used. Similar to our previous work on CBD-ZnO [84], It was noticed that adding ammonia is necessary to dissolve the Cd(OH)₂ formed upon mixing the Cd-source and EA or MA. CdSO₄, (NH₄)₂SO₄, and the desired complexing agent were mixed at room temperature before being added to the main solution. Appropriate amounts of hydrogen peroxide were then added to the main solution. Films were grown on 38 mm x 38 mm x 1 mm glass substrates (Schott Borofloat glass). With the help of a Teflon holder, the glass substrate was kept vertically in the solution. All substrates were held in the bath prior to the addition of any of the reagents. To ensure deposition of high-quality, adhesive, and specularly reflecting films, the substrate was removed from the solution when the solution becomes turbid and the homogeneous reaction starts to take place. The cleaning steps of the substrate are reported elsewhere [22].

Details of the specular transmittance/reflectance measurements, bandgap calculations, Hall effect measurements, XRD, SEM, and XPS measurements are
mentioned in sec. 3.1.2. Details of the TEM measurements are reported in sec. 3.2.2. Details of the RBS measurements can be found in sec. 2.1.2. Details of the FTIR micro-analysis are mentioned in sec. 4.1.2.

4.2.3 Results and Discussion

Fig. 76 shows the optical transmittance of as-grown films for all three complexing agents. As shown, all three films exhibit high transmittance that exceeds 80% in the visible region. The NH$_3$-based and EA-based films exhibit a sharp absorption edge around 365 nm – 370 nm, while the absorption edge of the MA-based film is around 270 nm. Such high transmittance and sharp absorption edge observed indicate the high quality of all three films. The calculated bandgap is 3.37 eV, 3.40 eV, and 4.64 eV for the EA-based, NH$_3$-based, and MA-based film respectively. The blue shift observed in the case of MA-based films can be understood by comparing its XRD pattern to that of EA-based film. According to Fig. 77, the as-grown EA-based film consists of a mixture of three different phases; cubic CdO [188], monoclinic / hexagonal Cd(OH)$_2$ [189, 190], and cubic CdO$_2$ [191]. However, as shown in Fig. 78, only cubic phase of CdO$_2$ is detected for as-grown MA-film. It should be noted that the XRD pattern of as-grown NH$_3$-film (not shown in this work) is similar to that of EA-based film. This may explain why both films almost share the same absorption edge, while a blue shift of more than 1.2 eV is observed in the case of MA-based film. After annealing at 400 °C in air for one hour, all three films are fully transformed into CdO. Fig. 79 shows the XRD pattern of annealed EA-based film, with only cubic phase of CdO [192] being detected. Similar XRD patterns are obtained for both MA-based and NH$_3$-based films annealed under the same conditions.
Fig. 76 Specular transmittance of as-grown films deposited using three different complexing agents

Fig. 77 XRD pattern of as-grown EA-based film
Fig. 78 XRD pattern of as-grown MA-based film

Fig. 79 XRD pattern of annealed EA-based film
Such transformation to CdO after annealing is responsible for the red shift observed in the optical transmittance (Fig. 80) and the optical bandgap (Fig. 81) of EA-based film. The bandgap of annealed CdO films is 2.53 eV, which agrees with the 2.55 eV [58], 2.57 eV [55], and 2.58 eV [158] bandgap values reported earlier in the literature for CdO.

FTIR absorption measurements shown in Fig. 82 agree with the XRD findings. Similar to what we have previously observed for CBD-ZnO [84], FTIR of as-grown EA-based film (Fig. 82a) detects a broadband around 3300 cm\(^{-1}\) which is assigned to the O-H stretching mode of the hydroxyl group. This confirms the presence of the Cd(OH)\(_2\) phase in as-grown EA-based films. This broadband disappears after annealing, as shown in Fig. 82(b). However, as shown in Fig. 82(c), such broadband does not exist in the case of as-grown MA-based film. It should be noted that peaks detected between 2840 cm\(^{-1}\) and 2930 cm\(^{-1}\) (Fig. 82a) are due to the C-H stretching vibration mode, which corresponds to the CH\(_2\) group of ethanolamine, which disappears after annealing as EA-film is fully transformed into CdO. Absorbance peaks observed between 650 cm\(^{-1}\) and 1500 cm\(^{-1}\) are due to Si-O and B-O stretching vibrations [193] from the Borofloat glass substrate. It is worth noting that the boron content of Borofloat glass is about 5.2%.

Fig. 83 shows the RBS spectra of as-grown EA-based film. Simulation using Rutherford Universal Manipulation Program (RUMP) [121] was implemented to obtain the best possible match to the raw RBS spectra. As shown, the Cd:O ratio obtained for the as-grown film is (1.00: 1.74 ±0.01). This confirms the presence of CdO in as-grown EA-based films. Should the film contains only mixed phases of CdO\(_2\) and Cd(OH)\(_2\), a ratio of about (1.00: 2.00) will be observed.
Fig. 80 Specular transmittance and reflectance of as-grown and annealed EA-based film

Fig. 81 Optical band gap calculations of as-grown and annealed EA-based film
Fig. 82 FTIR absorbance spectrum of (a) as-grown EA-based film, (b) annealed EA-based film, and (c) as-grown MA-based film.

Fig. 83 RBS spectrum and RUMP simulation of as-grown EA-based film.
Such ratio is obtained in the case of as-grown MA-based film (not shown in this work). Fig. 84, however, shows RBS of MA-annealed film, where a ratio of $(1.00: 1.00 \pm 0.01)$ is observed. This indeed confirms that, after annealing at 400 °C in air, film is fully transformed into CdO.

The XPS multiplex spectra of the Cd 3d$_{5/2}$ and 3d$_{3/2}$ peaks of as-grown as well as annealed EA-based films are shown in Fig. 85. As shown, Cd 3d$_{5/2}$ and 3d$_{3/2}$ peaks of the annealed film are symmetric and located at 405 eV and 411.8 eV which agrees well with the 6.74 eV spin-orbit energy splitting between Cd 3d$_{5/2}$ and 3d$_{3/2}$ states [148]. However, both peaks of as-grown film are asymmetric. As shown in Fig. 86, deconvolution of the Cd 3d$_{5/2}$ peak renders three peaks with binding energies of 403.7 eV, 404.5 eV, and 405.4 eV. These three binding states can be assigned to CdO$_2$, Cd(OH)$_2$, and CdO, respectively [148]. This also confirms the XRD, FTIR, and RBS findings of the mixed phase nature of as-grown EA-based film. Similar deconvolution carried out for the Cd 3d$_{3/2}$ peak is also shown in Fig. 86. All three peaks obtained maintain a ~ 6.7 eV energy difference from their corresponding Cd 3d$_{5/2}$ peaks. Finally, it should be noted that both 405.4 eV and 405 eV values observed in as grown and annealed films lie within the accepted values of Cd 3d$_{5/2}$ binding energies of CdO [148].

Fig. 87 shows the XPS multiplex spectra of the O 1s peak for as-grown and annealed EA-based films. Similar to the Cd 3d peaks, the O 1s peak of annealed film is symmetric while that of as-grown films is asymmetric. The O 1s binding energy of annealed film is at 529.9 eV, which lies within the 527.7 eV to 530.6 eV range characteristic of O$^{2-}$ oxides [148, 174].
Fig. 84 RBS spectrum and RUMP simulation of annealed MA-based film

Fig. 85 XPS multiplex spectra of Cd 3d of as-grown and annealed EA-based film
Fig. 86 Deconvolution of the Cd 3d peaks of as-grown EA-based film

Fig. 87 XPS multiplex spectra of O 1s of as-grown and annealed EA-based film
As shown in Fig. 88, a deconvolution of the O 1s peak of as-grown film renders two doublets with the main doublet located at 531.1 eV and the smaller one located at 528.4 eV. According to Dupin et al. [174], binding energies in the range of 530.6 eV to 531.1 eV are characteristics of oxygen species integrated in the material as OH$^-$ or O$_2^{2-}$. Therefore, the main contribution observed at 531.1 eV is due to either cadmium peroxide or cadmium hydroxide, while the contribution at 528.4 eV is characteristic of cadmium oxide, which again agrees with the XRD, FTIR, and RBS findings of the mixed phase nature of as-grown EA-based film.

HRTEM image of annealed EA-film is shown in Fig. 89. As shown, the CdO layer is about 0.25 µm. Only small variations in film thickness are observed. Occasional cracks due to annealing are found, as indicated by arrows near the edge of the film. The electron diffraction pattern observed (Inset of Fig. 89) confirms that CdO film is polycrystalline with a cubic crystal lattice.

SEM micrographs of annealed MA, EA, and NH$_3$-based films are shown in Fig. 90. As shown, MA and EA-based films maintain their integrity after annealing while NH$_3$-based films deteriorate when annealed, as indicated by the high density of cracks shown in Fig. 90 (c). This could be attributed to stress in as-grown NH$_3$-based films, which caused films to lose their integrity after annealing. We have reported similar observation for EA-based ZnO films in a previous work [84]. Some pinholes have been observed in MA-based film (Fig. 90 a). It is also noticed that, when compared to EA-film, average grain size of MA-film is much smaller. EA-based film, however, is continuous with much smoother surface than the other two films. This will have a significant impact on film resistivity and mobility as will be shown.
Fig. 88 Deconvolution of the O 1s peak of as-grown EA-based film

Fig. 89 HRTEM and TEM diffraction pattern (inset) of annealed EA-based CdO film
Fig. 90 SEM micrographs of (a) annealed MA-based film, (b) annealed EA-based film, and (c) annealed NH$_3$-based film
Table 26

<table>
<thead>
<tr>
<th>Sample</th>
<th>Carrier density (cm⁻³)</th>
<th>Mobility (cm²V⁻¹S⁻¹)</th>
<th>Resistivity (Ω-cm)</th>
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<tr>
<td>EA-based</td>
<td>1.89 x 10^{20}</td>
<td>3.17 x 10⁰</td>
<td>1.04 x 10⁻²</td>
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<td>MA-based</td>
<td>4.35 x 10^{18}</td>
<td>3.91 x 10⁻¹</td>
<td>3.67 x 10⁰</td>
</tr>
<tr>
<td>NH₃-based</td>
<td>7.55 x 10^{17}</td>
<td>8.21 x 10⁻¹</td>
<td>1.01 x 10¹</td>
</tr>
</tbody>
</table>

Table 26 shows the carrier density, resistivity, and Hall mobility of annealed EA, MA, and NH₃-based CdO films as revealed by Hall measurements carried out at room temperature. As shown, EA-films have the highest mobility and lowest resistivity amongst all three films. Resistivity of MA-film is two orders of magnitude higher, while that of NH₃-films is three orders of magnitude higher. Hall mobility of both films is also much smaller than that of EA-film. We believe that pinholes, small grain size, and high density of cracks observed under SEM (Fig. 90 (a) & (c)) are responsible for such drop in film resistivity and Hall mobility. High carrier density observed in EA-film can be attributed to oxygen deficiency in the film due to annealing. It is widely believed that excess Cd content in CdO film will result in Cd ions occupying interstitial sites where they act as donors which, in turn, increases carrier density and lowers film resistivity.

SEM and Hall results suggest that EA-based CdO films are the best candidates for fabricating transparent conducting oxides using a simple technique such as chemical bath deposition. These films are found to be of high quality, good uniformity, exhibit high transmittance, and good crystallinity. In addition, high conductivity is observed in EA-based films where a carrier density as high as 1.89 x 10^{20} cm⁻³ and a film resistivity as low as 1.04 x 10⁻² Ω-cm are achievable.
4.2.4 Conclusion

CBD of CdO using three different complexing agents is investigated. All three complexing agents proved to be successful where high quality; adherent, uniform, transparent, and specularly reflecting CdO films were obtained. XRD revealed that As-grown EA-based films consist of mixture of cubic CdO$_2$, cubic CdO, and monoclinic / hexagonal Cd(OH)$_2$ while only cubic CdO$_2$ phase has been detected in as-grown MA-based film. Annealing at 400 °C in air for one hour fully transformed as-grown films into cubic CdO. Optical bandgap of as-grown EA, NH$_3$, and MA-based films are 3.37 eV, 3.40 eV, and 4.64 eV, respectively. Annealed films have optical bandgap of 2.53 eV. Both as-grown and annealed films exhibit high transmittance that exceeds 80% in the visible region.

FTIR of as-grown EA-based film showed a broad absorption band around 3300 cm$^{-1}$, which is assigned to the O-H stretching mode of the hydroxyl group confirming the Cd(OH)$_2$ phase detected by XRD. Such absorption band disappeared after annealing and did not exist in as-grown MA-based film. RBS observations are consistent with the XRD and FTIR results. Deconvolution of the XPS multiplex of Cd 3d and O 1s peaks of as-grown EA-based film revealed three binding states of CdO$_2$, Cd(OH)$_2$, and CdO, two of which disappeared after annealing which agree with the observations of XRD, FTIR, and RBS. HRTEM showed small variations in film thickness and occasional cracks, due to annealing. The electron diffraction pattern observed confirms the polycrystalline nature of the CdO film. SEM micrographs show high density of cracks in annealed NH$_3$-based film. Some pinholes were detected in annealed MA-based films. SEM and Hall results revealed that EA-based CdO films are the best candidates for fabricating transparent
conducting oxides using CBD, where a carrier density as high as $1.89 \times 10^{20} \text{ cm}^{-3}$ and a film resistivity as low as $1.04 \times 10^{-2} \Omega\text{-cm}$ are achievable.
4.3 Investigation of Chemical Bath Deposition of SnO$_2$ and Cd$_2$SnO$_4$ Thin Films

4.3.1 Introduction

Transparent conducting oxides (TCO) such as indium tin oxide (ITO) play an important role in solar cells, light emitting diodes, as well as other optoelectronic devices. Seeking alternatives to ITO has been the focus of attention for a long time. As a result, other TCO layers such as ZnO, CdO, and Cd$_2$SnO$_4$ are heavily investigated. Although several techniques are currently in use to grow such layers, chemical bath deposition present a simple, low temperature, and inexpensive large-area deposition alternative. For over forty years, it has been widely used to grow group II-VI semiconductors, such as CdS [18, 20-47], CdSe [48-54], CdO [55-58], HgS [59-61], HgSe [54, 62, 63], ZnS [64-75], ZnSe [76-83], and ZnO [84-94].

In a previous work [84], we investigated CBD of ZnO using six different complexing agents, four of which proved to be successful in growing high quality ZnO thin films with a bandgap of 3.3 eV, a carrier density as high as $2.24 \times 10^{19}$ cm$^{-3}$, and a resistivity as low as $6.48 \times 10^{-1} \Omega$-cm. In another work [194], we succeeded to grow CBD-CdO thin films using three different complexing agents. Annealed CdO films have a bandgap of 2.53 eV, a carrier density as high as $1.89 \times 10^{20}$ cm$^{-3}$, and a resistivity as low as $1.04 \times 10^{-2} \Omega$-cm.

SnO$_2$ thin films reported in the literature have been obtained mainly by RF magnetron sputtering [195], metal organic chemical vapor deposition [196], vacuum evaporation [197], pulsed laser deposition [198], pulsed electron beam deposition [199], spray pyrolysis [200], sol-gel [201], chemical vapor deposition [202], and successive
ionic layer adsorption and reaction [203]. However, very few attempts to grow SnO$_2$ thin films using CBD have been reported [204, 205]. In both cases, the deposition time was of the order of hours; 15-24 hours in the work of Tsukuma et al [204] and 5-12 hours in the work of Supothina and De Guire [205]. Tsukuma et al [204] reported a growth rate that ranged from 2 nm / h at 40 °C to 50 nm / h at 80 °C. Supothina and De Guire [205] reported growing SnO$_2$ films, 60-70 nm thick, after 12 hours of deposition, with a growth rate of approximately 9 nm / h during the first 4 hours. Clearly, the small growth rate is a big limitation to using CBD as a viable technique to grow SnO$_2$ thin films.

In this work, we report a new approach of CBD-SnO$_2$ that enabled us to grow a 0.2 µm thick SnO$_2$ film using multi-dip deposition, with a deposition time as little as 8-10 minutes. We also investigate the possibility of fabricating a TCO layer of CBD-Cd$_2$SnO$_4$ by growing CBD-SnO$_2$ layer first, followed by CBD-CdO layer, and then annealing at different temperatures in air as well as in argon ambient.

Transmittance, reflectance measurements and band gap calculations are carried out for as-grown films as well as annealed films. Resistivity, carrier density, and Hall mobility of annealed films are acquired using Hall effect measurements. Crystal structure as well as crystal quality are determined using X-ray diffraction, transmission electron microscopy. Film morphology, composition, and binding energy are studied using atomic force microscopy (AFM), Rutherford backscattering spectroscopy, and X-ray photoelectron spectroscopy, respectively.
4.3.2 Experimental Details

SnO$_2$ films were prepared using aqueous solutions of tin chloride pentahydrate (0.028 M). Each bath contained 120 ml of de-ionized water (resistivity $\sim$ 18.2 M$\Omega$-cm) that was kept under stirring at 55 °C. Films were grown on 38 mm x 38 mm x 1 mm glass (Schott Borofloat glass) as well as quartz substrates (supplied by Quartz Scientific Inc.). With the help of a Teflon holder, the glass substrate was kept vertically in the solution. The cleaning steps of the substrate are reported elsewhere [22]. To ensure deposition of high-quality and adhesive films, the substrate was removed from the solution when the solution becomes turbid and the homogeneous reaction starts to take place. The deposition time was about 8-10 minutes. In order to grow SnO$_2$ films with a $\sim$ 0.2 µm thickness, the deposition process was repeated four times, with fresh solutions being used every time.

After annealing the SnO$_2$ film at 500 °C in air for one hour, a 0.2 µm layer of CdO is grown on top of the SnO$_2$ layer using CBD. Both layers are then annealed at different temperatures in air and in argon ambient so that cadmium diffuses into the SnO$_2$ layer to form Cd$_2$SnO$_4$. CdO thin films are grown using ammonia and ethanolamine as complexing agents, CdSO$_4$ as cadmium source, (NH$_4$)$_2$SO$_4$ as a buffer, and H$_2$O$_2$ as an oxidation agent. Details of CBD of CdO thin films are reported elsewhere [194].

Details of the specular transmittance/reflectance measurements, bandgap calculations, Hall effect measurements, XRD, and XPS measurements are mentioned in sec. 3.1.2. Details of the TEM measurements are reported in sec. 3.2.2. Details of the RBS measurements can be found in sec. 2.1.2. AFM images were acquired using Veeco Multimode SPM in tapping mode.
4.3.3 Results and Discussion

It is worth noting that SnO$_2$ films grown are extremely adhesive; highly concentrated sulfuric acid (98 %) and nitric acid (96 %) could not etch them. Therefore, in order to perform optical measurements, for example, two substrates were mounted together on the Teflon sample holder so that there is deposition on only one side of the substrate. Film thickness was determined using TEM, as will be shown later.

Fig. 91 shows the optical transmittance of as-grown and annealed SnO$_2$ films as well as CdO+SnO$_2$ films annealed at 500 °C and 700 °C. As shown, all films exhibit high transmittance that, in the case of SnO$_2$ films, exceeds 90% in the visible region. A red shift is observed due to formation of Cd$_2$SnO$_4$, which increases with increasing annealing temperature. The sharp absorption edge observed in Cd$_2$SnO$_4$ indicates that films still maintain high quality even after annealing at temperatures as high as 700 °C. Films annealed at a temperature of 800 °C or higher did not maintain the same quality. Fig. 92 shows the optical bandgap calculated for annealed SnO$_2$ films as well as CdO+SnO$_2$ films annealed at 500 °C and 700 °C. As shown, the bandgap is 4.42 eV, 2.67 eV, and 2.52 eV, for annealed SnO$_2$, Cd$_2$SnO$_4$ annealed at 500 °C, and 700 °C, respectively. It should be noted that the bandgap we observed for CdO films annealed at 400 °C is 2.53 eV [194]. Clearly, as the annealing temperature increases, films tend to behave more like CdO rather than Cd$_2$SnO$_4$. It should be noted that though the typical bandgap of SnO$_2$ is 3.6 eV, much higher bandgap values have been reported in the literature. Rakhshani et al [206] reported a direct bandgap of 4.11 eV, while Dawar and Joshi [207] reported bandgap values in the range of 3.9 eV – 4.6 eV for SnO$_2$. 

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Fig. 91 Specular transmittance of as-grown and annealed SnO$_2$ films and CdO+SnO$_2$ films annealed at 500 °C and 700 °C

Fig. 92 Optical band gap calculations of annealed SnO$_2$ films and CdO+SnO$_2$ films annealed at 500 °C and 700 °C
Fig. 93 XRD pattern of annealed SnO$_2$ film

Fig. 94 RBS spectrum and RUMP simulation of annealed SnO$_2$ film
The XRD pattern of annealed SnO$_2$ film is shown in Fig. 93. Annealed film is polycrystalline with a main (113) reflection and four weak reflections characteristic of the (023), (200), (106), and (117) planes of orthorhombic SnO$_2$ [208]. As grown SnO$_2$ films are found to be amorphous. Fig. 94 shows the RBS spectra of annealed SnO$_2$ film. Simulation using Rutherford Universal Manipulation Program (RUMP) [121] was implemented to obtain the best possible match to the raw RBS spectra. As shown, the film is highly stoichiometric with a Sn: O ratio of about (1.00: 2.00 ±0.01). The XPS multiplex spectra of the Sn 3d$_{5/2}$ and 3d$_{3/2}$ peaks of annealed SnO$_2$ film is shown in Fig. 95. As shown, Sn 3d$_{5/2}$ and 3d$_{3/2}$ peaks of the annealed film are symmetric and located at 486.4 eV and 494.8 eV which agrees well with the 8.41 eV spin-orbit energy splitting between Sn 3d$_{5/2}$ and 3d$_{3/2}$ states [148]. Also, the observed binding energy of 486.4 eV of Sn 3d$_{5/2}$ lies within the accepted range of binding energy values for SnO$_2$ [148]. Fig. 96 shows the XPS multiplex spectra of the O 1s peak of annealed SnO$_2$ film. The O 1s peak of annealed film is symmetric and located at 530.3 eV, which lies within the 527.7 eV to 530.6 eV range characteristic of O$^{2-}$ oxides [148, 174].

2-D and 3-D AFM images of as-grown as well as annealed SnO$_2$ film are shown in Fig. 97 and Fig. 98, respectively. Both films are continuous, uniform, and relatively smooth. The surface features of the films are comparable and the calculated surface roughness values are ~ 37.5 nm and 26.8 nm for as-grown and annealed SnO$_2$ films, respectively. Clearly, annealing reduced film roughness. Occasional crystallite overgrowth is observed on the surface of both films. This is attributed to colloidal particulates formed in solution and then adsorbed on the film.
Fig. 95 XPS multiplex spectra of Sn 3d of annealed SnO$_2$ film

Fig. 96 XPS multiplex spectra of O 1s of annealed SnO$_2$ film

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SnO$_2$-as grown

Fig. 97 2-D and 3-D AFM images of as-grown SnO$_2$ film

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Fig. 98 2-D and 3-D AFM images of annealed SnO$_2$ film
Fig. 99 HRTEM and TEM diffraction pattern (inset) of annealed SnO$_2$ film
HRTEM image of annealed SnO$_2$ film is shown in Fig. 99. As shown, the SnO$_2$ layer is about 0.20 µm. Film surface is uniform with only small variations in film thickness being observed. The electron diffraction pattern observed (Inset of Fig. 99) confirms that SnO$_2$ film is polycrystalline with orthorhombic crystal lattice structure.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Carrier density (cm$^{-3}$)</th>
<th>Mobility (cm$^2$V$^{-1}$S$^{-1}$)</th>
<th>Resistivity (Ω·cm)</th>
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</thead>
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<td>CdO</td>
<td>$1.89 \times 10^{20}$</td>
<td>$3.17 \times 10^{1}$</td>
<td>$1.04 \times 10^{-2}$</td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>$5.15 \times 10^{12}$</td>
<td>$1.61 \times 10^{1}$</td>
<td>$7.53 \times 10^{4}$</td>
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<tr>
<td>Cd$_2$SnO$_4$</td>
<td>$3.74 \times 10^{19}$</td>
<td>$3.49 \times 10^{-1}$</td>
<td>$4.78 \times 10^{-1}$</td>
</tr>
</tbody>
</table>

Table 27 shows Hall effect measurements carried out at room temperature for CdO film annealed at 400 °C, SnO$_2$ film annealed at 500 °C, and Cd$_2$SnO$_4$ layer annealed at 500 °C. As shown, the carrier density and resistivity values of the Cd$_2$SnO$_4$ film are intermediate between those of CdO film and SnO$_2$ film. Clearly, using a simple technique like CBD, we have succeeded to grow a TCO layer with a bandgap of ~ 2.7 eV and a carrier density as high as $3.74 \times 10^{19}$ cm$^{-3}$ and a resistivity ~ $4.78 \times 10^{-1}$ Ω·cm.

4.3.4 Conclusion

CBD of SnO$_2$ as well as Cd$_2$SnO$_4$ is investigated. A 0.2 µm thick CBD-SnO$_2$ films are grown using multi-dip deposition, with a deposition time as little as 8-10 minutes. Films are extremely adhesive and cannot be etched. Films are highly transparent with a bandgap of ~ 4.42 eV and a transmittance exceeding 90 % in the visible region of the spectrum. Annealed films are orthorhombic with a preferred orientation along the [113] direction. According to RBS data, annealed film is highly stoichiometric with a Sn: O...
ratio of about (1.00: 2.00 ± 0.01). AFM images show as-grown and annealed SnO$_2$ films to be continuous, uniform, and relatively smooth. An average roughness of ~ 37.5 and 26.8 nm is estimated for as-grown and annealed films, respectively. The electron diffraction pattern observed under TEM confirms that SnO$_2$ film is polycrystalline with orthorhombic crystal lattice structure.

Cd$_2$SnO$_4$ layer with a wide bandgap of ~ 2.7 eV and a carrier density as high as 3.74 x 10$^{19}$ cm$^{-3}$ and a resistivity ~ 4.78 x 10$^{-1}$ Ω-cm is achieved using a simple technique like CBD. Although promising, we believe that further work is needed to reach a bandgap of ~ 3.0 eV or higher, and a resistivity of the order of 10$^{-3}$ Ω-cm or lower, in order to fabricate a viable CBD-TCO layer. This work merely reports a preliminary step towards using CBD to fabricate a TCO layer of Cd$_2$SnO$_4$. Careful studies of post-heat treatments as well as further investigations of CBD-Cd$_2$SnO$_4$ stoichiometry are still needed to achieve this goal.
CONCLUSION

We have succeeded to optimize CBD of CdS thin films using NTA, NTA+N$_2$H$_4$, and NTA+NH$_3$. The effect of the cadmium salt on the deposition process of CdS has been studied using four different cadmium sources. Higher growth rate is achieved when CdSO$_4$ is used as cadmium precursor. Films grown using CdSO$_4$ have higher bandgap, better crystallinity, higher mobility, and lower resistivity. Highly stoichiometric films are obtained when CdCl$_2$ as well as CdI$_2$ are used as cadmium sources.

*In-situ* doping of CBD-CdS using group III elements, such as aluminum, boron, and gallium proves to be successful. We have demonstrated that the dark resistivity of CBD-CdS could be reduced by four orders of magnitude using this approach; a dark resistivity of the order of $10^{-2}$ $\Omega$-cm and a carrier density as high as $\sim 10^{19}$ cm$^{-3}$ are achieved. We have also shown that due to extremely low solubility product of indium sulfide ($K_{sp} = 10^{-73.24}$) compared to that of Cadmium Sulfide ($K_{sp} = 10^{-27.94}$) [96], it is highly unlikely, if not impossible, to incorporate indium in CdS, using CBD.

CBD of ZnO using six different complexing agents has been investigated, four of which prove to be successful. Adhesive, uniform, specularly reflecting, and transparent high quality ZnO films are obtained. Aluminum *in-situ* doping of CBD-ZnO shows promising results where a carrier density as high as $2.49 \times 10^{19}$ cm$^{-3}$ and a resistivity as low as $9.32 \times 10^{-2}$ $\Omega$-cm are achieved.

CBD of CdO using three different complexing agents has been achieved. EA-based CdO films are found to be the best candidates for fabricating transparent conducting oxides using CBD, where a carrier density as high as $1.89 \times 10^{20}$ cm$^{-3}$ and a
film resistivity as low as $1.04 \times 10^{-2} \, \Omega \cdot \text{cm}$ are achievable. SnO$_2$ thin films grown using CBD are uniform, transparent, and extremely adhesive. Cd$_2$SnO$_4$ layer with a wide bandgap of $\sim 2.7$ eV and a carrier density as high as $3.74 \times 10^{19} \, \text{cm}^{-3}$ and a resistivity $\sim 4.78 \times 10^{-1} \, \Omega \cdot \text{cm}$ is achieved using CBD. Although promising, we believe that further work is needed to reach a bandgap of $\sim 3.0$ eV or higher, and a resistivity of the order of $10^{-3} \, \Omega \cdot \text{cm}$ or lower, in order to fabricate a viable CBD-TCO layer.

We believe that our work on CBD of metal oxides, such as ZnO, CdO, and SnO$_2$ merely serves as a preliminary step towards using CBD to fabricate a TCO layer of Al-doped ZnO as well as Cd$_2$SnO$_4$.

Finally, we believe that the future of CBD resides in growing metal oxides as well as TCO layers that could be used in the fabrication of light emitting diodes (LEDs) and batteries. We also believe that, although difficult, fabricating and entire CIGS-based solar cell using only CBD is possible. We have demonstrated that CBD of high quality CdS, ZnO, CdO, SnO$_2$, as well as Cd$_2$SnO$_4$ thin films is achievable. The challenge now is to grow the CIGS absorber layer using CBD. We believe that the right approach is to optimize CBD of copper sulfide, indium sulfide, and gallium sulfide separately. The next step is to find the optimum pH value of the solution in each case that will ensure that film grown will not be etched when dipped again in the solution, so that three different layers of copper sulfide, indium sulfide, and gallium sulfide could be grown using the multi-dip deposition approach. Post heat treatment of all three layers should result in the formation of the CIGS layer.
Should this approach succeed, the goal of fabricating an entire solar cell device using only CBD could become a reality. This indeed will have a significant impact on solar cells industry.
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