Preparation of In_2Se_3 Thin Films by MOCVD with a New In-Se Single Source Precursor

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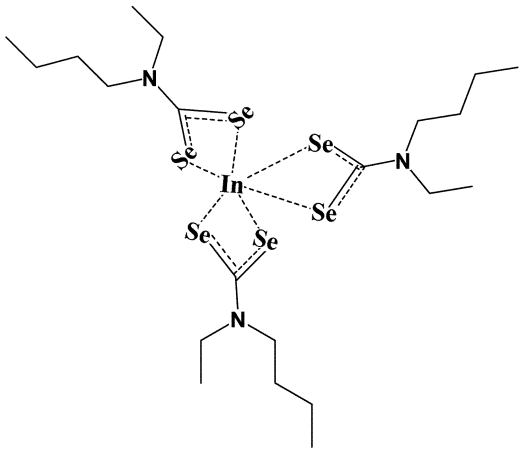
In_2Se_3 is a binary compound, which is attracting wide attention because it can be used as an important material for polycrystalline thin film solar cell. It has various structural modifications of α, β, and γ-phase, and they have quite different electronic properties;[1,2] α-phase of In_2Se_3 has low band gap, 1.2-1.3 eV at the temperature below 200 °C. As temperature goes up to above 200 °C, it is transformed to β-phase with a band gap of 1.4 eV. In addition, when temperature goes to higher temperature, 350 °C, it is converted to γ-In_2Se_3 with a band gap of 1.8 eV.[3,4] Particularly, γ-In_2Se_3 is interesting since it can be adopted as a suitable absorber layer in CdS/In_2Se_3 or In_2S_3/In_2Se_3 photovoltaic cells because of its high absorption coefficient and the band gap which is in an optimum range for solar energy conversion.[5-7]

Moreover, it can be used as a starting material to obtain $CuInSe_2$ or Cu(InGa)Se_2 thin films. The In_2Se_3 thin films can be prepared through various methods such as thermal evaporation,[8] spray pyrolysis,[9] metal organic chemical vapor deposition (MOCVD),[10] electrochemical atomic layer epitaxy,[11] electrodeposition,[12] and many other methods. Among them, MOCVD method has many practical benefits than any other methods; especially, the composition, structure, and morphology of the In_2Se_3 thin films can be properly controlled. Furthermore, its process is rather simple and less expensive if a suitable single source precursor[13,14] is available. In this research, two single source precursors, containing indium and selenium atoms: tris(*N,N*-ethylbutyldiselenocarbamato)indium(III) and tris(2-ethylpiperidinediselenocarbamato)indium(III), designated as In(ebdsc)$_3$ and In(epdsc)$_3$, respectively, were synthesized with high purity, and using them, γ-In_2Se_3 thin films were prepared by MOCVD.

Experimental Details

All reagents were used from Sigma-Aldrich-Corporation except CSe_2. CSe_2 was prepared through the reaction with selenium powder and excess dichloromethane.[15] However, the concentration of prepared CSe_2 in this process was too low to be used. Therefore, the solution was condensed by solvent evaporation and 20% CSe_2 solution was obtained. Ethanol was refluxed over molecular sieves 3 Å (pellets, 3.2 mm) to remove water molecules and distilled before using it.

Synthesis of Tris(*N,N*-ethylbutyldiselenocarbamato)-indium(III): Tris(*N,N*-ethylbutyldiselenocarbamato)indium (III) was obtained by the reaction of *N,N*-ethylbutyldiselenocarbamate of sodium and $InCl_3$. *N,N*-ethylbutyldiselenocarbamate of sodium was prepared by reacting sodium hydroxide (120.0 mg, 3 mmol), *N*-ethylbutylamine (0.410 mL, 3 mmol), and CSe_2 in dichloromethane (1.734 mL, 3 mmol); CSe_2 solution was slowly dropped to the ethanol (30 mL) solution of sodium hydroxide and *N*-ethylbutylamine at 0 °C for 1 hr. After addition, the color of the solution turned transparent yellow. To this solution, $InCl_3$ (225.7 mg, 1 mmol) was slowly added. Then, yellow In(ebdsc)$_3$ product was immediately precipitated. This precipitate was filtered, dried under vacuum, and recrystallized. The yield of this product was 79%.

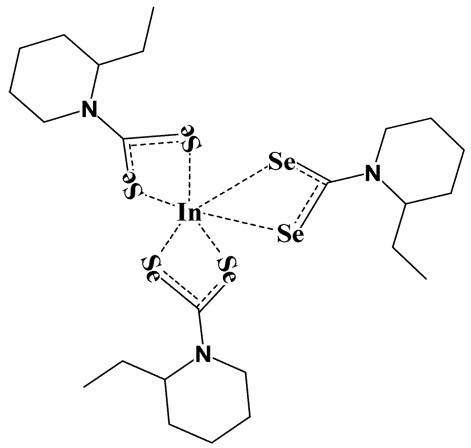


[In(ebdsc)$_3$]

Synthesis of Tris(*N,N*-2ethylpiperidinediselenocarbamato)indium(III): This precursor was synthesized exactly as above process except using 2-ethylpiperidine (0.340 mL, 3 mmol) and the yield was 75%. These two precursors were easily characterized by ^{1}H-NMR (Varian Gemini 2000, 300 MHz (USA)), IR (Jasco FT/IR-5300), DIP-FAB MASS (Mass Spectrometer, Autospec EBE), Elemental Analyzer (Elemental Analysis, EA-1110 Fisous), and Thermal Analyzer (Setaram LABSYS). The results are listed in Table 1.

Table 1. Results of the characterization for $In(ebdsc)_3$ and $In(epdsc)_3$ precursors

precursor	yield (%)	^{1}H NMR			MASS (m/z)	FT-IR bands (cm^{-1})			Elemental Analysis observed value (calculated value)		
		δ(ppm)			(M^+)	υ(C=S)	υ(N-CS_2)	υ(C-N)	C	H	N
$In(Se_2CNC_6H_{14})_3$	79	q	2H	3.87	926	971	1432	1499	28.10 (27.2)	4.7 (4.5)	4.8 (4.5)
		t	3H	3.75							
		m	2H	1.82							
		m	2H	1.38							
		t	3H	1.34							
		T	3h	0.94							
$In(Se_2CNC_7H_{14})_3$	75	m	1H	5.07	962	987	1423	1474	30.4 (29.9)	4.5 (4.4)	4.4 (4.3)
		m	1H	4.96							
		m	1H	3.08							
		m	2H	1.85							
		m	2H	1.75							
		m	2H	1.67							
		m	2H	1.59							
		t	3H	0.96							



$[In(epdsc)_3]$

Fabrication of In_2Se_3 Thin Films: In_2Se_3 films were deposited through MOCVD method in vacuum condition as previous reports.[16-18] In_2Se_3 films were well grown without any other flow gases because $In(ebdsc)_3$ was quite volatile. These precursors were stable at room temperature in air and no photo decomposition was observed. To set the pertinent bubbler temperature and substrate temperature, $In(ebdsc)_3$ was analyzed by thermal analyzer (Setaram LABSYS). Thermal analysis showed that melting point was 165 °C and weight loss was started from 215 °C. Total weight loss was 74.2% at 300 °C, corresponding to the theoretical weight loss of 74.9% and this result reveals that very pure In_2Se_3 remains after decomposition reaction. On the base of this result, bubbler temperature was fixed at 200 °C and substrate temperature was set to 330 °C.

In case of $In(epdsc)_3$, its melting point was nearly 220 °C, and the onset of its decomposition was about 240 °C. The decomposition temperature was about 300 °C. At this point, the total weight loss was 73.2%. This was quite close to the calculated value of 74.8%, but the deposited In_2Se_3 thin films using $In(epdsc)_3$ through MOCVD were quite poor in their crystallinity and film growth rate was very small. This result is assumed to arise from short temperature range between melting point and decomposition temperature. In other words, since this range is too narrow of about 20 °C, lots of precursors are very likely to be already decomposed at the bubbler right after their melting and evaporation. Therefore, only $In(ebdsc)_3$ was chosen as a proper precursor for the preparation of In_2Se_3 thin films in this study. The resulting In_2Se_3 films were characterized by x-ray diffractometer (Scintag XDS-2000), scanning electron microscope (J.S.I-DS-130), energy dispersive x-ray spectroscopy (EDAX Phoenix EDS), and UV/VIS spectroscopy (JASCO U-550).

The synthesized precursor is quite stable in ambient conditions and has relatively low melting points with lower decomposition temperature in comparison to the known similar precursors.[3,19]

Using $In(ebdsc)_3$ precursor, In_2Se_3 thin films were deposited on glass and ITO glass and their color was red. They appear from the substrate temperature of 330 °C, which is a little higher than the decomposition temperature of the

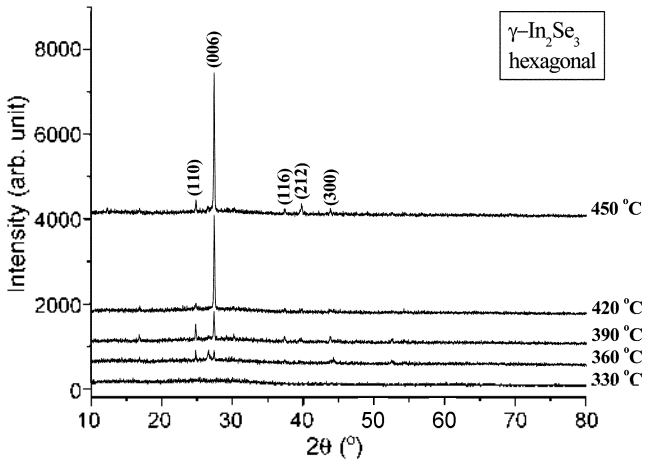


Figure 1. XRD data of hexagonal γ-In_2Se_3 deposited on glass at various substrate temperatures.

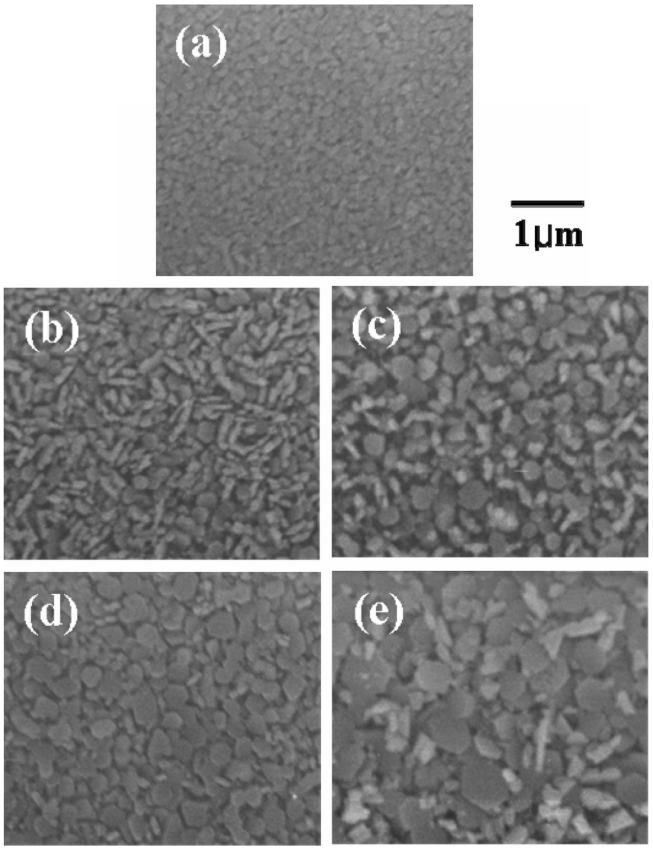


Figure 2. SEM images of hexagonal γ-In_2Se_3 330 °C (b) 360 °C (c) 390 °C (d) 420 °C (e) 450 °C.

precursor. As shown Figure 1, they become more highly crystalline as temperature goes up and the intensities of peaks in their XRD pattern increase as the substrate temperature increases. The XRD data show that the obtained In_2Se_3 is in hexagonal phase (γ-In_2Se_3).[20,21] In addition, interestingly, there are no other phases such as InSe, In_2Se_2, In_6Se_7, and In_2O_3.[3,9]

As shown Figure 2, SEM images show the highly crystalline state of the deposited In_2Se_3 films and their homogeneity. It was found that the grain size and the growth rate were drastically increased according to the elevation of the substrate temperature from 330 °C to 450 °C: the grain size and the film thickness at 330 °C were about 100 nm and 150 nm, respectively. But at 450 °C, they were nearly 770 nm and 1 μm., respectively.

Also, EDX data show that the ratio of indium to selenium in these films is 2.01 : 3.04, corresponding to the stoichiometric ratio of In_2Se_3 in all deposited films. There are no other appreciable impurities such as O, C, and N atoms, nor other phase such as In_xSe_y.

The optical band gap of those films is about 1.87 eV in 330-450 °C range, which coincides well with that of the typical hexagonal γ-In_2Se_3[1,21,22] as shown Figure 3.

In conclusion, homogeneous phase-pure γ-In_2Se_3 thin films were successfully prepared on glass or ITO glasses, using a single source precursor of In(ebdsc)$_3$ with high purity through MOCVD. They are in hexagonal phase

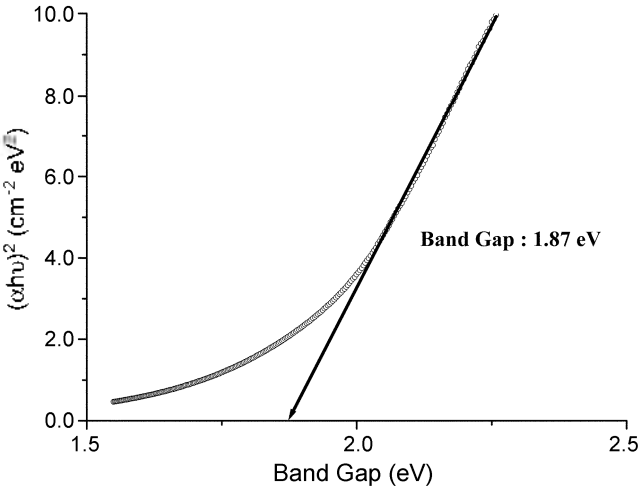


Figure 3. Plot of $(\alpha h\upsilon)^2$ *vs.* band gap of In_2Se_3 films (α: the absorption coefficient, $h\upsilon$: the photon energy).

without any other appreciable impurities, and their band gap is 1.87 eV at substrate temperature range from 330 °C through 450 °C.

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