Preparation of In$_2$S$_3$ Thin Films by MOCVD Using Single Source Precursors:
Tris(N,N-ethylbutyldithiocarbamato)indium(III) and Tris(2-ethylpiperidinedithiocarbamato)indium(III)

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The ternary chalcopyrite semiconductor CuInSe$_2$ (CIS) or related Cu(In,Ga)Se$_2$ (CIGS) are well known materials for high efficiency thin film solar cells. In ease of CIGS absorber film prepared through chemical bath deposition method, photovoltaic conversion efficiency was reported to be higher than 19%.$^1$ Such high efficiency has been reached with a CdS buffer layer processed in a wet chemical bath and the CdS has been found to be best suited as a buffer layer material. However, cadmium is toxic and has a negative effect on environment. Therefore, there have been many studies to find replacement materials for cadmium negative effect on environment. Therefore, there have been many studies to find replacement materials for cadmium

Experimental Details

All used reagents were from Sigma-Aldrich-Corporation, and methanol was refluxed over Molecular Sieves 3 Å (pellets, 3.2 mm) to remove water molecules and distilled before using them.

Preparation of tris(N,N-ethylbutyldithiocarbamato)-
indium(III). NaOH (120.0 mg, 3 mmol) and N,N-ethylbutylamine (0.410 mL, 3 mmol) were dissolved in methanol (30 mL). In this solution, CS$_2$ (0.186 mL, 3 mmol) was slowly dropped at 0°C for 1 hour. After stirring the solution, InCl$_3$ (221.2 mg, 1 mmol) was slowly added. Immediately, white precipitates were obtained. They were filtered, dried under vacuum and recrystallized. The product, In(epdtc)$_3$, was obtained with high yield, 89%, and was easily characterized by $^1$H-NMR (Varian Gemini 2000, 300 MHz), IR (Jasco FT/IR-5300), DIP-EI MASS (mass spectrometer, Autospec EBE), elemental analyzer (Elemental Analysis, EA-1110 Fisous), and thermal analyzer (Setaram LABSYS).

Preparation of tris(2-ethylpiperidinedithiocarbamato)
indium(III). This precursor was similarly prepared except with 2-ethylpiperidine (0.340 mL, 3 mmol) and characterized as above. The yield of the precursor, In(epdc)$_3$, was 83%. The results are summarized in Table 1 and 2.

Deposition of In$_2$S$_3$ thin films through MOCVD. The In$_2$S$_3$ thin films were prepared by MOCVD method and all processes were treated in vacuum as previously reported.$^{3,11}$ In deposition process using In(epdc)$_3$, the bubbler temperature was controlled at 150°C, and In$_2$S$_3$ thin films were deposited on the various substrates at temperature range from 370°C to 490°C for 3 hr. In thermal analysis, the total

| Table 1. Results of characterization for two precursors |
|-----------------|-----------------|-----------------|-----------------|
| Precursor       | Yield (%)       | $^1$H NMR       | \(\delta\) ppm |
| In(S$_3$CNC$_6$H$_{13}$)$_3$ | 89              | q 2H 3.84, t 3H 0.94, d 2H 1.73, m 2H 1.76, m 2H 1.34, t 3H 0.95 | 643 994 1425 1503 1493 38.27 6.5 6.4 |
| In(S$_3$CNC$_6$H$_{13}$)$_3$ | 83              | m 1H 5.06, m 1H 4.92, m 1H 3.11, m 2H 1.81, m 2H 1.69, m 2H 1.65, m 2H 1.50, t 3H 0.94 | 678 988 1434 1478 42.1 (4.24) 6.3 6.2 |

weight loss of the precursor at 350 °C was 76.39%, indicative of \( \text{In}_2\text{S}_3 \) formation. In another case of \( \text{In} \text{(epdtc)} \) as a precursor, bubbler temperature was 250 °C, and substrate temperature started from 350 °C. At 300 °C, the total weight loss of this precursor was 75.12% which is quite comparable to the theoretical loss. These thin films obtained by MOCVD process were characterized by X-ray diffractometer (Scintag XDS-2000), scanning electron microscope (SEM I.S.I-DS-130), energy dispersive X-ray spectroscopy (EDAX Phoenix EDS), UV/VIS spectroscopy (JASCO U-550), and atomic force microscope (AFM XE-100).

The synthesized precursors are quite stable in ambient conditions and have relatively low melting points with short decomposition temperature ranges in comparison to the known similar precursors, suggesting that these can be used in the MOCVD process under relatively milder conditions. The X-ray diffraction pattern of the resulting dark red \( \text{In}_2\text{S}_3 \) thin films on glass or ITO glass made from \( \text{In} \text{(ebdtc)} \), coincides quite well with that of the known tetragonal \( \text{In}_2\text{S}_3 \) up to 450 °C without any dependence of the three substrates. But it is transformed to cubic \( \beta \text{In}_2\text{S}_3 \) phase above 470 °C as shown in Figure 1. The intensities of the peaks increase as the substrate temperature increases. EDX analyses of these films show an In/S ratio of nearly 2 : 3 in whole substrate temperature range, indicating the formation of \( \text{In}_2\text{S}_3 \) without any appreciable amount of impurities such as carbon, oxygen and nitrogen. In addition, it is quite noteworthy that there are no other phases such as \( \text{InS} \) or \( \text{In}_6\text{S}_7 \).

The growth rate of these films was 2.8 nm/min in average at low temperature region near 370 °C. However, the rate notably increased to 43.3 nm/min, at high temperature region of 490 °C. In addition, the grain size in diameter increases from about 50 nm to 1.5 μm due to active nucleation and following crystal growth process as the substrate temperature increases from 370 °C to 490 °C, as shown in Figure 2.

The optical band gap of these films increases from 2.0 eV to 2.4 eV according to grain size and thickness of thin films;

<table>
<thead>
<tr>
<th>Precursor</th>
<th>State</th>
<th>Melting Point</th>
<th>Decomposition Temperature Range (DSC Peak Temperature)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{In} \text{(S}_2\text{CNC}<em>6\text{H}</em>{14})_3 )</td>
<td>white powder</td>
<td>140 °C</td>
<td>270-350 °C (340 °C)</td>
</tr>
<tr>
<td>( \text{In} \text{(S}_2\text{CNC}<em>7\text{H}</em>{14})_3 )</td>
<td>white powder</td>
<td>230 °C</td>
<td>270-340 °C (290 °C)</td>
</tr>
</tbody>
</table>

Figure 1. XRD patterns from \( \text{In}_2\text{S}_3 \) thin films deposited at several temperatures on glass. The phase of the films is tetragonal from 370 °C to 490 °C and cubic above 470 °C.

Figure 2. SEM images at 15 KV of \( \text{In}_2\text{S}_3 \) thin films deposited on glass at the temperatures. (a) 370 °C (b) 390 °C (c) 410 °C (d) 430 °C (e) 450 °C (f) 470 °C (g) 490 °C.
the band gap is 2.0 eV at the substrate temperature of 430°C. At this point, the average grain size and film thickness are about 900 nm and 2.2 μm, respectively. However, it increases to 2.4 eV at 370°C, in which the grain size and film thickness are about 50 nm and 420 nm. These results reveal that the higher the substrate temperature is, the lower the energy band gap becomes as previously reported.15

The surface morphology of the prepared In$_2$S$_3$ films at 430°C can be seen in Figure 3. Figure 3(a) and (b) show two-dimensional (2D) and three-dimensional (3D) AFM images of In$_2$S$_3$ films, respectively. 2D image shows the film is well covered to the substrate surface. At the left hand side of the image, an intensity strip is shown, indicating the depth of the surface grains along z-axis. The SEM images and 3D image reveal the formation of islands and the grains of about 900 nm in diameter on the substrate. The thickness of the In$_2$S$_3$ film is estimated to lie in the range from about 120 to 160 nm in average.

Similarly, the same In$_2$S$_3$ film were successfully grown on CIGS film as shown in Figure 4.17,18 In case of the other precursor, In(epdtc)$_3$, the same quality films were obtained but the substrate temperature could be lowered to 350°C since it has relatively low decomposition temperature.

In conclusion, very pure In$_2$S$_3$ thin films through MOCVD method using two single source precursors were successfully deposited on various substrates and the deposition rate was relatively quite good under mild conditions. The phase of these films obtained at the substrate temperature up to 450°C is tetragonal, but cubic above 470°C. Optical band gap varies from 2.0 to 2.4 eV according to the grain size and thickness of film. The SEM and AFM images of the films show that they have highly microcrystalline morphology and compact surface.

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