Preparation of In_2S_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 case 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 sulfide. The possible candidates for the cadmium free solar cells are ZnS,[2] In_2S_3,[3] ZnSe,[4] In_xSe_y.[5] Among these materials, In_2S_3 is nontoxic and exhibits optical and electrical properties similar to those of CdS. Also, In_2S_3 thin film deposited by ALCVD using $In(acac)_3$ and H_2S was reported to be an n-type semiconductor and was found to properly function as a buffer layer for the heterojunction solar cells.[6]

For the preparation of In_2S_3 thin films without using toxic H_2S gas, various single source precursors suitable to the MOCVD process are possible.[7] Among them, the precursors containing dialkyldithiocarbamate ligands with non-symmetrical structure are interesting since they were found to have better thermal properties compared to symmetrical ones.[8]

In this work, two single source precursors, tris(*N,N*-ethylbutyldithiocarbamato)indium(III) and tris(2-ethylpiperidinedithiocarbamato)indium(III) (designated as $In(ebdtc)_3$ and $In(epdtc)_3$, respectively) were synthesized with high purity and yield. Using them, In_2S_3 thin films were successfully grown on various substrates, such as glass, ITO glass, and CIGS film through MOCVD process.

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, $In(ebdtc)_3$ 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, $In(epdtc)_3$ was 83%. The results are summarized in Table 1 and 2.

Deposition of In_2S_3 thin films through MOCVD. The In_2S_3 thin films were prepared by MOCVD method and all processes were treated in vacuum as previously reported.[9-11] In deposition process using $In(ebdtc)_3$, the bubbler temperature was controlled to 150 °C, and In_2S_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	MASS (m/Z)	FT-IR Bands (cm^{-1})			Elemental Analysis; observed value (calculated)		
		δ(ppm)	(M^+)	υ(C=S)	υ(N-CS_2)	υ(C-N)	C	H	N
$In(S_2CNC_6H_{14})_3$	89	q 2H 3.84, t 3H 0.94, d 2H 3.73, m 2H 1.76, m 2H 1.34, t 3H 0.95	643	994	1425	1503 1493	38.27 (39.19)	6.5 (6.5)	6.4 (6.5)
$In(S_2CNC_7H_{14})_3$	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 1.59, t 3H 0.94	678	988	1434	1478	42.1 (42.4)	6.3 (6.2)	6.2 (6.2)

Table 2. Thermal properties of prepared precursors

Precursor	State	Melting Point	Decomposition Temperature Range (DSC Peak Temperature)
$In(S_2CNC_6H_{14})_3$	white powder	140 °C	270-350 °C (340 °C)
$In(S_2CNC_7H_{14})_3$	white powder	230 °C	270-340 °C (290 °C)

weight loss of the precursor at 350 °C was 76.39%, indicative of In_2S_3 formation. In another case of $In(epdtc)_3$ 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,[12,13] suggesting that these can be used in the MOCVD process under relatively milder conditions. The X-ray diffraction pattern of the resulting dark red In_2S_3 thin films on glass or ITO glass made from $In(ebdtc)_3$ coincides quite well with that of the known tetragonal In_2S_3[14] up to 450 °C without any dependence of the three substrates. But it is transformed to cubic β-In_2S_3 phase above 470 °C[15] 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 In_2S_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 InS or In_6S_7.[7]

The growth rate of these films was 2.8 nm/min in average

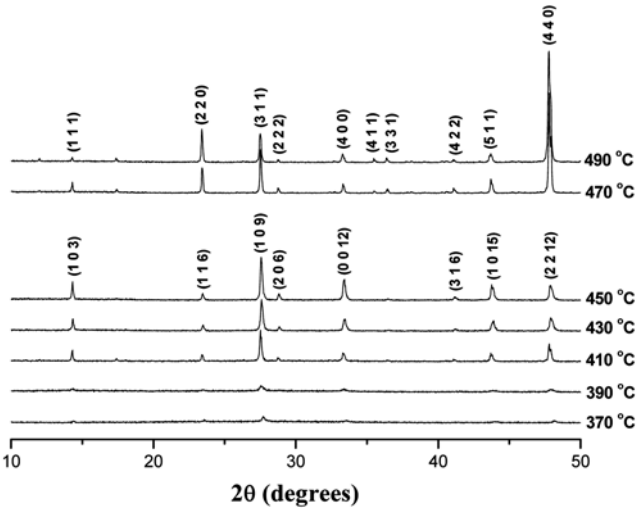

Figure 1. XRD patterns from In_2S_3 thin films deposited at several temperatures on glass. The phase of the films is tetragonal from 370 °C to 450 °C and cubic above 470 °C.

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;

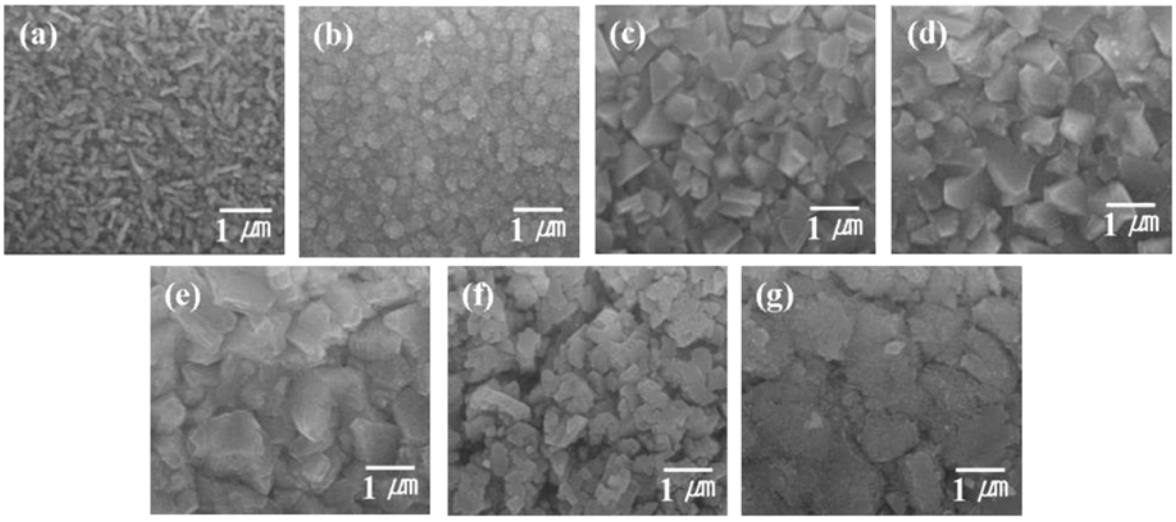

Figure 2. SEM images at 15 KV of In_2S_3 thin films deposited on glass at the temperatures. (a) 370 °C (b) 390 °C (c) 410 °C (d) 430 °C (e) 450 °C (f) 470 °C (g) 490 °C.

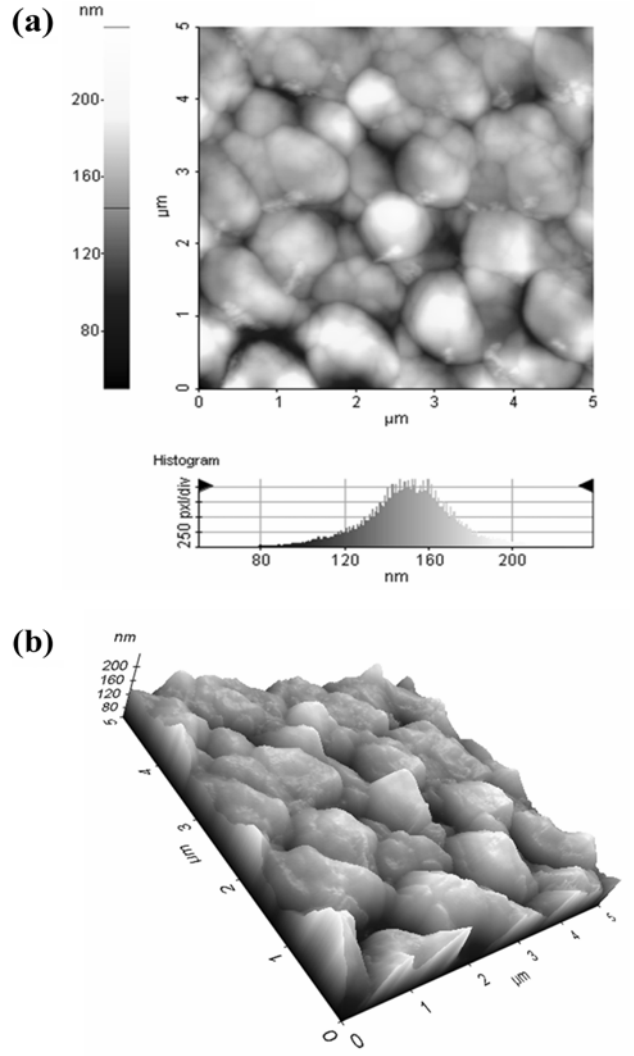

Figure 3. AFM images of the prepared In_2S_3 film on glass at 430 °C; (a) 2D, (b) 3D image.

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.[16]

The surface morphology of the prepared In_2S_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_2S_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_2S_3 film is estimated to lie in the range from about 120 to 160 nm in average.

Similarly, the same In_2S_3 film were successfully grown on CIGS film as shown in Figure 4.[17,18] In case of the other

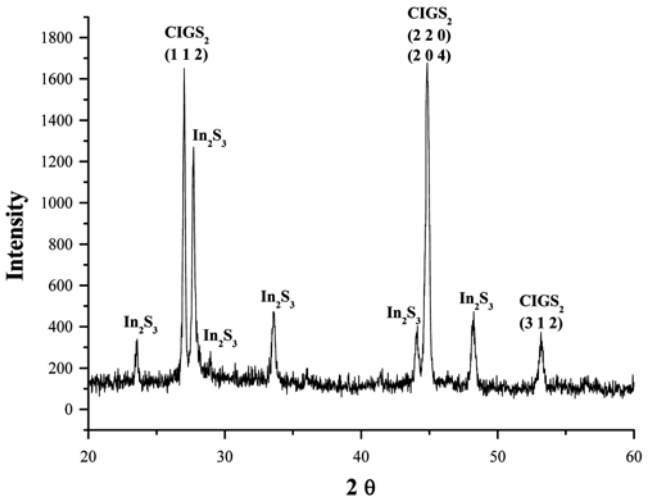

Figure 4. XRD patterns from In_2S_3 thin films deposited on CIGS film.

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_2S_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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