Metal–Organic Chemical Vapor Deposition of Semiconducting III/VI In_2Se_3 Thin Films from the Single-Source Precursor: $In[SeC(SiMe_3)_3]_3$

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Thin films of In_2Se_3 have been prepared by metal–organic chemical vapor deposition (MOCVD) using volatile $In[SeC(SiMe_3)_3]_3$ as the precursor. The influence of growth parameters on the formation of crystalline phases and on the morphologies of In_2Se_3 films were examined by X-ray diffraction and scanning electron microscopy. The stoichiometry of the films was determined by Rutherford backscattering spectroscopy (RBS).

Introduction

Indium selenide compounds are of potential importance as binary sources for the synthesis of several chalcopyrite-type semiconductors used in the manufacturing of solar cells such as $CuInSe_2$ or $Cu(InGa)Se_2$.[1,2] In_2Se_3 is a semiconductor that exhibits at least three different crystalline phases denoted as α, β, γ, with energy gaps E_g of 1.42, 1.55, and 2 eV, respectively.[3] The relatively highly conductive α phase transforms to the intrinsically conductive β phase at approximately 200 °C. The phase transformation of the β phase to the insulating γ phase occurs at about 650 °C.[4,5]

The growth of In_2Se_3 thin films has been studied using various techniques, such as flash evaporation of single-source powdered In_2Se_3,[6] flash evaporation of indium and selenium,[7] molecular beam deposition of elemental components under ultrahigh vacuum,[8] and electrodeposition of indium and selenium in aqueous solution with a postannealing process.[9] In contrast to the extensively studied MOCVD of II/VI and III/V materials, there have been very few MOCVD approaches to III/VI materials (especially In_2Se_3). Kanatzidis and co-workers have developed an indium polyselenide precursor $(Ph_4P)_2[In_2Se_{21}]$ for generating In_2Se_3 thin films by solid-state pyrolysis.[10,11] His group also reported the synthesis of ternary molecular precursors $(Ph_3P)_2CuIn(QR)_4$ (Q = S; Se, R = Et; ^iBu) for the preparation of photovoltaic materials $CuInQ_2$.[12] Recently, Gysling et al. have successfully used spray MOCVD to grow InSe and In_2Se_3 thin films from the single-source precursors $Me_2In(SePh)$ and $In(SePh)_3$, respectively.[13] However, to our knowledge, there has not been any report of growth of In_2Se_3 by conventional MOCVD using a volatile single-source precursor.

In the last few years, the use of molecular compounds as precursors to solid-state materials has been extensively explored. There are many excellent examples of the uses of single-source precursors for binary materials (e.g., TiC,[14] AlN,[15–17] GaAs,[18–20] ZnSe,[21,22] etc.) by MOCVD. A single-source precursor is designed so that it contains the elements of the binary compounds to be deposited, covalently bonded in a single molecule. By using single-source precursors, the MOCVD process can in principle be simplified since the deposition proceeds from only one compound. Since these precursors are solids, the use of high-pressure gas cylinders is avoided. Due to their low vapor pressure at room temperature, their handling during the process is safer and rather easy. More importantly, they also provide the potential of stoichiometry control of the materials at the molecular level. Also, it has been demonstrated that metastable phases (or materials) can be prepared by kinetically controlled reactions using single-source precursors (e.g., cubic-GaN,[23] cubic-TaN,[24] cubic-In_xSe_y,[13] cubic-GaS[25]). Low volatilities of single-source precursors have been a problem in the past. We have shown that one solution to this problem involves the use of large,

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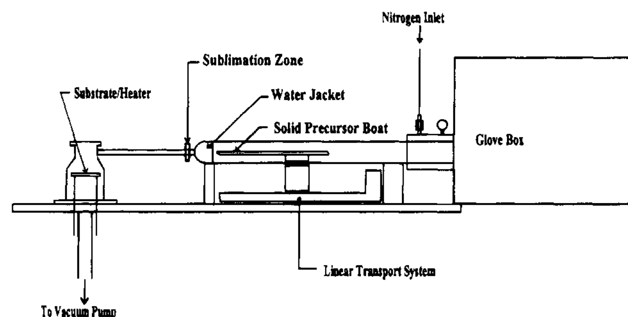

Figure 1. Schematic of the vertical cold-wall reactor for MOCVD.

sterically demanding new ligands of general formula R = -EX(SiMe$_3$)$_3$; E = Se, Te; X = C, Si. Metal complexes containing these ligand system are often volatile due to their monomeric or dimeric structures,[26-30] and they have been used successfully for growth of II/VI compounds by MOCVD.[22,31,32] Here we describe the thin film growth of In_2Se_3 from the volatile single-source precursor In(CSel)$_3$ [CSel = −SeC(SiMe$_3$)$_3$] by MOCVD.

Experimental Section

General Methods. All manipulations to make the precursor were carried out using standard Schlenk and cannula techniques under nitrogen or in vacuum.[33] The film thicknesses and stoichiometry were measured by combined Rutherford backscattering spectrometry (RBS) and particle-induced X-ray emission (PIXE) using a 1.8 MeV He ion beam. The RBS and PIXE spectra were accumulated simultaneously using a silicon surface barrier detector located at 165° and a Si(Li) detector at 150° with respect to the ion beam, respectively. X-ray powder diffraction (XRD) data were acquired using a Siemens D500 diffractometer using Cu Kα radiation with a power supply of 40 kV and 30 mA. Scanning electron micrographs (SEM) were obtained on a JEOL JSM-6400 instrument. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-400 instrument at 400 and 100.5 MHz in benzene-d_6, respectively.

Materials. HSeC(SiMe$_3$)$_3$ and InCp$_3$ were prepared by literature methods.[26,34] In(CSel)$_3$ [CSel = −SeC(SiMe$_3$)$_3$] was prepared by the following modifications of the literature procedure:[27]

InCp$_3$ (0.48 g, 1.6 mmol) and HSeC(SiMe$_3$)$_3$ (1.4g, 4.8 mmol) were combined as solids to which 50 mL of hexanes was added. The homogeneous orange solution was stirred for 1 day at room temperature. The reaction mixture was pumped dried under vacuum and the solid residue was extracted with hexane (2 × 30 mL). The hexane extracts were combined and concentrated. Cooling the dark orange solution to −40 °C yielded orange microcrystals of In[SeC(SiMe$_3$)$_3$]$_3$ (1.0 g); yield 60%, mp 195 °C. ^{1}H NMR (C_6D_6, 25 °C) δ 0.41(s).

MOCVD Studies. The growth experiments were carried out in a low-pressure vertical cold-wall quartz reactor (Figure 1). The growth chamber can be evacuated with a mechanical pump to about 10^{-2} Torr. The precursor is loaded in nitrogen atmosphere in a drybox located next to the reactor and introduced into the reactor through a load lock. Nitrogen is used as the carrier gas. The reactor is evacuated prior to growth and the boat containing the precursor is moved into a locally heated sublimation zone about 5 mm long. Heating of the zone is provided by the resistive heating of a Ni−Cr wire. A narrow sublimation zone is obtained by using a water-cooled jacket to prevent sublimation of the precursor prior to reaching the sublimation zone. The boat (5 mm height, 5 mm width, 300 mm long) is attached to a magnetic holder coupled to a motor driven shaft for automatic transfer from the load-lock to the reactor and control of the sublimation rate. This system is designed so that the sublimation rate can be controlled by both the amount of precursor loaded in the tube and the translation rate of the boat. The translation rate was nominally set at 1 mm/min. The flow of nitrogen was regulated by a mass flow controller at 50 sccm/min. The glass tube connecting the sublimation zone and the growth chamber is heated with heating tape to prevent any condensation of the sublimed precursor. The substrates are mounted on a molybdenum holder designed for 2 in. wafers. Boron nitride is used to isolate the Mo substrate carrier from the graphite heater. The substrate temperature is monitored by a thermocouple in contact with the top surface of the Mo holder. During the CVD experiments, exhaust gases are collected in a liquid nitrogen cold trap. The organic byproducts collected were dissolved in C_6D_6 and analyzed by ^{1}H and ^{13}C NMR spectroscopy. We could confirm RSeSeR (50%), RSeH (38%), and RH (12%) as major byproducts along with small amounts of unidentified organic-by-products at 400 °C under static vacuum condition.

Deposition of In_2Se_3 Films. The total amount of precursor In(CSel)$_3$ used, about 0.2 g, was spread evenly along the sublimation boat. The boat was slowly moved through the sublimation zone at a speed of 1 mm/min. The sublimation temperature was 120 °C, and the depositions were conducted using nitrogen as a carrier gas at a flow rate of 50 sccm, maintaining a total chamber pressure of 0.5 Torr. Successive depositions of In_2Se_3 were carried out with substrate temperatures of 330, 380, 430, and 500 °C. GaAs(100), Si(111), and Si(100) wafers of dimensions about 2 × 2 cm were used as the substrates. After completion of the experiment, the growth chamber was allowed to cool to room temperature under vacuum. The samples were analyzed by XRD, RBS, and SEM. Typical deposition time was about 2 h and films a few hundred nanometers thick were obtained.

Results and Discussion

Precursor Synthesis and Properties. The In(CSel)$_3$ precursor was prepared by the literature procedure similar to that recently described by our group.[27] Simple metathesis reaction of In(III) chloride with lithium selenolate gives In(CSel)$_3$ in relatively low yield (~30%). The best method involves selenolysis of InCp$_3$ compound with HSeC(SiMe$_3$)$_3$, which gives cleaner product in higher yield (~60%). It has been reported that In(SePh)$_3$ can serve as a thin-film precursor for In_2Se_3 by *spray* MOCVD;[13] however, the precursor itself is not volatile under normal MOCVD conditions. In comparison, In(CSel)$_3$, is sublimable and volatile enough to be used under low-pressure MOCVD conditions.

Chemical Vapor Deposition of In_2Se_3. The depositions of films from In(CSel)$_3$ were carried out on various substrates [GaAs(100), Si(100), Si(111)] at 330, 380, 430, and 500 °C at a pressure of 0.5 Torr with the nitrogen carrier gas flow set at 50 sccm. The precursor was slowly sublimed at the rate of 0.1 g/h (1.6 μmol/min) by passing the precursor containing boat through the sublimation zone heated to 120 °C. Using this

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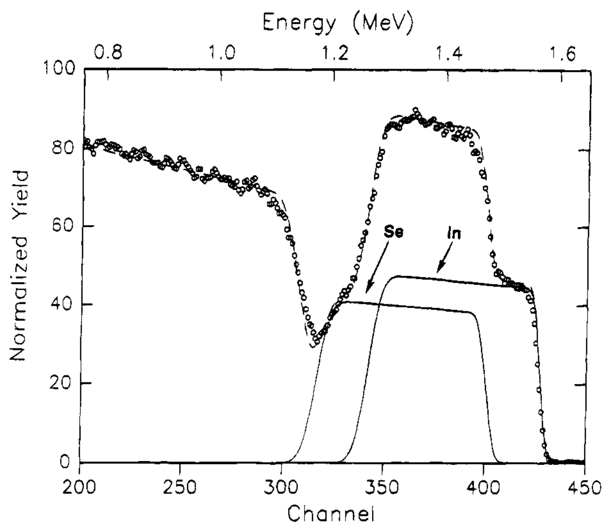

Figure 2. Rutherford backscattering spectrum of In_2Se_3 films deposited on GaAs(100) from $In(CSeI)_3$ at 380 °C. Data fitting was carried out using RUMP simulation for In:Se ratio of 1:1.7.

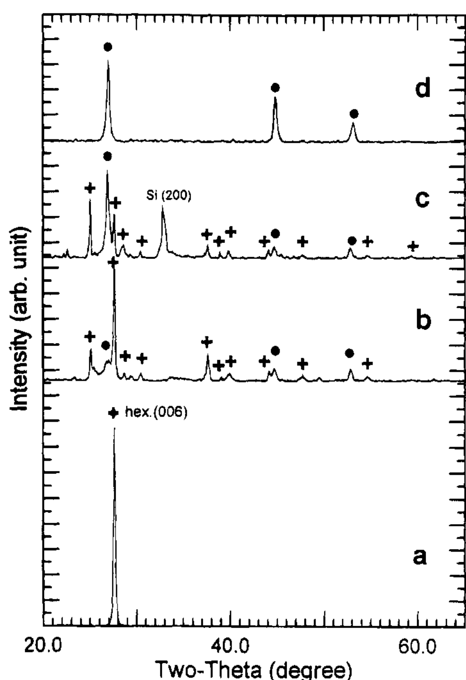

Figure 3. X-ray diffraction patterns of In_2Se_3 films on Si (100) grown at four different temperatures: (a) 330 °C; (b) 380 °C; (c) 430 °C; (d) 500 °C. The peaks labeled (●) correspond to the cubic phase and those labeled (+) correspond to the hexagonal phase.

Table 1. Summary of RBS Results of In_2Se_3 Films Grown from $In(CSeI)_3$

growth temp (°C)	substrate	In:Se
330	GaAs(100)	2:3.6
	Si(100)	2:3.4
380	GaAs(100)	2:3.4
	Si(100)	2:3.2
430	GaAs(100)	2:3.3
	Si(100)	2:3.4
	Si(111)	2:3.3
500	GaAs(100)	2:3.4
	Si(100)	2:3.4
	Si(111)	2:3.5
	av In:Se =	1:1.7

procedure, we could eliminate the commonly observed prepyrolysis of the solid precursor before sublimation. The films grown at 330 °C were nonreflective, dark brown, whereas films grown at higher temperatures were mirror like, reflective smooth films with various color shades indicating thickness inhomogeneities.

RBS analyses of the films (Figure 2) indicate an In to Se ratio of 1:1.7, from which we determined that the film is In_2Se_3 with a Se-rich composition. This composition remained constant for four different growth temperatures and three different substrates (Table 1). Due to high background signal of the substrates (GaAs and Si) in our In_2Se_3 samples, we could not estimate the amount of light elements (such as C, Si, and O) accurately by conventional RBS analysis. In general, trace amounts of light elements in heavy elements containing samples cannot be determined accurately due to kinematics and the atomic number (Z^2) dependence on the scattering cross section. However, by aligning the substrate (100) axis with respect to the analyzing beam (i.e., in the channeling orientation), we could reduce the substrate signal and hence enhanced the C, O, and Si detection limit. In these experiments, trace amounts of Si and C signals were detected and these are very close to the background noise level of the RBS detection limit ($<3\%$) in the films studied. We could not detect any O signal ($<2\%$). Also, particle-induced X-ray emission (PIXE) experiments of the samples show that there were trace amounts of Si ($\sim0.3\%$) and C ($\sim0.3\%$). We cannot know at this time what is the source of these elements; they can be from decomposition of the precursor or contamination from the growth chamber which contains quartz and graphite parts.

The crystal structures of the films were examined by X-ray diffraction. The films grown at 330 °C showed the highly preferentially oriented β-phase hexagonal In_2Se_3 (JCPD 23-294; Figure 3a). As the growth temperature is increased to 380 °C, the intensity of the peaks corresponding to the preferentially oriented hexagonal β-phase decreases and three new peaks are detected with d spacings of 3.314, 2.023, and 1.724 Å (Figure 3b). With further increase in growth temperature, these peak intensities still increase while the peaks due to β-hexagonal phase continue to decrease (Figure 3c). Finally at a growth temperature of 500 °C, only three peaks, due to a new phase, were observed (Figure 3d). The three observed diffraction peaks can be indexed as the (111), (220), and (311) peaks of a cubic In_2Se_3 phase with a lattice parameter of 5.71 Å. Within the 2θ range of our XRD measurements, there are no missing major diffraction peaks from a cubic In_2Se_3 phase and the identification is successful. We do not observe any substrate effect on the formation of the new cubic phase. The modification from hexagonal to cubic phase is identical on all of the substrates used [GaAs(100), Si(100) and Si(111)]. Similar observations were seen in films grown by spray-CVD from $Me_2In(SePh)$ and $In(SePh)_3$ by Gysling[13] (Table 2). The identity of the new phase was not completely confirmed. These authors concluded that the new phase In_xSe_y, where $x = 1$, $1 \leq y \leq 1.5$ could be either InSe or In_2Se_3 with a zinc blend-type cubic structure. According to our RBS results on the films grown at 500 °C, the ratio of In:Se is 1:1.7, which suggests that the new phase is Se-rich In_2Se_3. We suggest that an excess of Se resulted from the decomposition of the CVD byproduct RSeR to give Se and R−R (see below). Our XRD and RBS analyses indicate that the new phase is cubic. For comparison between the CVD process and bulk pyrolysis, we did two

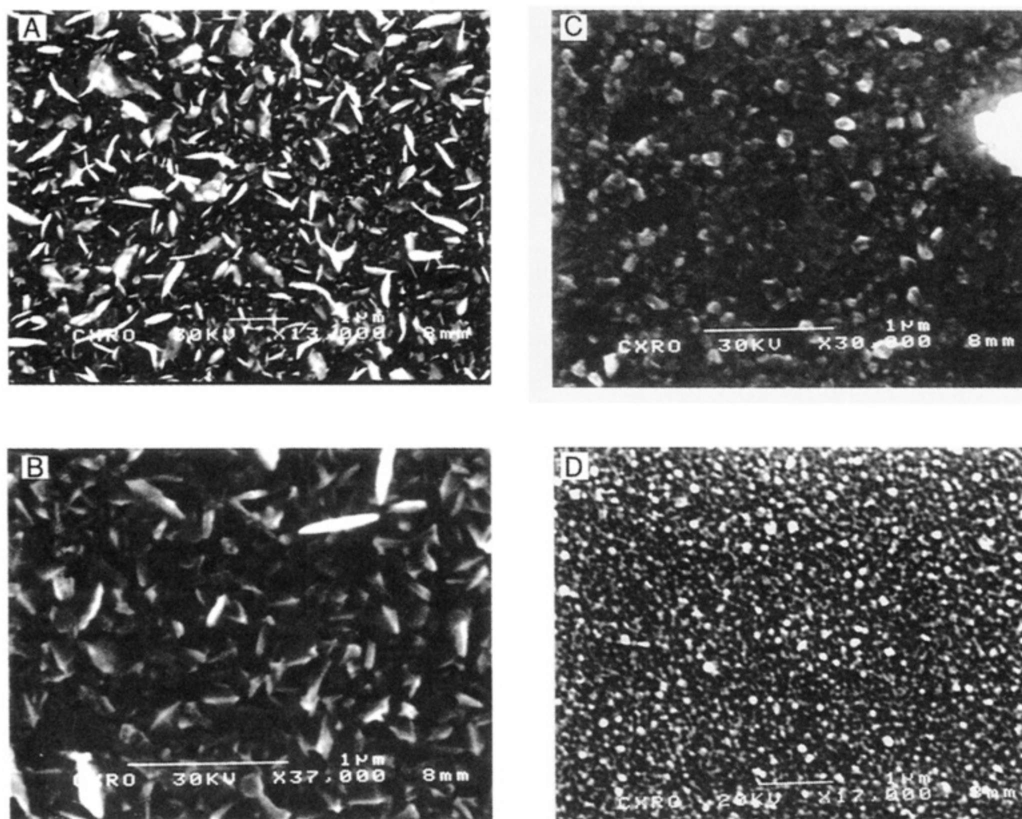

Figure 4. Scanning electron micrographs of In_2Se_3 films grown on Si (100) substrate at four different temperatures: (a) 330; (b) 380; (c) 430; (d) 500 °C.

Table 2. Comparison of Lattice Constants and Intensities for Cubic Phase In_2Se_3. Our In_2Se_3 Films Are Grown on Si(100) at 500 °C from $In(CSeI)_3$

	this study		Gysling's study[13]	
hkl	*d* spacing (Å)	I/I_0	*d* spacing (Å)	I/I_0
(111)	3.314	100	3.303	100
(200)			2.861	1
(220)	2.023	56	2.023	27
(311)	1.724	27	1.727	10

bulk pyrolysis of the $In(CSeI)_3$, one at 400 °C and one at 500 °C. XRD studies of the resulting black powder indicates obtention of both the cubic and hexagonal phase at 400 °C, which is identical to the results obtained in the CVD condition. However, bulk pyrolysis done at 500 °C also resulted in the formation of cubic and hexagonal phase (there was no indication of oriented crystal growth in the cubic or hexagonal phase), which is different from the formation of only the cubic phase in the CVD condition. The new modification (new cubic phase) was not obtained from bulk pyrolysis of the precursor.

Scanning electron microscopy (SEM) studies indicate that the morphology of the films also changes depending on the growth temperature. The film grown at 330 °C consists of fine needles (about 0.6 μm long; Figure 4a). Platelet crystals are dominant in the films grown at 380 °C with needles as minor component (Figure 4b). The film grown at 430 °C shows granular (about 100 nm in diameter) with irregular shapes (Figure 4c). Higher growth temperatures result in films with only round granular shapes (about 60 nm in diameter; Figure 4d). It appears that the needles correspond to the hexagonal phase with a preferential growth direction along the *c* axis and that the granular shapes are the preferred morphology of the cubic phase.

Decomposition Pathways. In addition to the formation of the solid state product (In_2Se_3), various organic byproducts, including RSeSeR (50%), RSeH (38%), and RH (12%) [$R = -C(SiMe_3)_3$] along with some unidentified species were isolated in a cold trap after pyrolysis of the precursor at 400 °C under vacuum. Formation of these organic byproducts are possibly due to radical decomposition of RSeR.[35] Reactive $RSe^{\bullet}$ can recombine to give diselenide or could abstract hydrogen to form RSeH. Similarly, $R^{\bullet}$ can abstract hydrogen to give stable RH. Related radical processes involving $SePh_2$ have been reported from the bulk pyrolysis of $In(SePh)_3$.[13] Thermally or photochemically induced extrusion and insertion reactions of diselenide and monoselenide are known to involve radical pathways.[36] Our previous pyrolysis experiment of $Zn(CSeI)_2$ gave similar organic byproducts,[32] which may be due to a radical process of RSeR. It is quite interesting to note that the related analogue $Se[Si(SiMe_3)_3]_2$ is much more stable than $Se[C(SiMe_3)_3]_2$, and only $Se[Si(SiMe_3)_3]_2$ was observed as an exclusive byproduct in CVD of precursors featuring this ligand system.[22,31]

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