In-situ boron doping of chemical-bath deposited CdS thin films

Hani Khallaf, Guangyu Chai, Oleg Lupan, Lee Chow, Helge Heinrich, S. Park, and Alfons Schulte

1 Department of Physics, University of Central Florida, Orlando, FL 32816, USA
2 Apollo Technologies, Inc., 205 Waymont Court, Suite 111, Lake Mary, FL 32746, USA
3 Department of Microelectronics and Semiconductor Devices, Technical University of Moldova, 168 Stefan cel Mare Boulevard, 2004 Chisinau, Republic of Moldova
4 Advanced Materials Processing and Analysis Center, University of Central Florida, Orlando, FL 32816, USA
5 Department of Mechanical, Materials, Aerospace Engineering, University of Central Florida, Orlando, FL 32816, USA

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1 Introduction
Due to its wide bandgap (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)Se₂ [1, 2]. Chemical-bath deposition (CBD) is one of the most commonly used techniques to grow CdS thin films [3, 4]. It is 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 1.7 × 10⁻² Ω cm [5], 10⁹ Ω cm [6], and 10¹⁰ Ω cm [7] has been reported earlier for CBD–CdS. In a previous study [3], 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 × 10⁸ Ω cm to 8.01 × 10⁸ Ω cm, depending on the Cd precursor used and film stoichiometry. Although a resistivity of 8.01 × 10⁸ Ω cm is low 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 [8–10], Cu [11, 12], Li [13, 14], and Na [15] has been reported. In this work, the effectiveness of B⁺⁺ dopant 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 a phase transition were detected by micro-Raman spectroscopy and transmission electron microscopy. The chemistry and morphology of films were unaffected by B doping.
2 Experimental details  Cds films were prepared using stock solutions of CdSO₄ (0.038 M), (NH₄)₂SO₄ (0.076 M), NH₂OH (29.4%), and (NH₄)₂CS (0.076 M). Films were grown on 38 mm × 38 mm × 1 mm glass substrates (Schott Borofloat glass, supplied by S.I. Howard Glass Co., Inc.). Boron doping was carried out by adding boric acid (H₃BO₃) as the 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 h. Details of the growth process have been previously reported [3]. The cleaning steps of the substrate are reported elsewhere [8].

Alpha-step 500 surface profilometer (Tencor) was used to determine film thickness. Specular transmittance measurements were carried out at room temperature with unpolarized light at normal incidence in the wavelength range from 350 nm to 1200 nm using a Cary 500 (Varian) double-beam UV/VIS spectrophotometer. Specular reflectance measurements were carried out at an angle of incidence of 7° in the same wavelength range. The optical absorption coefficient \( \alpha \) was calculated for each film using the equation [16]:

\[
T = (1 - R)^2 \exp(-\alpha t),
\]

where \( T \) is transmittance, \( R \) is reflectance, and \( t \) is film thickness (Table 1).

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

\[
\alpha = \frac{K(h\nu - E_g)^n}{h\nu},
\]

where \( K \) is a constant, \( E_g \) is the optical bandgap, and \( n \) is equal to 1 for direct bandgap materials such as Cds. The bandgap was determined for each film by plotting \( (ah\nu)^2 \) versus \( h\nu \) and then extrapolating the straight-line portion to the energy axis. XRD was carried out using a Rigaku D XRD unit (with 40 kV, 30 mA Cu Kα radiation, \( \lambda = 0.15406 \) nm). The sample was mounted at 2.5° and scanned from 25–55° in steps of 0.02° with a scan rate of 1.2° min⁻¹. 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 a FEI 200 focused ion beam system. Resistivity, Hall mobility, and carrier density 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 system (Ecopia HMS-3000, Bridge Technology, Chandler Heights, AZ, USA) with a 0.55 T magnetic induction. Micro-Raman scattering was performed at room temperature with a Horiba Jobin Yvon LabRam IR system at a spatial resolution of 2 μm in a backscattering configuration. A 632.8 nm line of a helium-neon laser was used for off-resonance excitation with less than 4 mW power at the sample. The spectral resolution was 2 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 Kα radiation at 1253.6 eV. Each of the XPS spectra was acquired from 30 repeated sweeps. XPS spectra were corrected from charging effects by referencing the adventitious C 1s peak to 284.6 eV.

3 Results and discussion  Figure 1 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 \( 8.5 \times 10^{-3} \) to 0.1. Adding higher concentrations of (H₃BO₃) resulted in a homogeneous reaction that quickly dominated the deposition process and affected the quality of doped Cds films (films were porous, nonadherent, 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 noted in all doped films. This red shift was found to increase as the [B]/[Cd] ratio increases. Using transmittance and reflectance data, the absorption coefficient \( \alpha \) was calculated and was then used to determine the bandgap, as

<table>
<thead>
<tr>
<th>[B]/[Cd] ratio</th>
<th>film thickness (Å)</th>
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<tbody>
<tr>
<td>0.0</td>
<td>1400</td>
</tr>
<tr>
<td>8.5 × 10⁻³</td>
<td>1600</td>
</tr>
<tr>
<td>1.7 × 10⁻²</td>
<td>1100</td>
</tr>
<tr>
<td>3.4 × 10⁻²</td>
<td>1200</td>
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<tr>
<td>5.1 × 10⁻²</td>
<td>1200</td>
</tr>
<tr>
<td>6.8 × 10⁻²</td>
<td>1300</td>
</tr>
<tr>
<td>0.1</td>
<td>1300</td>
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Figure 1 (online colour at: www.pss-a.com) Specular transmittance and reflectance spectra of B-doped Cds films grown at different [B]/[Cd] ratios, \( R (R = 0.0 \) is assigned to the undoped film).
Figure 2 (online colour at: www.pss-a.com) Optical bandgap calculations of B-doped CdS films grown at different [B]/[Cd] ratios, $R$.

Figure 3 Optical bandgap of B-doped CdS films as a function of [B]/[Cd] ratio.

Figure 4 XRD pattern of B-doped CdS films grown at different [B]/[Cd] ratios, $R$.

Figure 5 Average (111)/(0002) interplanar distance $d_{(111)}/d_{(0002)}$ as a function of [B]/[Cd] ratio.

shown in Fig. 2. Figure 3 shows the bandgap dependence on [B]/[Cd] ratio. The bandgap of B-doped films decreases as the [B]/[Cd] ratio increases. Undoped film has a bandgap of 2.41 eV that agrees well with the 2.42 eV bandgap of single-crystal CdS [17]. Such a drop in bandgap due to boron doping is similar to what we have reported earlier for Al-doped CdS films [8]. We believe that 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 the 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, which reduces the bandgap.

XRD patterns of B-doped films and undoped CdS film are shown in Fig. 4. Only one peak is detected, which is either the (111) peak of cubic (zinc-blende) 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 a phase transition is believed to be 300 °C [18], above which the cubic phase transforms into hexagonal phase. 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. 4, no peaks of B, BS, or B$_2$S$_3$ were detected, which indicates that incorporation of B$^{3+}$ ions does not affect the crystal structure of CdS film. The average (111)/(0002) interplanar distance $d_{(111)}/d_{(0002)}$ was calculated...
Figure 6: High-resolution TEM of film grown at a [B]/[Cd] ratio of $5.1 \times 10^{-2}$.

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. 5, as the [B]/[Cd] ratio increases, the spacing of the (111)/(0002) lattice planes decreases further below that of undoped film. Since the ionic radius of $\text{B}^{3+}$ (0.20 Å) is smaller than that of $\text{Cd}^{2+}$ (0.97 Å) [19], this suggests that $\text{B}^{3+}$ ions replace the $\text{Cd}^{2+}$ ions in the lattice substitutionally, which in turn results in a smaller $d$ value than that of undoped CdS film. There is always the possibility that some of the $\text{B}^{3+}$ ions enter the lattice interstitially, but since the $d$ value continues to decrease as the [B]/[Cd] ratio increases, it is more likely that the majority of $\text{B}^{3+}$ ions are replacing $\text{Cd}^{2+}$ ions substitutionally.

High-resolution TEM of film grown at a [B]/[Cd] ratio of $5.1 \times 10^{-2}$ 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 that are characteristic of the zincblende structure. The wurtzite structure is, however, dominating, as shown in Fig. 6, 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. 7 was taken from a small area of the CdS layer with only a few grains. Instead of diffraction rings, the spot pattern shows distinct 0002 diffraction spots of the wurtzite structure. However, the high stacking-fault density is responsible for streaks in the diffraction pattern instead of sharp $11\bar{2}0$ and $110\bar{2}$ reflections.

Figure 7: TEM diffraction pattern of film grown at a [B]/[Cd] ratio of $5.1 \times 10^{-2}$.

Figure 8: Carrier concentration (CC) dependence on [B]/[Cd] ratio.

Figure 9: Dark resistivity as a function of [B]/[Cd] ratio.
Figure 10 Variation of Hall mobility ($\mu$) with [B]/[Cd] ratio.

Ti02 reflections. These streaks indicate that the stacking sequence of the wurtzite structure is imperfect.

Figure 8 shows the carrier concentration (CC) as a function of [B]/[Cd] ratio. The undoped film has a CC of about $4 \times 10^{16}$ cm$^{-3}$. The CC increases as the [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. 9. The resistivity of undoped film is about $1.03 \times 10^{2}$ $\Omega$ cm. As shown, the resistivity of boron-doped films gradually decreases as the [B]/[Cd] ratio increases. The lowest resistivity obtained was $1.7 \times 10^{-2}$ $\Omega$ cm at a ratio of 0.1. This gradual increase of CC and decrease of resistivity as the [B]/[Cd] ratio agrees 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 ($\mu$) values shown in Fig. 10 are consistent with what we reported earlier for Al-doped CdS films [8].

Figure 11 shows micro-Raman spectra for all B-doped films. All films show 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.

Figure 12 shows the deconvolution of the 303 cm$^{-1}$ peak of film grown at [B]/[Cd] ratio of $5.1 \times 10^{-2}$, using a Gaussian fit from which peak position and FWHM have been obtained. Similar to what we have observed in Al-doped films [8], this peak consists of a superposition of three different peaks; the cubic 1LO [20] or hexagonal...
Figure 14 XPS multiplex spectra of undoped CdS film, and B-doped film grown at a $[B]/[Cd]$ ratio of $1.7 \times 10^{-2}$. (a) S 2p peak. (b) Cd 3d peak.

$A_1$(LO)/$E_1$(LO) peak [21] 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$^{-1}$. This Raman shift in the TO peak (originally at 246 cm$^{-1}$ [20]) 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 a phase transition in CdS due to annealing. We have shown earlier [8] 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. Figure 13 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 $[B]/[Cd]$ ratio used. The average position of the $E_2$ peak was found to be 258 cm$^{-1}$ (Fig. 13(a)) which agrees well with the 256 cm$^{-1}$ [22] and the 257 cm$^{-1}$ [23] values of $E_2$ mode that have been reported earlier. The average position of the TO peak (Fig. 13(b)) is 288 cm$^{-1}$, which agrees with what we have reported earlier for Al-doped films [8]. However, as shown in Fig. 13(c), the FWHM of the cubic 1LO or hexagonal $A_1$(LO)/$E_1$(LO) peak is sensitive to $[B]/[Cd]$ 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 1.7 $\times$ 10$^{-2}$. In both cases, the binding energy of the S 2p peak (Fig. 14(a)) is 161.7 eV, which is in the range characteristic of sulfides. No peak shift was detected due to B-doping. Also, no sulfur oxides (166–171 eV) or elemental sulfur (164 eV) [25] 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. 14(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 [25].

SEM images show that B doping did not affect the morphology of the CdS film. As shown in Fig. 15, 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 crystallites are most probably aggregates due to the formation of colloidal particles in solution that are later adsorbed on the film.

4 Conclusion In-situ boron doping of CdS using CBD proved to be successful. A resistivity as low as $1.7 \times 10^{-5}$ 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 $[B]/[Cd]$ ratio of 0.1. XRD measurements did not detect any new peaks due to B doping, indicating that incorporation of B$^3+$ ions does not change the crystal structure of the CdS film. It was also shown 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 of cubic and hexagonal phases were detected. An increase in the FWHM of cubic 1LO or hexagonal A\text{1}\text{LO}/E\text{1}\text{LO} peak with [B]/[Cd] ratio was observed, which implies an increase in induced lattice defects as the [B]/[Cd] ratio increases. A high density of defects, like stacking faults and partial dislocations, is observed by TEM. XPS spectra showed that B doping did not affect the chemistry of the CdS film. SEM images showed that B doping did not affect the morphology of the CdS film.

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**References**


