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Amorphous effect on the advancing of wide-range absorption and structural-phase transition in γ -In₂Se₃ polycrystalline layers

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The exploitation of potential functions in material is crucial in materials research. In this study, we demonstrate a III-VI chalcogenide, polycrystalline γ -In₂Se₃, which simultaneously possesses the capabilities of thickness-dependent optical gaps and wide-energy-range absorption existed in the polycrystalline layers of γ -In₂Se₃. Transmission electron microscopy and Raman measurement show a lot of γ -phase nanocrystals contained in the disordered and polycrystalline state of the chalcogenide with medium-range order (MRO). The MRO effects on the γ -In₂Se₃ layers show thickness-dependent absorption-edge shift and thickness-dependent resistivities. The amorphous effect of MRO also renders a structural-phase transition of $\gamma \rightarrow \alpha$ occurred inside the γ -In₂Se₃ layer with a heat treatment of about 700 °C. Photo-voltage-current (Photo V-I) measurements of different-thickness γ -In₂Se₃ layers propose a wide-energy-range photoelectric conversion unit ranging from visible to ultraviolet (UV) may be achieved by stacking γ -In₂Se₃ layers in a staircase form containing dissimilar optical gaps.

Nanocrystals contained in a polycrystalline solid with a grain size in the nanometer range have received considerable attention because the relationship between nanocrystals and amorphous states^{1,2}. These effects are usually present in absorption-edge change or variations in optoelectronic property of the disordered and polycrystalline materials^{2–4}. The amorphous effect that involves the nanocrystalline, disordered, and interfacial states of a polycrystal may push the amorphous material possessing numerous potential functions for fabrication of optical, data storage, energy, and optoelectronics devices.

In₂Se₃ is a crucial III-VI compound that possesses at least five crystal modifications of α , β , γ , δ , and κ ^{5–7}. It is suitable for application in solar-cell material⁸, nanostructural phase-change memory⁹, and wide-energy-range photodetectors^{10–12}. The diversified crystal phases and various applications of In₂Se₃ may be attributed to the misvalency of the In^{III} and Se^{VI} atoms in the indium chalcogenide to form various crystalline and amorphous states¹³ as well as diversified crystal phases and lattice forms^{14,15}. The α -phase In₂Se₃ belongs to a hexagonal layer structure ($E_g \sim 1.45$ eV)¹² and the γ phase is a defective wurtzite structure ($E_g \sim 2$ eV)¹⁴. The α and γ phases are the two most stable phases of In₂Se₃ stabilized at room temperature. In contrast to the other Group III-V and Group IV compounds have the strongest covalent bond, the misvalency and weaker bond strength between the III and VI elements allow In₂Se₃ to exhibit an amorphous (disordered and polycrystalline) state and to present a phase transition (change) in the chalcogenide compound easily. For example, the γ -In₂Se₃ glassy-state thin film was easy to grow on substrates that available for state-change (amorphous $\leftrightarrow$ crystalline in the same γ phase) memory use^{4,13}. However, it is believed that the amorphous γ -In₂Se₃ maybe has the character of phase transition (e.g. γ to α) that can be made in an optical-memory disc with long-time reservation of data. Despite the applications of γ -In₂Se₃, the experimental study on the optical, electrical and structural properties of amorphous γ -In₂Se₃ is still relatively rare. The understanding of optical properties of amorphous γ -In₂Se₃ should be crucial. It is important to push this chalcogenide material for application in long-term-storage optical memory and cascaded wide-energy-range solar cells.

In this paper, we report that the γ -In₂Se₃ layers (exhibiting medium-range order and nanocrystalline states) possess several specific characteristics of thickness-dependent absorption-edge shift, thickness-dependent

resistivities, wide-energy-range optical absorption in visible to ultraviolet (UV) range as well as γ to α phase transition by heat treatment. The layer-type γ - In_2Se_3 polycrystals were grown by chemical vapor transport method using ICl_3 as a transport agent. The as-grown layer crystals show varying colors from dark red, red, orange, to light-yellow because the crystals have dissimilar thicknesses. The thickness-dependent optical gaps in the γ - In_2Se_3 layers were evaluated by thermoreflectance (TR) measurements. The optical band-gap change in the γ - In_2Se_3 layered samples was determined to be from 2.52 eV (6 μm) to approximately 2.08 eV (290 μm), which agrees well with the color change of the as-grown crystals. The thickness-dependent optical gaps also cause a variation in resistivity of the different-thickness samples. The measurement results of Photo V-I (i.e. using a white LED and a halogen lamp) propose a staircase-stacking structure of the amorphous γ - In_2Se_3 layers with dissimilar thicknesses (optical gaps). It may promote a wide-energy-range optical absorption from the visible to UV region. Raman and TR results of an annealed γ - In_2Se_3 layer indicate that the structural phase transition of In_2Se_3 from γ to α phase can occur at 700 °C with a heat treatment in a tube furnace. Laser induced structure change (γ to α) by using a 405-nm laser has also been done to verify the phase transition. The phase-transition character makes γ - In_2Se_3 a potential material applied for long-term-storage optical memory disc.

Results

Crystal morphology and crystallinity. Displayed on the left side of Fig. 1(a) are the crystal morphology and crystal color of an as-grown γ - In_2Se_3 crystal (see inset) and the corresponding scanning electron microscope (SEM) image. The crystal thickness of the sample is approximately 200 μm , and the crystal exhibits a transparent red color. In addition, the magnification image of the SEM picture reveals a stacking-layer structure of the as-grown In_2Se_3 . The evidence of SEM image indicates that the defective wurtzite structure of γ - In_2Se_3 crystal also displays a layered-type outline similar to that of α - In_2Se_3 ¹⁰. The easily formed face of the layered γ - In_2Se_3 may be the c plane. The right hand side of Fig. 1(a) shows the high-resolution transmission electron microscope (TEM) image of the as-grown In_2Se_3 layer-type crystal. The TEM image shows somewhat nanocrystalline states (marked by yellow dashed polygons: “C”) and a few amorphous and disordered states (denoted by light green: “A”), as displayed on the right side of Fig. 1(a). The crystallinity of the as-grown In_2Se_3 exhibited slightly polycrystalline and disordered states (i.e. amorphous with approximately medium-range order). The sizes of the In_2Se_3 nanocrystallites displayed in the TEM image were from about 1 nm to larger than 10 nm. According to the TEM image, the average interatomic distance between two nearest neighbors in the nanocrystalline area [see Fig. 1(a)] was approximately 2.38 Å. The γ -phase In_2Se_3 is a defective wurtzite structure with structural vacancies disordered in a screw form and surrounded along c -axis^{14,15}. In the screw form of the defective wurtzite structure, one-third of the cation sites (i.e. In) were left vacant to satisfy the octet rule of sp^3 hybridization in the In_2Se_3 compound. This signifies that the lattice constants of a and b for the γ - In_2Se_3 shown in Fig. 1(a) were $a = b = 7.14$ Å (i.e., 2.38×3 Å). The X-ray diffraction pattern of the c plane of the layered γ - In_2Se_3 (not shown) also indicates a lattice constant of $c \approx 19.36$ Å for the γ - In_2Se_3 , similar to that of the α - In_2Se_3 ¹⁰. The experimental SEM and X-ray results confirmed that the as-grown colored crystals are γ -phase In_2Se_3 . The layered material possessed a slightly disordered and nanocrystalline state (medium-range order) inside the crystals.

Fig. 1(b) shows the Raman spectrum of the c -plane-layered γ - In_2Se_3 between 100 and 350 cm^{-1} . The Raman spectrum exhibits several broadened peak features of the vibration modes (not showing sharp and narrow), which are caused by the layered γ - In_2Se_3 typically being in a polycrystalline and medium-range ordering state, as

Figure 1 | (a) SEM and TEM images of γ - In_2Se_3 . The crystal morphology and crystal color of the as-grown In_2Se_3 crystal is shown in the inset. The SEM image verifies the stacking-layer structure of γ - In_2Se_3 , and the TEM image displays the nanocrystalline and disordered states (amorphous) of the γ - In_2Se_3 . (b) Raman spectrum of the layered γ - In_2Se_3 at room temperature.

evident in the TEM image of Fig. 1(a). Although the layered γ - In_2Se_3 contains both nanocrystallites (size up to larger than 10 nm) and disordered states the bond angle disorder and lattice deformation of the disordered states make stronger contribution of Raman intensity for the broadened features than those of the other nanocrystallites with narrow line width. As shown in the lower portion of Fig. 1(b), the Lorentzian fits to the Raman spectrum can be analyzed to reveal four peak features positioned at 125 ± 5 , 150 ± 5 , 183 ± 4 , and 228 ± 5 cm^{-1} for In_2Se_3 . The modes are tentatively assigned and referred to previously reported data. The energy region below 115 cm^{-1} is the system detection limit, where a rapid decrease in the Raman spectra is occurred. The broadened peaks of the 125 ± 5 and 228 ± 5 cm^{-1} modes had been observed in an amorphous $\text{In}_{40}\text{Se}_{60}$ thin film deposited on a glass substrate. The two modes are closely related to the γ phase of In_2Se_3 ¹⁶, and the 150 cm^{-1} feature is related to the zone center mode of the γ - In_2Se_3 crystal¹⁷. The other 183 ± 4 cm^{-1} peak was determined to be a characteristic mode for γ - In_2Se_3 ^{18,19}. It is possible to contain some modes from the local structures in In_2Se_3 due to the structural disorder such as InSe_2 at 150 cm^{-1} ¹⁷. However, the respective peak features are too broad to distinguish owing to the amorphous state of In_2Se_3 . The Raman result of the layered plane in Fig. 1(b) approximately verifies and maintains the hypothesis that the as-grown In_2Se_3 layers are γ phase crystals, which exhibit amorphous state.

Thickness dependent optical gaps and thickness dependent resistivities. Fig. 2(a) shows the thickness-dependent TR spectra of γ - In_2Se_3 with various thicknesses ranging from approximately 6 μm

Figure 2 | (a) Thickness-dependent TR spectra of the γ -In₂Se₃ layered crystals. The side-view SEM image facilitates the estimation of sample thickness. (b) The dark resistivities of 6-, 68-, and 212- μ m thick samples according to the V-I measurement. The representative crystal colors of the three samples are also included for comparison.

to 290 μ m at room temperature. The crystal thickness of each sample was estimated using a cross-sectional view of the SEM image. The right insets of Fig. 2(a) display the representative SEM images for the estimated thickness of the 30- and 125- μ m-thick samples. The TR measurement was previously proven to be a powerful tool for evaluating the direct band-edge transition of semiconductors²⁰. The derivative line shape of the transition feature enhances the ability to determine the exact energy location of the direct transition in semiconductor. As shown in Fig. 2(a), the dashed lines are the experimental TR spectra and the solid lines are the least-square fits to a derivative Lorentzian line-shape function expressed as^{21,22}:

$$\Delta R/R = \text{Re} \left[\sum A \cdot e^{j\varphi} (E - E_g^d + j\Gamma)^{-m} \right], \quad (1)$$

where A and φ are the amplitude and phase of the line shape, and E_g^d and Γ are the energy and broadening parameter of the interband transition. The value of $m = 0.5$ is used for the first derivative line shape analysis of direct band-edge transition of γ -In₂Se₃²¹. The obtained transition energies of direct band edge of γ -In₂Se₃ were determined to be $E_g^d = 2.08$ eV (290 μ m), 2.09 eV (212 μ m), 2.13 eV (125 μ m), 2.22 eV (68 μ m), 2.31 eV (38 μ m), 2.33 eV (30 μ m), and 2.52 eV (6 μ m), respectively. With decreasing the thickness of the samples, the direct optical gap E_g^d of γ -In₂Se₃ demonstrates an energy blue-shift behavior. The crystal colors of

the as-grown crystals varied from dark red to light yellow also verified this behavior. The thickness-dependent optical-gap change of the γ -In₂Se₃ layers may be attributed to the amorphous effect together with the nanocrystals' quantum sized effect and we may discuss this behavior later. To check the thickness-dependent optical-gap change of the γ -In₂Se₃ layers, dark resistivity measurements were also carried out. Fig. 2(b) shows the dark V-I measurements used for the determination of resistivities of several selected 6-, 68-, and 212- μ m-thick samples for γ -In₂Se₃. The representative crystal color for the different-thickness γ -In₂Se₃ sample is also displayed in Fig. 2(b) for comparison. The measurement configuration of the dark V-I is depicted in the upper inset of Fig. 2(b). The experimental results of the 6-, 68-, and 212- μ m-thick samples are respectively displayed by solid squares, solid triangles, and solid circles in Fig. 2(b). The solid lines represent the resistance fits. In general, for two layered semiconductors with dissimilar thicknesses (but the same area), the measured resistances of the two samples are different, but the resistivity should be equal. However, based on the V-I measurements shown in Fig. 2(b), a high resistivity of $\rho = 6.63 \times 10^8 \Omega\text{-cm}$ (see lower inset) was measured for the 6- μ m-thick sample and the lowest resistivity of $\rho = 2.88 \times 10^8 \Omega\text{-cm}$ was obtained for the 212- μ m-thick sample. The resistivity value of the 68- μ m-thick sample was $\rho = 3.80 \times 10^8 \Omega\text{-cm}$. The resistivity value of γ -In₂Se₃ reveals thickness dependent with a lower resistivity occurred in a thick sample. This behavior approximately verifies the occurrence of band-gap reduction in the thick sample. For a general semiconductor, the resistivity can be expressed as

$$\rho = \frac{1}{\sigma} = \frac{1}{n_i \cdot q \cdot (\mu_n + \mu_p)}, \quad (2)$$

$$n_i \propto \exp\left(\frac{-E_g}{2kT}\right), \quad (3)$$

and therefore

$$\rho \propto \exp\left(\frac{E_g}{2kT}\right), \quad (4)$$

for the semiconductor (i.e. simple model). Where σ is the conductivity, μ_n and μ_p are the mobilities of electron and hole of the semiconductor. Because the thickness-dependent optical band edge of γ -In₂Se₃, the thin sample may exhibit an equivalent larger band gap and consequently possesses a lower carrier density and higher resistivity at room temperature. This behavior may also cause γ -In₂Se₃ being a resistor-logic material by changing the film thickness for electrical memory use.

Discussion

According to the shift of absorption edge with different thicknesses in the amorphous γ -In₂Se₃ layers, the main causes are maybe owing to some effects of amorphous effect, defects, nano-sized quantum confinement²³, and layer-type crystallography²⁴.

Amorphous effect, defects, nano-sized quantum confinement, and layer-type crystallography. For an amorphous semiconductor with medium-range order, it is believed that the void fraction (by vacancies), amorphous effect (disorder), and one-dimensional quantum confinement (ODQC) are closely related to the thickness-dependent optical gap change. Regarding a thin polycrystalline layer with poor crystallization quality, the band-gap energy of γ -In₂Se₃ was typically larger than that of a single crystal or a high-quality crystalline film (e.g., $E_g \approx 2$ eV)¹⁸ because of the existence of quantum localization of nanocrystals with ODQC effect. For the intra-layer plane, if a nanocrystal (with particle size smaller than 10 nm) was confined to a region in x-axis of length Δx . The

Figure 3 | (a) The representative schemes of band tailing and potential fluctuations by spatial distribution of disordered and nanocrystalline states of $\gamma\text{-In}_2\text{Se}_3$ near band edge. (b) The representative scheme of a thicker (by stacking layers) $\gamma\text{-In}_2\text{Se}_3$ sample with $E_g^d \sim 2.0$ eV. (c) The representative scheme of a thinned $\gamma\text{-In}_2\text{Se}_3$ layer that can pass through the higher-energy photons in the layered plane (e.g. $E_g^d \sim 2.52$ eV for a $6 \mu\text{m}$ -thick sample).

momentum of electron is $\Delta P_x \sim \hbar/\Delta x$ and the increment of kinetic energy is about $\Delta E \sim (\Delta P_x)^2/2m \sim \hbar^2/2m \cdot (\Delta x)^{-2}$. For thickness dependence of the optical-gap change, the confinement can be considered only in the thickness t direction (i.e. c -axis) with ODQC effect described by:

$$E_g^d(t) = E_{g(\text{bulk crystal})} + \frac{\pi^2 \hbar^2}{2m_r^*} \cdot \frac{1}{t^2}, \quad (5)$$

where $\frac{1}{m_r^*} = \frac{1}{m_e^*} + \frac{1}{m_h^*}$ is the reduced mass. For the amorphous effect as shown in the left-hand side of Fig. 3(a), localized-state tails of the conduction band and valence band by high-density defects may occur in $\gamma\text{-In}_2\text{Se}_3$. Potential fluctuations by spatial distribution of disordered and nanocrystalline states²⁵ may cause deformation potential near band edge existed in an amorphous material as displayed in right-hand side of Fig. 3(a) for one single layered plane of $\gamma\text{-In}_2\text{Se}_3$ (e.g. $t = 6 \mu\text{m}$). It is noticed that the deformation potential in amorphous layered $\gamma\text{-In}_2\text{Se}_3$ is arisen from lattice deformation and which may cause strain exerted on the nanocrystalline grains. The induced strain makes the nanocrystalline grains deformed and distorted. It will narrow down the optical gap of nanocrystals, especially in a thicker sample with stacking layers (i.e. increased strain by increasing thickness)²³.

For the defect effect in amorphous $\gamma\text{-In}_2\text{Se}_3$, the void (vacancy) fraction affects the optical gap. A thin sample (i.e. $t = 6 \mu\text{m}$) has highly defective vacancy fraction and open In_2Se_3 network will increase its optical gap because the ODQC effect is dominant²³. As

in a thick sample, the networks are more compact and the void fraction decreases. It leads an equivalent higher crystallinity and renders a smaller optical gap such as a bulk crystal. Furthermore, for the contribution of layer-type crystallography on optical band gap, the optical absorption of the layer compound is considered to be different from that of a cubic system with the planes parallel and perpendicular to the c axis. In the layered plane of $\gamma\text{-In}_2\text{Se}_3$, the system is similar to a 2D-like environment with strong intra-layer covalent bonding. However, the inter-layer interaction between the individual layers is only a weak van der Waals bond. This property may also make significance to the thickness-dependent optical gap change of the layer crystals in the micro-scale range. It was found that the single crystals of layered TlInS_2 had shown an energy-gap decrease of $\Delta E_g \approx 0.078$ eV as the sample thickness increased from 27 to $66 \mu\text{m}$ ²⁴. As shown in Fig. 3(b), in a thick $\gamma\text{-In}_2\text{Se}_3$ sample, the crystallinity and exerted strain on the nanocrystals would be higher than those of a thin layer. The optical gap decreases to comparable with a single crystal with $E_g^d \sim 2$ eV. When a white light impinges on the thick sample, only the lower-energy photons (red and near infrared) can pass through the $\gamma\text{-In}_2\text{Se}_3$ sample. However, for a thin layered sample with $t = 6 \mu\text{m}$, as illustrated in Fig. 3(c), the nanocrystals with ODQC provide a path through which higher-energy photons (yellow and green portion) can pass. The averaged optical gap of a thin $\gamma\text{-In}_2\text{Se}_3$ sample is thus increased to about 2.52 eV, which can be evident by Fig. 2(a). During the crystal growth of $\gamma\text{-In}_2\text{Se}_3$, the layers are likely to have different crystallinity in different regions in the layered plane. The thick $\gamma\text{-In}_2\text{Se}_3$ sample should have the averaged better crystallinity and hence own a typical lower band

Figure 4 | (a) Photo V-I measurements of a 68- μm -thick sample. (b) Photo V-I measurements of a 6- μm -thick sample. The inset shows a proposed wide-energy-range absorption scheme that involves stacking dissimilar absorption edges (thicknesses) of $\gamma\text{-In}_2\text{Se}_3$. (c) The light emission spectra and spot-light patterns of the white LED and halogen lamp at a power density of ~ 9 mW/cm².

gap close to 2 eV. This behavior would also be verified by the decreased resistivity in the thick samples as evident in Fig. 2(b).

White-light Photo V-I property. To further verify the thickness-dependent absorption edge shift and evaluate the photoelectric conversion behavior of $\gamma\text{-In}_2\text{Se}_3$, Photo V-I measurements of different-thickness $\gamma\text{-In}_2\text{Se}_3$ photoconductors were implemented. Figs. 4(a) and 4(b) show the Photo V-I and dark V-I measurement results for the two thickness samples of $t = 68$ μm and $t = 6$ μm , respectively. The measurement setup is shown in the lower inset of Fig. 4(a). Two white light sources comprising one white LED and one halogen lamp were used. The white LED covers a wide spectral range from visible to infrared (IR) with two hump peaks centered at approximately 2.81 eV and 2.26 eV [see Fig. 4(c)]. The halogen lamp shows a broadband blackbody radiation with a main hump peak close to approximately 1.83 eV, which also decreases in intensity toward the IR range. Two white-light-spot patterns of halogen lamp and white LED display different color temperatures as evident in Fig. 4(c). The color temperature for the white LED is typically “cold” whereas the halogen lamp possesses a more

“warm” color temperature. The spectral contribution of the white LED approaches the visible-to-UV region, whereas the halogen lamp approaches the visible-to-NIR range. The optical-gap values for the two thickness samples (obtained by TR) were $E_g = 2.22$ eV (68 μm) and $E_g = 2.52$ eV (6 μm), respectively. The Photo V-I slopes (photoconductivities) in Figs. 4(a) and 4(b) clearly show that the photoresponsivity of the halogen lamp in the low band-gap sample (68 μm , 2.22 eV) was similar to that of the white LED, whereas for the large band-gap sample (6 μm , 2.52 eV), the Photo V-I slope by the halogen lamp approaches the dark condition, as evident in Fig. 4(b). The resistivity values of $\gamma\text{-In}_2\text{Se}_3$ under various light-source illuminations are included in Figs. 4(a) and 4(b) for comparison. It is more reasonable to show that the wide optical-gap sample (e.g., $t = 6$ μm , $E_g = 2.52$ eV) exhibits less responsivity to the visible-NIR light but demonstrates high sensitivity to the blue-UV illuminations. Since the character of thickness-dependent absorption edge change of $\gamma\text{-In}_2\text{Se}_3$, a wide-energy-range absorption unit using a staircase-stacking structure of $\gamma\text{-In}_2\text{Se}_3$ layers can be proposed. The lower inset of Fig. 4(b) depicts the representative scheme of the unit. The structure may

γ to α transition by thermal annealing at 700 °C

Figure 5 | (a) Raman and TR spectra of an annealed γ - In_2Se_3 sample at 700 °C. The upper-left inset shows the crystal color and morphology of the annealed sample. (b) The Raman and TR spectra of an as-grown α - In_2Se_3 layered crystal. The upper-left inset displays the crystal outline of the α - In_2Se_3 .

integrate the maximal photoresponses of γ - In_2Se_3 induced by various optical-gap (thicknesses) layers, and it can also render a wide-energy range and high-efficiency optical absorption responsively to the white lights.

The γ to α phase transition. In general, the amorphous materials can usually present crystalline state or phase transition treated by heating process at high temperatures. To see any polymorphism transformation behavior occurred in the γ - In_2Se_3 layers, thermal annealing test has been implemented in an evacuated tube furnace. Fig. 5(a) shows the Raman spectra of a ~ 10 - μm thick γ - In_2Se_3 (yellow color) annealed at 700 °C for 20 minutes. The upper-left inset of Fig. 5(a) shows the color and morphology of the annealed γ - In_2Se_3 sample. It is essentially black color after annealing and we believe that the In_2Se_3 crystal undergoes a phase transition from γ to α polytype by the heat treatment of 700 °C. The TR spectrum displayed in the upper-right inset of Fig. 5(a) confirms a broadened feature of band-edge transition (E_g) at about 1.45 eV, matches well with the direct gap of an as-grown α - In_2Se_3 layered crystal (measured by TR), as shown in the upper-right inset of Fig. 5(b). The value of E_g^d (~ 1.45 eV) of α - In_2Se_3 is different from those of 2–2.52 eV for the γ - In_2Se_3 layers with different thicknesses in Fig. 2(a). As shown in the Raman spectra of Fig. 5(a), the vibration modes of the annealed sample (undergoing γ to α transition) essentially demonstrate five

peak features positioned at 142, 174, 202, 236, and 253 cm^{-1} . They are different from those of the amorphous γ - In_2Se_3 layer with broadened 125, 150, 183, and 228 cm^{-1} features in Fig. 1(b). The five peak features of 142, 174, 202, 236, and 253 cm^{-1} measured at different positions of the layered plane [i.e. POS1 and POS2 in Fig. 5(a)] show somewhat relative intensity change because the annealed sample does not have a smoothly and flatly layered-plane surface after annealing. Many α -polycrystalline grains with different orientations and areas are maybe contained and randomly distributed on the layered plane of the annealed sample. Despite the orientation effect, the five vibration modes of 142, 174, 202, 236, and 253 cm^{-1} in the annealed sample can also be detected in the as-grown α - In_2Se_3 crystal [see Fig. 5(b)]. The α - In_2Se_3 has a hexagonal layered structure [i.e. as the outline of the as-grown crystal in Fig. 5(b)]. The vibration modes in Fig. 5 are tentatively assigned and compared to previous results. The 142 cm^{-1} peak is related to the vibration mode of $A_1(\text{TO})$ of α - In_2Se_3 crystal²⁶, and the 174 cm^{-1} mode closely correlates with the In-Se vibrations in a α - In_2Se_3 thin film¹⁷. The 202 cm^{-1} peak is the $A_1(\text{LO})$ mode of α - In_2Se_3 , which is stronger if the Raman measurement was done on the basal plane ($k \parallel c$ -axis)²⁶. The 236 cm^{-1} mode also possesses the A_1 symmetry and which usually presents a little bit higher intensity on the edge plane with the incident light of $k \perp c$ -axis operation. The feature of 253 cm^{-1} is related to a vibration mode by Se_8 rings that had ever been detected in an α - In_2Se_3 thin film¹⁷. The thermal annealing test of the polycrystalline γ - In_2Se_3 layer indicates that the defect-wurtzite γ - In_2Se_3 is a low-temperature phase, and which can be transformed into the high-temperature 2H (two-layer hexagonal) structure of α - In_2Se_3 at ~ 700 °C. The values of lattice constant c (c -axis) in both α - and γ - In_2Se_3 are similar, which is determined to be $c \approx 19.3$ Å. The γ - In_2Se_3 is a defect-wurtzite structure with the atomic arrangement in the cation sheet being $\blacksquare$ -In-In- $\blacksquare$ -In-In, where “ $\blacksquare$ ” is the indium vacancy. For α - In_2Se_3 , the monolayer may be consisted of Se-In-Se-In-Se tetrahedral configuration. For the amorphous γ - In_2Se_3 under the heat treatment of 700 °C, the same lattice constant c of the layered plane provides a suitable environment for the $\gamma \rightarrow \alpha$ transition in the same layered plane of In_2Se_3 (i.e. intra-layer phase transformation). Furthermore, in order to promote the optical memory use of the γ - In_2Se_3 , laser-induced photodarkening test by using a 405-nm solid-state laser was also implemented. The spot size (diameter) of the laser is of ~ 0.5 mm and the output power can be adjusted from 0 to 300 mW. The sample area of γ - In_2Se_3 is about 2×2 mm² and thickness is $t \approx 6$ μm (i.e. yellow color). Figure 6 shows the real crystal colors and Raman spectra of the γ - In_2Se_3 layered sample with photodarkening test using laser heat treatment. As the laser power increases, the spot color of the γ - In_2Se_3 gradually changes from yellow, orange, red, dark red, brown, and black ($P \approx 50$ mW, power density ≈ 6.36 W/cm²). The induced black spot should be an α -polytype area and whose Raman spectrum consisted of a much broadened feature and five α -related Raman modes as evident in Fig. 6. For the dark-red (brownish) area near the black spot of the photodarkened γ - In_2Se_3 (see Fig. 6), the Raman spectrum shows similar line shape with that of the yellow sample excepting that the line widths of the dark-red area are narrowed and the peak energies are blue shift a little bit. The dark-red (brownish) area may be still a γ - In_2Se_3 with better crystallinity whereas the black spot is an α - In_2Se_3 phase (i.e. phase transition). From the result, the laser treatment also has the same effect as the thermal annealing by furnace. According to the experimental results, the most stable and highly crystalline phase of In_2Se_3 should be the α phase. The phase-change property of diindium triselenide renders γ - In_2Se_3 a potential usage for being an optical memory material with long-time storage capability.

In summary, γ -phase In_2Se_3 layered crystal with a little bit amorphous state has been grown by chemical vapor transport method using ICl_3 as the transport agent. Owing to the misvalency

γ -In₂Se₃ Laser Treatment - Raman

Figure 6 | Raman spectra and crystal pictures of a 6- μm thick γ -In₂Se₃ under different laser treatments (photodarkening test) for the verification of phase transformation of γ to α .

of In^{III} and Se^{VI} and a lot of nanocrystalline states in the amorphous γ -In₂Se₃ layer, many fundamental properties and probable applications of the chalcogenide have been explored. At first, thickness-dependent absorption-edge shift of γ -phase In₂Se₃ layers ranging from 2.52 eV ($t = 6 \mu\text{m}$) down to 2.08 eV ($t = 290 \mu\text{m}$) have been detected due to amorphous effect and quantum localization of nanocrystals. The resistivity of γ -In₂Se₃ also reveals thickness dependent. It verifies the absorption edge change with the variation in thickness. This property can be utilized as resistor logic by changing the film thickness as an electrical memory. The Photo V-I measurements indicate that the white lights of the visible to UV portion can be efficiently absorbed to achieve photoelectric conversion in the γ -In₂Se₃ layered compound exhibiting various thicknesses. The thermal annealing test verifies that the transition temperature of γ to α phase in In₂Se₃ is about 700°C. The state and phase changes were also verified by laser-induced photodarkening experiments. The polytype change of γ to α can be simultaneously occurred in the same In₂Se₃ sheet identifies that both α -In₂Se₃ and γ -In₂Se₃ are belonging to the layered-type structure. The amorphous effect on the feasible improvement of the optoelectronic property of γ -In₂Se₃ causes the layer crystal being a multifunctional material owning electrical logic, optical memory, and photoelectric-conversion capabilities.

Methods

Preparation of In₂Se₃ layered crystals. The In₂Se₃ crystals were grown by applying chemical vapor transport using ICl₃ as a transport agent²⁷. The growth was conducted in a horizontal three-zone tube furnace with a temperature gradient setting as 500°C $\leftarrow$ 650°C $\rightarrow$ 500°C for growing two sealed quartz ampoules simultaneously. Prior to the crystal growth, the pure elements of In and Se with proper stoichiometry combined with a small amount of transport agent (ICl₃) were put into the quartz ampoule, which was then cooled using liquid nitrogen, evacuated to approximately 10⁻⁶ Torr, and then sealed. The reaction was maintained for 200 h for growing large single crystals. After the growth was completed, the as-grown crystals exhibited two distinct color groups: shiny black (α -In₂Se₃, at higher-temperature position) and red to yellow (γ -In₂Se₃, at lower-temperature side). These are essentially layer-type crystals with varying optical gaps. By using a razor blade or Scotch tape, both of them were thinned out to obtain thinner samples because weak van der Waals bonding existed between the individual layers.

Optical measurements. The TR experiments were implemented using indirect heating manner with a gold-evaporated quartz plate as the heating element. The thin layered samples of γ - and α -In₂Se₃ were closely attached on the heating element by silicone grease²⁸. The on-off heating disturbance uniformly modulates the layered sample periodically. The incident and reflected lights can be guided by a silica fiber. 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 is focused onto the sample with a spot size less than hundred μm^2 . An EG&G type HUV-2000B Si photodetector acted as the detection unit and the TR signal was

measured and recorded via a NF 5610B lock-in amplifier. For the 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 In₂Se₃ materials. The laser spot size (diameter) of Raman measurement was about 0.2 mm (i.e. the minimum size can be down to 5 μm) and the laser power was adjusted to be about 2 mW. Photo V-I experiments were performed using two dissimilar white-light sources as the solar emulators. The first was a commercialized InGaN-based phosphorus white-light light-emitting diode array (denoted as white LED), and the second was a tungsten halogen lamp (denoted as halogen lamp). The averaged power density of the white LED and the halogen lamp was adjusted and maintained at approximately 9 mW/cm² by using the monitor of an OPHIR optical power meter equipped with a broadband high-sensitivity thermal sensor (0.15–6 μm). To prepare the samples for the Photo V-I measurements, each specimen of the layered γ -In₂Se₃ was cut into a rectangular shape. The two ends of each specimen were then coated with Au/In, which served as the ohmic-contact electrodes by sputtering. To perform the optical measurements, the ohmic-contact electrodes on each sample were shielded with light. The Photo V-I measurements were implemented using the auxiliary of a semiconductor parameter analyzer. The voltage scanning range was set at -500 to 500 V.

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Author contributions

C.H.H. conceived the idea and conducted the experiments. C.H.H. also grew the samples, analyzed the data, and wrote the manuscript.

Additional information

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