Research Article

Structural and Optical Characteristics of γ -In₂Se₃ Nanorods Grown on Si Substrates

M. D. Yang,^{1,2} C. H. Hu,¹ S. C. Tong,¹ J. L. Shen,¹ S. M. Lan,³ C. H. Wu,² and T. Y. Lin⁴

¹ Department of Physics and Center for Nano-Technology, Chung Yuan Christian University, Chung-Li 32023, Taiwan

² Institute of Nuclear Energy Research, Longtan, Taoyuan 32546, Taiwan

³ Department of Electronic Engineering, Chung Yuan Christian University, Chung-Li 32023, Taiwan

⁴ Institute of Optoelectronic Sciences, National Taiwan Ocean University, Keelung 20224, Taiwan

Correspondence should be addressed to J. L. Shen, jlshen@cycu.edu.tw

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This study attempted to grow single-phase γ -In₂Se₃ nanorods on Si (111) substrates by metal-organic chemical vapor deposition (MOCVD). High-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) confirmed that the In₂Se₃ nanorods are singularly crystallized in the γ phase. The photoluminescence of γ -In₂Se₃ nanorods at 15 K was referred to as free and bound exciton emissions. The bandgap energy of γ -In₂Se₃ nanorods at room temperature was determined to be ~ 1.99 eV, obtained from optical absorption.

The III-VI semiconductors have been the subject of many investigations due to their peculiar electrical and optical properties, and their potential applications in electronic and optoelectronic devices, such as phase-change random access memories (PRAMs), solid-state batteries, and solar cells [1–4]. Among these III-VI semiconductors, In₂Se₃ is a defective structure of tetrahedral bonding, where one-third of the sites is vacant and forms a screw array along the *c* axis. Due to many different crystalline phases existing in In₂Se₃, growth of high-quality In₂Se₃ with a single phase is a challenging task. Several different methods have been demonstrated to grow In₂Se₃ epilayers, such as evaporation [5, 6], the Bridgman-Stockbarger Method [7, 8], and metal-organic chemical vapor deposition (MOCVD) [9–11]. Recently, one-dimensional III-VI semiconductor nanostructures, such as nanowires and nanotubes, exhibited novel and device applicable physical properties, which can be used in a wide variety of applications in nanoelectronic and nano-optoelectronic devices [12–17]. For example, α -phase layer-structured In₂Se₃ nanowires have been grown and have shown a large anisotropy in both structure and conductivity [12]. These III-VI semiconductor nanostructures can afford an efficient charge carrier transfer while maintaining

a small cross-section for the applications. However, so far, little attention has been given to γ -phase In₂Se₃ (γ -In₂Se₃) nanorods. Bulk γ -In₂Se₃ has been of particular interest for photovoltaic applications because it can be an absorbing layer in a solar cell. The one-dimensional γ -In₂Se₃ nanostructures may be more interesting materials since they exhibit excellent light absorption owing to their high surface-to-volume ratio. To be an absorbing layer in solar cells, γ -In₂Se₃ requires deposition on different substrates with a high crystalline quality. It is well known that Si can be a good substrate to grow nanostructures because it offers many attractive advantages, such as good doping properties and thermal conductivity. If Si substrate can be utilized in growing γ -In₂Se₃ nanostructures, various devices on Si-based integrated circuits could be developed in the future.

In our previous work, energy relaxation of hot electrons in γ -In₂Se₃ nanorods has been investigated [16]. It was found that the main path of energy relaxation for the hot electrons is LO-phonon emission. In this study, the detailed structures of the γ -In₂Se₃ nanorods on Si substrates were investigated by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and selected area electron diffraction (SAED). Also, the optical properties

FIGURE 1: (a) Cross-section SEM image, (b) TEM image, and (c) HRTEM image of γ - In_2Se_3 nanorods grown on Si (111) substrates. The inset of (c) shows the SAED pattern along the [006] axis.

of γ - In_2Se_3 nanorods were explored by photoluminescence (PL), cathodoluminescence (CL), and the optical absorption spectra.

The γ - In_2Se_3 nanorods were directly grown on Si (111) substrates without any buffer layers using an MOCVD system with a vertical reactor [16]. The nanorods were grown using liquid MO and a trimethyl-indium (TMIn) compound at atmospheric pressure. Gaseous H_2Se was employed as the reactant source material. Gaseous N_2 was used as the carrier gas in this process. Before growth, Si substrates were baked at 1100°C for 10 min in gaseous HCl and H_2 in order to remove the native oxide. After the thermal etching process, the reactor cooled down to 425°C and then started to grow γ - In_2Se_3 nanorods. The total growth time was 50 min. The gaseous flow rate was kept at $3 \mu\text{mol}/\text{min}$ for TMIn and $40 \mu\text{mol}/\text{min}$ for H_2Se . Gaseous H_2Se was mixed with 85% hydrogen and 15% H_2Se . The gaseous flow rate and temperature play an essential role in growing nanorod structures in γ - In_2Se_3 . The TEM lattice image and the SAED pattern of an individual In_2Se_3 nanorod were taken by a JSM-2100F (JEOL Company) Transmission Electron Microscope. The room temperature CL measurement and morphology of the nanorods image were measured by using the JSM-7001F (JEOL Company). The PL measurements were performed using a 532 nm semiconductor laser as the excitation source. The temperature-dependent PL spectra were measured by a

close-cycle helium cryostat and were analyzed by means of a 0.75 m monochromator and silicon detector.

A cross-section image of the SEM for the grown In_2Se_3 nanorods is shown in Figure 1(a). The SEM image was taken with 10 keV of electron energy to present a magnification of 30,000. As shown in Figure 1(a), the In_2Se_3 nanorods are straight and not tapered. The average diameter and the average height of the In_2Se_3 nanorods are about 64 and 460 nm, respectively. To understand the structural and morphological characteristics of nanorods, TEM investigations were carried out. Figure 1(b) shows a low magnification TEM image of In_2Se_3 nanorods. The diameter and height of In_2Se_3 nanorods are in good agreement with the SEM image shown in Figure 1(a). Figure 1(c) is a high-resolution TEM (HRTEM) image recorded from a segment of an In_2Se_3 nanorod. The image exhibits the ordering feature across its entire width, with a uniform periodicity of ~ 1.7 nm. This superlattice structure within the nanorods is a structural characteristic due to the effect of the vacancy ordering [12]. A similar behavior was also reported for the vacancy ordering in α - In_2Se_3 nanowires and CuInSe_2 -CdS Core-Shell nanowires [12, 13]. The SAED pattern taken along the [006] zone axis of In_2Se_3 nanorods is displayed in the inset of Figure 1(c). The SAED pattern shows a rectangular array with characteristic distances of $d_1 = 28.9 \times 10^{-1}$ nm and $d_2 = 7.93 \times 10^{-1}$ nm, respectively. These regular spots in SAED suggest an epitaxial orientation relationship between the In_2Se_3 nanorods and substrates; that is, the In_2Se_3 nanorods are single crystalline. The SAED pattern is consistent with the previous established pattern for γ - In_2Se_3 with basis vectors of $(-1,1,0)$ and $(0,0,6)$ [17]. It is noted that the growth direction of the nanowire in Figure 1(c) is not along the [006] direction, but it makes an angle of 13.7° with respect to the [006] direction. Anyhow, the HRTEM image allows us to confirm that the grown In_2Se_3 nanorods are well crystallized in the γ phase.

The PL spectrum of the γ - In_2Se_3 nanorods on Si (111) substructure at 15 K is shown in Figure 2. Three Gaussian components, peaked at 2.126, 2.147, and 2.155 eV, are resolved in Figure 2. The full width at half maximum (FWHM) of the PL peak at 2.155 eV is 8 meV, indicating good crystal quality for the γ - In_2Se_3 nanorods. In previous reports, the PL peak of γ - In_2Se_3 epilayers at low temperatures was referred to as the exciton-related emission [9]. Therefore, the main PL peak positioned at 2.155 eV is suggested to be the free exciton emission and the peaks in the lower energy side are suggested to be the bond exciton emissions. Figure 3 shows the temperature-dependent PL spectra from 15 to 180 K. The peak energy of the PL in γ - In_2Se_3 nanorods is red-shifted with increased temperature. The open circles in the inset of Figure 3 show temperature-induced bandgap shrinkage extracted from the PL spectra in Figure 2. This relation was fitted by the Varshini Empirical Formula as

$$E(T) = E_0 - \frac{\alpha \cdot T^2}{(\beta + T)}, \quad (1)$$

where E_0 is the bandgap at 0 K, α is the average temperature coefficient and β is the Debye temperature of the material.

FIGURE 2: PL spectrum of γ - In_2Se_3 nanorods at 15 K. Three peaks are fitted with Gaussian line shape (solid line) to the experimental data (open circles).

Experimental data fitting is shown by the solid line in the inset in Figure 3. The experimental results show good agreement with data that fits using Varshini's Equation with $E_0 = 2.14$ eV, $\alpha = 1.1 \times 10^{-3}$ eV/K, and $\beta = 173$ K. By analyzing the variation of PL peak energy as a function of temperature and ability to fit with the Varshini Equation, the room temperature peak energy of the PL in the γ - In_2Se_3 nanorods was evaluated to be ~ 1.95 eV.

To explore the bandgap energy of γ - In_2Se_3 nanorods at room temperature, the CL and optical absorption spectra were investigated. The room temperature CL spectrum of γ - In_2Se_3 nanorods is shown in Figure 4(a). The peak energy of the CL is 1.95 eV, in good agreement with the predicated value by Varshini's relation, as displayed in the inset of Figure 3. The optical absorption spectrum taken at room temperature is displayed in Figure 4(b). It is known that γ - In_2Se_3 is a direct bandgap semiconductor. Thus, the absorption coefficient α near the band edge follows the relation of a direct bandgap transition [18] as

$$\alpha = \frac{A(h\nu - E_g)^{1/2}}{h\nu}, \quad (2)$$

where A is a constant, $h\nu$ is the photon energy and E_g is the energy gap between the valence band and the conduction band. The bandgap can be derived from extrapolating the linear part of the curve to zero absorption. The straight line in Figure 4(b) shows the extrapolation, and the bandgap energy was estimated to be ~ 1.99 eV. Obtaining the bandgap energy and absorption coefficient is essential for developing γ - In_2Se_3 nanorods as absorber layers in photovoltaic applications.

Figure 5(a) shows the PL spectrum of γ - In_2Se_3 nanorods at 15 K in the infrared spectral range. A broad PL peak located at 1.24 eV was observed. The sharp peak with energy at 1.16 eV is the emission related to the excitation laser. To find out origin of the 1.24 eV PL, the dependence of PL intensity on the excitation intensity was studied. The PL

FIGURE 3: The temperature dependence of PL spectra in the γ - In_2Se_3 nanorods. The inset shows the temperature dependence of peak position in PL (open circles). The solid line in the inset shows the fit according to (1).

FIGURE 4: (a) CL and (b) optical absorption spectra of γ - In_2Se_3 nanorods at room temperature. The red solid line shows the fit according to (2).

spectra with the excitation power density varied from 17 to 270 W/cm^2 were shown in Figure 5. The open circles in Figure 6 show the PL intensity as a function of the laser excitation density, indicating a linear increase of the PL intensity with excitation density. The dependence of the PL intensity I on the excitation density P can be fitted by a relation [19]:

$$I = CP^m, \quad (3)$$

where C and m are constants. The exponent m depends on the mechanism of recombination: for an excitonic recombination $m = 1$, while for free carrier recombination $m = 2$. When $m < 1$, it may indicate a transition associated with the donor-acceptor pair transition or free-to-bound transition [20, 21]. The solid line in Figure 6 displays the fit from (3). A value of m was determined to be around 0.6, which corresponds to the emission from the donor-acceptor pair transition or free-to-bound transition.

FIGURE 5: The infrared PL emission of γ - In_2Se_3 nanorods at 15 K on various excitation intensities: (a) 53 W/cm², (b) 88 W/cm², (c) 142 W/cm², and (d) 177 W/cm². The dashed line indicates that the PL peak shifts toward the high-energy side with increasing excitation density.

FIGURE 6: PL intensity of the 1.24 eV peak as a function of excitation density. The solid line shows the fit according to (3).

In Figure 6, the PL peak at 1.24 eV shifts to the high-energy spectral region with increasing the excitation density. This blue shift, originating from the increase of the interaction between more closed donor-acceptor pairs, is a characteristic of the donor-acceptor pair transition. Therefore, according to these observations, the observed PL peak at 1.24 eV can be ascribed to the donor-acceptor pair transition in γ - In_2Se_3 nanorods.

In summary, γ - In_2Se_3 nanorods deposited on Si (111) substrates were grown by MOCVD using dual-source precursors. The crystal structure and morphology of In_2Se_3 nanorods were characterized by SEM and HRTEM. The SAED analysis taken along [006] reveals a rectangle spot pattern, confirming the single crystalline in the γ phase. The optical absorption, CL, and temperature-dependent PL have been investigated. The PL at 15 K contains three peaks, which are identified with recombination of free excitons and bound excitons. The energy of the direct bandgap at

room temperature was found to be ~ 1.99 eV. An infrared PL, peaked at 1.24 eV, was observed in 15 K and assigned to be the donor-acceptor pair transition.

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