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Optical-memory switching and oxygen detection based on the CVT grown γ- and α-phase In_2Se_3

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ABSTRACT

Layered-type α- and γ-In_2Se_3 crystals were simultaneously grown by chemical vapor transport (CVT) method using ICl_3 as the transport agent. The crystalline state, surface state, and structural polytype of the as-grown In_2Se_3 were observed by high-resolution transmission electron microscopy (HRTEM). The direct band edges of α- and γ-In_2Se_3 were evaluated by thermoreflectance (TR) measurements. For α-In_2Se_3, a surface oxidation layer α-$In_2Se_{3-3x}O_{3x}$ ($0 \leq x \leq 1$) can easily form on the crystal face in environmental air by oxygen detection (~250 nm/day). The surface formation oxide can be easily removed by laser treatment (λ = 266 nm, P = 60 mW) and the oxygen detection can be repeated again. For γ-In_2Se_3, the HRTEM and Raman measurements reveal amorphous and polycrystalline state existing in the as-grown crystals. The amorphous effect renders erasable optical-memory switching of γ ↔ α inter-phase transition occurred inside the γ-In_2Se_3 layer with laser heating treatment. The phase transition of In_2Se_3 is fast and easily by using the laser treatment. The phase transformation of γ ↔ α was verified by Raman and TR measurements. The optical-memory switching and oxygen detection behavior for the as-grown γ- and α-phase In_2Se_3 are demonstrated herein.

1. Introduction

Diindium triselenide (In_2Se_3) is a III–VI compound which possesses at least five crystal modifications: α (two-layer hexagonal, 2H), β (three-layer rhombohedral, 3R), γ (defect wurtzite in hexagonal, H), δ, and κ [1,2]. The δ and κ are meta stable phases of diindium triselenide formed at different high temperatures. The β phase is similar to α on the layered plane excepting that a difference exists in between the monolayer's stacking along *c* axis (i.e. $c \cong 28.3$ Å for 3R β and $c \cong 19.2$ Å for 2H α). The α and γ modifications are two most stable phases of diindium triselenide stabilized at room temperature. Diindium triselenides of α and γ phases are suitable for application in solar-cell material [3], nanostructural phase-change memory [4,5], wide-energy-range photodetector [6,7], and thickness-tunable long pass filter [8]. The diversified crystal phases and various applications of In_2Se_3 are attributed to the misvalency of In^{III} and Se^{VI} atoms in the indium chalcogenide to form different crystalline and amorphous states [9] as well as diversified crystal phases and lattice forms [10,11]. Recently the individual study on respective α-In_2Se_3 or γ-In_2Se_3 has been implemented [6,8]. The surface of α-In_2Se_3 was been proven to contain oxide composition. The existence of the surface oxide on the α-In_2Se_3 was found to render a wide-energy-range photoelectric conversion from near infrared to ultraviolet region [6]. For γ-In_2Se_3, amorphous and nanocrystalline states were existed in the reported crystals [8] and the amorphous and nanocrystalline effect mainly dominated the thickness-dependent optical gap change of the diindium triselenide [8]. However, to date, no systematic study on the integration of crystal growth, structural, and sensing property of both α- and γ-In_2Se_3 has been reported.

In this study, the sensing properties of optical-memory switching and oxygen detection are, respectively, demonstrated in the γ- and α-phase In_2Se_3 polycrystals. The layered crystals of α and γ phases have been simultaneously grown by the CVT method at different high temperatures. The structural phases and optical properties of the layered γ- and α-In_2Se_3 have been evaluated and verified by high-resolution transmission electron microscopy (HRTEM), thermoreflectance (TR), surface photovoltage (SPV), surface photoconductive response (SPR), photoconductivity (PC), photoluminescence (PL) and Raman measurements. The

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experimental results of laser-induced photodarkening and annealing recovery test show that the γ-In_2Se_3 possesses an erasable read/write optical-memory function with well-behaved phase changed capability. The erasable read/write function can be attributed to the $\gamma \leftrightarrow \alpha$ inter-phase transition inside the microscale polycrystalline γ-In_2Se_3 layers. For the α-In_2Se_3, a surface oxidation layer of α-$In_2Se_{3-3x}O_{3x}$ ($0 \le x \le 1$) can easily form on the crystalline surface of α-In_2Se_3 in the air owing to the existing dangling bonds by chalcogen vacancy of the layered α-In_2Se_3. The surface-sensing oxide (layer) existing on the α-In_2Se_3 crystal assists photoelectric conversion in visible to ultraviolet range. The surface oxidation layer can be removed from the surface of α-In_2Se_3 via the laser treatment with higher power density. The oxygen sensing behavior on the α-In_2Se_3 surface is hence repeatable (re-used) after the laser treatment. PL, SPV, and SPR experiments verify the formation of surface oxide layer on the α-In_2Se_3. The surface formation oxide on the α-In_2Se_3 after oxygen detection can also be utilized as a photon emitter or a solar-energy converter. The function of the resultant is superior to that of the other O_2 gas sensors.

2. Experimental

2.1. Crystal growth

The In_2Se_3 crystals were grown by the CVT method using ICl_3 as a transport agent [12]. The growth was conducted in a horizontal three-zone tube furnace with the temperature gradient setting as 800 °C ← 950 °C → 800 °C (also tried 500 °C ← 650 °C → 500 °C) for simultaneously growing two sealed quartz ampoules (i.e. 2.2 cm OD, 1.9 cm ID, and 20 cm in length). The temperature gradient was −7.5 °C/cm. Prior to the crystal growth, the pure elements of In and Se with proper stoichiometry combined with a small amount of transport agent (ICl_3) were put into the quartz ampoule, which was then cooled using liquid nitrogen, evacuated to approximately 10^{-6} Torr, and then sealed with acetylene and oxygen torch. The mixture in the quartz tube was slowly heated to the growth temperatures to avoid any explosion. The reaction was maintained for 240 h for growing large single crystals. After the growth process, the as-grown crystals exhibited two distinct color groups: black shiny (α-In_2Se_3, at higher-temperature position) and red to yellow (γ-In_2Se_3, at lower-temperature side). They are essentially layer-type crystals with varying band gaps. By using a razor blade or Scotch tape, both of them could be thinned out to obtain thinner samples because weak van der Waals bonding was existed in between the individual monolayers.

2.2. Characterization

TR experiments of the In_2Se_3 layers were implemented using indirect heating manner with a gold-evaporated quartz plate as the heating element [13,14]. The thin layered sample was closely attached on the heating element by silicone grease. Thermal modulation of the samples was achieved by indirect heating manner of supplying current pulses to the Au heating element periodically. The on–off heating disturbance uniformly modulates the α- and γ-In_2Se_3 samples. An 150 W tungsten halogen lamp (or an 150 W xenon-arc lamp) filtered by a PTI 0.2-m monochromator provided the monochromatic light. The incident light was focused onto the sample with a spot size less than 1000 μm^2. An EG&G type HUV-2000B Si photodetector acted as the detection unit and the TR signal was measured and recorded via an EG&G model 7265 lock-in amplifier. PL experiments were carried out using a QE65000 spectrometer. The CCD array detections were employed in the PL measurements. The pumping light source was a Q-switched diode-pumped solid-state laser (λ = 266 nm). A set of neutral density filters was used to change and control the pumping power of the laser.

The SPV, SPR, and PC experiments are the optical techniques which do not need any optical sensor. The photodetector is the sample itself. For SPV measurement, the photoexcited electron–hole pairs from the surface band-bending region were extracted out from the top and bottom electrodes of a capacitor-like configuration, and then sent to a low-noise amplifier. The incident light was chopped at 20 Hz and photoelectric conversion response (from the low-noise amplifier) of α-In_2Se_3 was recorded via an EG&G model 7265 lock-in amplifier. For SPR measurements, an electric field was applied perpendicular to the *c* plane of α-In_2Se_3 between the top and bottom electrodes. It is similar to the electric-field operation of a thin-film solar cell. A load resistor connected in series with the sample was used for sensing the photocurrent under optical illumination. A DC voltage was supplied to the circuit. For PC measurements, α-In_2Se_3 sample was cut into a rectangular shape with indium coating two ends acted as the ohmic contact electrodes. The main difference between SPR and traditional PC measurements is the direction of applying electric field to the sample. The SPR is normal to *c* plane ($\varepsilon_{||} c$ axis) while PC is the in-plane photoconductivity of the *c* plane ($\varepsilon_{\perp} c$ axis) for the α-In_2Se_3 crystal. All the measured PC, SPV, and SPR spectral photoresponses are calibrated using a broadband thermal sensor with a measurement range from 1.25 to 4.5 eV. For Raman measurement, a Renishaw micro-Raman spectrometer equipped with a 514-nm Ar^+ ion laser was used for the structural characterization of phase change in the layered In_2Se_3 materials. The laser spot size (diameter) of Raman measurement was less than 0.2 mm and the laser power was adjusted to be about 2 mW.

X-ray photoemission spectroscopic (XPS) measurements were implemented by a Thermo Scientific K-Alpha system with a monochromatic Al K_α line source. The X-ray spot size in the system can be adjusted to 30–400 μm and the energy resolution can reach ~0.02 eV. The experiments were done on the as-grown (oxidized) plane of the layered α-In_2Se_3 in an analysis chamber with an ultimate vacuum reaching 10^{-9} mbar.

3. Results and discussion

3.1. Morphology and structure characterization

Fig. 1(a) shows a representative scheme of a sealed quartz ampoule after the CVT growth. Even the use of different growth conditions of 950 °C → 800 °C and 650 °C → 500 °C (the same gradient of −7.5 °C/cm), the CVT growth still results in two different color groups of black shiny (α-In_2Se_3, at higher temperature side ~10–15 cm) and red to yellow (γ-In_2Se_3, at lower temperature side ~15–20 cm). The temperature distribution (gradient) and crystal morphology for the as-grown α- and γ-In_2Se_3 are shown in Fig. 1(b) for comparison. The distinction of the grown phases for the as-grown In_2Se_3 crystals can be initially based on that the band gap of α-In_2Se_3 is in the near-infrared region (~1.45 eV, black) [6] and the γ-In_2Se_3 is in the visible range (≥2 eV, red to yellow with thickness dependence) [8]. The production ratio of the as-grown crystals for different growth temperature (i.e. α to γ phase) is about 9:1 for the temperature setting of 950 °C → 800 °C and 8:2 for that of 650 °C → 500 °C, respectively. With the decrease of the growth temperature, the formation of γ phase In_2Se_3 seems to be more productive than those obtained at higher temperatures. This result can also sustain that the γ-In_2Se_3 crystal is a lower temperature phase in the diindium triselenide while the α-In_2Se_3 belongs to a high-temperature phase. The materials are essentially sheet-type crystals with α-In_2Se_3 exhibiting hexagonal layer structure [6] but γ phase belongs to a defective wurtzite structure [8]. For α-In_2Se_3,