Chemical bath deposition of SnO$_2$ and Cd$_2$SnO$_4$ thin films

Hani Khallaf$^a$, Chia-Ta Chen$^{b,c}$, Liann-Be Chang$^{b,c}$, Oleg Lupan$^{a,d}$, Aniruddha Dutta$^{a,e}$, Helge Heinrich$^{a,e}$, Firoze Haque$^a$, Enrique del Barco$^a$, Lee Chow$^{a,b,c,e,*}$

$^a$ Department of Physics, University of Central Florida, Orlando, FL 32816, USA
$^b$ Graduate Institute of Electro-Optical Engineering, Chang Gang University, Kweishan, Taoyuan 333, Taiwan
$^c$ Green Technology Research Center, Chang Gang University, Kweishan, Taoyuan 333, Taiwan
$^d$ Department of Microelectronics and Semiconductor Devices, Technical University of Moldova, 168 Stefan cel Mare Boulevard, MD-2004 Chisinau, Republic of Moldova
$^e$ Advanced Materials Processing and Analysis Centre, Department of Mechanical, Materials, and Aerospace Engineering, University of Central Florida, Orlando, FL 32816, USA

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A new approach of chemical bath deposition (CBD) of SnO$_2$ thin films is reported. Films with a 0.2 µm thickness are obtained using the multi-dip deposition approach with a deposition time as little as 8–10 min for each dip. The possibility of fabricating a transparent conducting oxide layer of Cd$_2$SnO$_4$ thin films using CBD is investigated through successive layer deposition of CBD-SnO$_2$ and CBD-CdO films, followed by annealing at different temperatures. High quality films with transmittance exceeding 80% in the visible region are obtained. Annealed CBD-SnO$_2$ films are orthorhombic, highly stoichiometric, strongly adhesive, and transparent with an optical band gap of ~4.42 eV. Cd$_2$SnO$_4$ films with a band gap as high as 3.08 eV, a carrier density as high as $1.7 \times 10^{20}$ cm$^{-3}$, and a resistivity as low as $1.01 \times 10^{-2}$ Ω cm are achieved.

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1. Introduction

Transparent conducting oxides (TCOs) 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 due to the rising costs of indium. As a result, other TCO layers fabricated from ZnO, CdO, Cd$_2$SnO$_4$, and Zn$_2$SnO$_4$ are heavily investigated [1,2]. Although several techniques are currently in use to grow such layers, chemical bath deposition (CBD) presents a simple, low temperature, and inexpensive large-area deposition alternative. For over forty years, it has been widely used to grow wide-band gap group II–VI semiconductor thin films, such as CdS [3–9], CdO [10–14], and ZnO [15–20].

In a previous work [15], we have investigated CBD of ZnO using six different complexing agents, four of which proved to be successful in growing high quality ZnO undoped thin films with a band gap of 3.3 eV, a carrier density as high as $2.24 \times 10^{19}$ cm$^{-3}$, and a resistivity as low as $6.48 \times 10^{-1}$ Ω cm. More recently, we have succeeded to grow CBD-CdO thin films using three different complexing agents [14]. Annealed CdO undoped films with a band gap of 2.53 eV, a carrier density of $1.89 \times 10^{20}$ cm$^{-3}$, and a resistivity $1.04 \times 10^{-2}$ Ω cm were obtained.

SnO$_2$ thin films reported in the literature, however, have been obtained mainly by RF magnetron sputtering [21], metal organic chemical vapor deposition [22], vacuum evaporation [23], pulsed laser deposition [24], pulsed electron beam deposition [25], spray pyrolysis [26], sol–gel [27], chemical vapor deposition [28], and successive ionic layer adsorption and reaction [29]. However, very few attempts to grow SnO$_2$ thin films using CBD have been reported [30,31]. In both cases, the deposition time was of the order of several hours; 15–24 h in the work of Tsukuma et al. [30] and 5–12 h in the work of Supothina and De Guire [31]. Tsukuma et al. [30] reported a growth rate that ranged from 2 nm/h at 40 °C to 50 nm/h at 80 °C. Supothina and De Guire [31] reported growing SnO$_2$ films, 60–70 nm thick, after 12 h of deposition, with a growth rate of approximately 9 nm/h during the first 4 h. Clearly, the slow growth rate is a major 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 film using multi-dip deposition, with a deposition time as little as 8–10 min for each dip. We also investigate the possibility of fabricating a TCO layer of CBD-Cd$_2$SnO$_4$ thin film through growing CBD-CdO layer on top of the CBD-SnO$_2$ layer followed by heat treatments in air at different temperatures. 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 at room temperatures using Hall effect measurements. Crystal structure as well as crystal quality of CBD-SnO2 films are determined using X-ray diffraction (XRD), transmission electron microscopy (TEM), and Fourier transform infrared spectroscopy (FTIR). Film morphology, composition, and binding energy of CBD-SnO2 are studied using atomic force microscopy (AFM) and scanning electron microscopy (SEM), Rutherford backscattering spectroscopy (RBS), and X-ray photoelectron spectroscopy (XPS), respectively.

2. Experimental details

SnO2 films were prepared using aqueous solutions of tin chloride pentahydrate (0.028 M). Each bath contained 120 ml of de-ionized water (resistivity ~18.2 MΩ·cm) that was kept under stirring at 55 °C. Films were grown on 38 mm × 38 mm × 1 mm Schott Borofloat glass as well as quartz substrates. 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 [6]. To ensure deposition of high-quality and adhesive films, the substrate was removed from the solution whenever the solution becomes turbid and the homogeneous reaction starts to take place. The deposition time was about 8–10 min for each dip. In order to grow SnO2 films with a ~0.2 μm thickness, the deposition process was repeated four consecutive times, with fresh solutions being used every time.

After annealing the SnO2 film at 400 °C in air for 1 h, a 0.2 μm layer of CdO is grown on top of the SnO2 layer using CBD. Both layers are then annealed at different temperatures in air. CdO thin films are grown using ammonia and ethanolamine as complexing agents, CdSO4 as cadmium source (NH4)2SO4 as a buffer, and H2O2 as an oxidation agent. Details of CdO thin films are reported elsewhere [14].

Specular transmittance measurements were carried out at room temperature in the wavelength range from 200 to 1200 nm, using a Cary 500 (Varian) double beam UV/vis spectrophotometer. Specular reflectance measurements were performed at an angle of incidence of 7° in the same wavelength range. The optical absorption coefficient α was calculated for each film using the equation [32]:

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

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

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

\[ \alpha = \frac{K(N - E_g)^{1/2}}{hv} \]  

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 CdO. The band gap was determined for each film by plotting (αhv)^2 versus hv and then extrapolating the straight line portion to the energy axis. 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. XRD was carried out using Rigaku D XRD unit (with 40 kV, 30 mA CuKα radiation, λ = 0.15406 nm). The sample was mounted at 2.5° and scanned from 20° to 80° in steps of 0.02° with a scan rate of 1.2° min^-1. TEM was performed using a Tecnai F30 STEM system operating at an acceleration voltage of 300 kV. Cross sections of CdO films were prepared with FEI 200 focused ion beam system. SEM micrographs were obtained using a JEOL 6400F SEM at an acceleration voltage of 10 kV. The FTIR micro-analysis was performed at room temperature using contact ATR optimized objective that covers a range of wavenumbers from 650 cm^-1 to 4000 cm^-1. RBS measurements were acquired using a 2.25 MeV α-particles IONIX 1.7 MU Tandetron, with a surface barrier detector with energy resolution <15 keV (full width at half maximum – FWHM), positioned at a scattering angle of 165°. 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. AFM images were acquired using Veeco Multimode SPM in tapping mode.

3. Results and discussion

It was observed that as-grown SnO2 films are extremely adhesive, where highly concentrated sulfuric acid (98%) and nitric acid (96%) could not etch them. Therefore, in order to perform optical measurements, two substrates were tightly mounted together on the Teflon sample holder to ensure deposition on only one side of the substrate. Film thickness was determined using TEM, as will be shown later. Fig. 1 shows the optical transmittance of as-grown and annealed SnO2 films as well as CdO + SnO2 films annealed at 200, 300, 400, 500, and 600 °C. As shown, all films exhibit high transmittance that, in most cases, exceeds 80% in the visible region. A red shift in the optical absorption edge is observed due to formation of Cd2SnO4, which increases with increasing annealing temperature. The sharp absorption edge observed in Cd2SnO4 layers indicates that films still maintain high quality, even after annealing at temperatures as high as 600 °C. Films annealed at higher temperatures did not maintain the same quality and were discarded from any further characterizations. We have previously reported similar thermal-induced degradation of some CBD-ZnO and CBD-CdO films [14,15] that was attributed to stress in as-grown layers which caused films to lose their integrity after annealing, even at temperatures as low as 200–300 °C [15]. Since SnO2 films initially annealed at 400 °C maintained their integrity as will be shown later in this work, it is likely that the CdO top-layer is responsible for this degradation. However, because CBD-SnO2 films grown in this work were not separately subjected to heat treatments at temperatures higher than 400 °C, we cannot rule out the possibility of thermal-induced degradation of this layer at higher temperatures. Furthermore, growing CdO layer on top of SnO2 using CBD typically exposes the SnO2 film to a high pH environment due to
the high alkalinity of the solutions used, which may have a deep impact on the integrity of the SnO bottom-layer. We have faced this challenge in a previous work when we tried to grow thick ZnO layers using the multi-dip deposition approach. We found out that 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 followed by deposition of a non-uniform and porous new ZnO layer with inferior quality [15]. Although, such etching was not observed in this work, we cannot rule out the possibility of formation of cracks in the SnO layer when dipped in the CdO-based solution. A future work will be dedicated to study this complex issue in detail.

Fig. 2 shows the optical band gap calculated for annealed SnO films as well as CdSbO films annealed at different temperatures. The transmittance data shown in Fig. 1 and the corresponding reflectance data (not shown in this work) were used to calculate the absorption coefficient according to Eq. (1). As shown, band gap values of 4.42 eV, 3.02, 3.08, 2.68 eV, and 2.53 eV are observed for SnO films annealed at 400 °C and CdSbO films annealed at 200, 300, 500, and 600 °C, respectively. The band gap calculated for films annealed at 400 °C is 2.83 eV. It is worth noting that the band gap we observed for CdO films annealed at 400 °C is 2.53 eV [14]. It should also be noted that, although the typical band gap of SnO2 is around 3.75 eV [1], much higher values have been reported in the literature. Rakhshani et al. [33] reported a direct band gap of 4.11 eV, while Dawar and Joshi [34] reported band gap values in the range of 3.9–4.6 eV for SnO2 thin films. On the other hand, Nozik [35], who was the first to prepare amorphous CdSbO films by RF sputtering, reported band gap values ranging from 2.06 eV to 2.85 eV for sputtered CdSbO films, depending on films conductivity. He also reported that the conductivity increase of CdSbO films is accompanied by a large shift of the fundamental optical absorption edge toward the UV. This was confirmed by the observations of Mamazza et al. [2], where a 15% rise in charge carrier density increased the optical band gap of CdSbO films from 2.97 eV to 3.18 eV. Coutts et al. [1] reported typical band gap values of CdSbO films of about 3.1 eV. As will be shown later, Hall measurements of annealed films, in accordance with the observations of Nozik [35] and Mamazza et al. [2], may give an explanation for the significant red-shift observed in Fig. 2 for CdSbO films annealed at temperatures higher than 400 °C. However, other factors such as SnO2 film degradation and formation of secondary phases due to annealing cannot be ruled out.

The XRD pattern of annealed SnO2 films is shown in Fig. 3. Annealed films are polycrystalline with a major (1 1 3) reflection and four weak reflections characteristic of the (0 2 3), (2 0 0), (1 0 6), and (1 1 7) planes of orthorhombic SnO2 [36]. As grown SnO2 films are found to be amorphous. In order to rule out the formation of secondary phases such as tin hydroxide during film deposition, FTIR measurements were carried out for both as-grown and annealed films. FTIR absorption measurements shown in Fig. 4 are identical for both films, where the broadband around 3300 cm⁻¹ typically assigned to the O–H stretching mode of the hydroxy group has not been detected. Such band was detected for both CBD-CdO and CBD-ZnO as-grown films [14,15]. Absorbance peaks observed between 650 cm⁻¹ and 1500 cm⁻¹ are due to Si–O and B–O stretching vibrations [37] originating from the “Borofloat” glass substrate. It is worth noting that the boron content in “Borofloat” glass is about 5.2%. XRD measurements of annealed CdSbO films revealed that all films are amorphous. According to Wu et al. [38], CdSbO4...
films grown by RF magnetron sputtering start to crystallize at an annealing temperature of about 580 °C. Mamazza et al. [2], on the other hand, reported that Cd2SnO4 films deposited by RF magnetron co-sputtering from cadmium oxide and tin oxide targets in argon ambient begin to crystallize at an annealing temperature of about 525 °C. In this work, however, there was no indication of film crystallization, even after annealing at temperatures as high as 600 °C.

Fig. 5 shows the RBS spectra of annealed SnO2 film. Simulation using Rutherford universal manipulation program (RUMP) [39] 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). The XPS multiplex spectra of the Sn 3d5/2 and 3d3/2 peaks of annealed SnO2 film is shown in Fig. 6(a). As shown, Sn 3d5/2 and 3d3/2 peaks of the annealed film are located at 486.4 eV and 494.8 eV which agrees well with the 8.41 eV spin-orbit energy splitting between Sn 3d5/2 and 3d3/2 states [40]. Also, the observed binding energy of 486.4 eV of Sn 3d5/2 lies within the accepted range of binding energy values for SnO2 [40]. Fig. 6(b) shows the XPS multiplex spectra of the O 1s peak of annealed SnO2 film. The O 1s peak of annealed film is located at 530.3 eV, which lies within the 527.7–530.6 eV range characteristic of O2− oxides [40,41].

2-D and 3-D AFM images of as-grown as well as annealed SnO2 film are shown in Figs. 7 and 8, 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 SnO2 films respectively. Clearly, annealing reduced film roughness. Occasional crystallite overgrowth is observed on film surface, as revealed by SEM images (inset of Fig. 7b). This is attributed to colloidal particulates formed in solution and then adsorbed on the film. We have previously reported similar observations for CdS, CdO, and ZnO thin films grown by CBD [5,14,15].

HRTEM image of annealed SnO2 film is shown in Fig. 9. As shown, the SnO2 layer is about 0.20 μm thick. Film surface is smooth, in accordance with the AFM and SEM observations. Furthermore, SnO2 layer is uniform with only small variations in film thickness being observed. The small area electron diffraction (SAED) pattern observed (inset of Fig. 9) confirms that SnO2 film is polycrystalline with orthorhombic crystal lattice structure.

Table 1 shows a summary of Hall effect measurements and band gap calculations carried out at room temperature for SnO2 film annealed at 400 °C, and Cd2SnO4 films annealed at 200–600 °C. The typical carrier density and resistivity values obtained for annealed SnO2 films are of the order of 1012 cm−3 and 102 Ω cm, respectively. Comparing these values with their counterparts acquired for Cd2SnO4 films, it is clear that while the carrier density increased by 6–8 orders of magnitude, the resistivity of Cd2SnO4 films is only 4–5 orders of magnitude lower than that of SnO2, depending on annealing temperatures. This has to do with the low mobility of amorphous Cd2SnO4 films compared to the much higher (2–3 orders of magnitude) mobility obtained for polycrystalline SnO2 films. Hall mobilities as high as 65 (cm2 V−1 s−1) were achieved by Wu et al. [38] for Cd2SnO4 films annealed in argon ambient. They have shown that electron mobility increases with increasing film crystallinity and concluded that annealing in a reducing atmosphere not only raises the free electron concentration but also increases electron mobility. They have reported film resistivity as low as 1.28 × 10−4 Ω cm. Nozik [35], on the other hand, reported that heat treatment in H2 ambient at 280 °C for 10 min caused a significant reduction of film resistivity, where a sheet resistance as low as 2.3 Ω/sq was achieved. Mamazza et al. [2] reported 15% increases in carrier density for films subsequently annealed in H2 after being annealed in He ambient. In this work, however, all samples were
Furthermore, carrier observations annealed shown, cannot mitigated in achieving subsequent heating films. As-grown Cd$_2$SnO$_4$ 600 is noted in Fig. 1. As shown, films annealed at 200 and 300 °C which have very close carrier density values almost share the same absorption edge. Furthermore, at annealing temperatures higher than 400 °C, the band gap clearly decreases with decreasing carrier density. These observations agree well with the observations of Nozik [35] and Mamazza et al. [2]. However, such dependence on carrier density cannot explain the red shift observed for films annealed at 400 °C. In addition, it is noted that as the annealing temperature increases, the band gap values start to get closer to that of CBD-CdO films [14]. As a result, other factors such as SnO$_2$ film degradation and formation of secondary phases due to annealing cannot be ruled out.

Finally, comparing the band gap values with the corresponding carrier density of annealed films, it is obvious that the decrease in carrier density is responsible for the red shift observed in Fig. 1. As shown, films annealed at 200 and 300 °C which have very close carrier density values almost share the same absorption edge. Furthermore, at annealing temperatures higher than 400 °C, the band gap clearly decreases with decreasing carrier density. These observations agree well with the observations of Nozik [35] and Mamazza et al. [2]. However, such dependence on carrier density cannot explain the red shift observed for films annealed at 400 °C. In addition, it is noted that as the annealing temperature increases, the band gap values start to get closer to that of CBD-CdO films [14]. As a result, other factors such as SnO$_2$ film degradation and formation of secondary phases due to annealing cannot be ruled out.

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Annealing temperature (°C)</th>
<th>$E_g$ (eV)</th>
<th>Carrier density (cm$^{-2}$)</th>
<th>Mobility (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>Resistivity ($\Omega$ cm)</th>
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<tr>
<td>SnO$_2$</td>
<td>400</td>
<td>4.42</td>
<td>$5.15 \times 10^{12}$</td>
<td>$1.61 \times 10^2$</td>
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<td>200</td>
<td>3.02</td>
<td>$1.13 \times 10^{20}$</td>
<td>$2.97 \times 10^8$</td>
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<tr>
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<td>3.08</td>
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<tr>
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<tr>
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<tr>
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<td>600</td>
<td>2.53</td>
<td>$2.86 \times 10^{18}$</td>
<td>$1.17 \times 10^{-1}$</td>
<td>$1.86 \times 10^1$</td>
</tr>
</tbody>
</table>

Table 1 shows the Hall effect measurements and optical band gap calculations carried out at room temperature for SnO$_2$ films annealed at 400 °C, and Cd$_2$SnO$_4$ films annealed at 200–600 °C.

![Fig. 7. 2D AFM images and SEM micrograph (inset) of (a) as-grown SnO$_2$ film and (b) annealed SnO$_2$ film.](image7)

![Fig. 8. 3D AFM images of (a) as-grown SnO$_2$ film and (b) annealed SnO$_2$ film.](image8)
4. Conclusion

CBD of SnO₂ as well as Cd₂SnO₄ is investigated. A 0.2 μm thick CBD-SnO₂ films are grown using multi-dip deposition, with a deposition time as little as 8–10 min. Films are extremely adhesive and cannot be etched using concentrated sulfuric or nitric acid. Films are highly transparent with a band gap of ~4.42 eV and a transmittance exceeding 80% in the visible region of the spectrum. Annealed films are orthorhombic with a preferred orientation along the [1 1 3] direction. According to RBS data, annealed film is highly stoichiometric with a Sn:O ratio of ~1.00:2.00. AFM images show as-grown and annealed SnO₂ 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 SnO₂ film is polycrystalline with orthorhombic crystal lattice structure.

Cd₂SnO₄ films with an optical band gap as high as 3.08 eV; a carrier density as high as 1.7 × 10²⁰ cm⁻³; and a resistivity as low as 1.01 × 10⁻² Ω cm are obtained using CBD. Although promising, we believe that further work is needed to reach a resistivity of the order of 10⁻⁶ Ω cm, in order to fabricate a viable CBD-TCO layer. Careful studies of post-heat treatments as well as doping investigations [6,42,43] could lead to further improvement of the conductivity.

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