

# Epitaxial Growth of $\gamma$ -InSe and $\alpha$ , $\beta$ , and $\gamma$ -In<sub>2</sub>Se<sub>3</sub> on $\epsilon$ -GaSe

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## Abstract

We demonstrate that  $\gamma$ -InSe and the  $\alpha$ ,  $\beta$  and  $\gamma$  phases of  $\text{In}_2\text{Se}_3$  can be grown epitaxially on  $\epsilon$ -GaSe substrates using a physical vapour transport method. By exploiting the temperature gradient within the tube furnace, we can grow selectively different phases of  $\text{In}_x\text{Se}_y$  depending on the position of the substrate within the furnace. The uniform cleaved surface of  $\epsilon$ -GaSe enables the epitaxial growth of the  $\text{In}_x\text{Se}_y$  layers, which are aligned over large areas. The  $\text{In}_x\text{Se}_y$  epilayers are characterised using Raman, photoluminescence, X-ray photoelectron and electron dispersive X-ray spectroscopies. Each  $\text{In}_x\text{Se}_y$  phase and stoichiometry exhibits distinct optical and vibrational properties, providing a tuneable photoluminescence emission range from 1.3 eV to  $\sim 2$  eV suitable for exploitation in electronics and optoelectronics.

## KEYWORDS

Indium Selenide, III-VI van der Waals layered crystals, 2D materials, physical vapour transport

## Introduction

Multi-layer van der Waals (vdW) heterostructures have the potential to extend the range of functionalities of optoelectronic devices [1]. These artificial structures, which are prepared by mechanical exfoliation and stacking of the component crystalline layers, have physical properties of fundamental and technological interest [2]. However, this method is not easily scalable for large-area device fabrication. This drawback can be overcome by the direct growth of 2D layers using vdW epitaxy [3]. Since vdW crystals have no dangling bonds and weak inter-layer forces, they can be grown on a vdW crystal or other substrates ( $\text{SiO}_2$ , mica, quartz, *etc.*) with low levels of in-plane strain and form clean, sharp interfaces even in highly lattice mismatched heterostructures [4–6].

To date, epitaxial growth by chemical vapour deposition (CVD), physical vapor transport (PVT) or molecular beam epitaxy (MBE) has been used for the synthesis of hexagonal boron nitride (hBN) [7–10], graphene [11–13], metal dichalcogenides [14–21] and metal chalcogenides [22–29]. Within this large family of vdW crystals, the epitaxial growth of metal chalcogenides containing In and Se, *e.g.*  $\text{In}_x\text{Se}_y$ , is now attracting increasing interest. These crystals can exist in different polytype phases, *e.g.*  $\alpha$ ,  $\beta$ ,  $\gamma$ , and/or stoichiometries, *i.e.* different In/Se atomic ratio [30], each with a band structure that is strongly dependent on the number of atomic layers when the layer thickness is reduced below  $\sim 20$  nm [31,32]. Studies of exfoliated  $\gamma$ -InSe flakes have revealed properties that are distinct from those of other vdW crystals [33–35]. They are optically active with a band gap that increases markedly with decreasing layer thickness down to a single layer [33,35]. In addition, the hybridization of the In and Se atomic orbitals leads to electron effective masses in the layer plane that are relatively small [34], giving rise to a high electron

mobility at room temperature ( $> 0.1 \text{ m}^2/\text{Vs}$ ) and at liquid-helium temperature ( $> 1 \text{ m}^2/\text{Vs}$ ) [35], considerably higher than for the transition metal dichalcogenides [36].

Although advances have been achieved using mechanically exfoliated films of two-dimensional (2D)  $\text{In}_x\text{Se}_y$  with different polytypes and stoichiometries, the scalable synthesis of layers and heterostructures is still in its infancy. Growth by CVD and PVT has been explored only recently, with some success in producing specific polytypes of  $\text{In}_2\text{Se}_3$  [22–24,26,27]. Different phases of InSe have also been produced by various techniques, such as pulsed laser deposition [37], atomic layer deposition [38] and molecular beam epitaxy [39,40]. Although these results are encouraging, the stoichiometry and polytype phase grown on specific substrates are generally difficult to predict and control; furthermore, different polytypes can coexist within the same structure. Addressing these challenges represents an important step towards the scalable production of high-quality materials and functional devices, thus overcoming the reliance on exfoliated crystals.

Here, we demonstrate the epitaxial growth by PVT on  $\epsilon$ -GaSe substrates of large-area ( $> 10^3 \mu\text{m}^2$ )  $\text{In}_x\text{Se}_y$  layers with a stoichiometry and phase that can be controlled by the temperature within the PVT furnace, see Figure 1. The cleaved surface of  $\epsilon$ -GaSe with its low density of dangling bonds enables the growth of uniform, large-area crystals of  $\gamma$ -InSe, and  $\alpha$ ,  $\beta$  and  $\gamma$  phases of  $\text{In}_2\text{Se}_3$ , despite the large lattice mismatch (between 6% and 47%) with the  $\epsilon$ -GaSe-substrate (in-plane lattice constant  $3.755 \text{ \AA}$ ). We show that high-quality epilayers with well-defined vibrational and optical properties can also be grown on thin exfoliated flakes of  $\epsilon$ -GaSe transferred onto a supporting  $\text{SiO}_2/\text{Si}$ -substrate. In particular, the different polytypes which we have grown exhibit bright photoluminescence (PL) emissions at room temperature covering a wide range from 1.3 eV for  $\gamma$ -InSe to 2 eV for  $\gamma$ - $\text{In}_2\text{Se}_3$ . The wide choice of potential energy band

alignments between the  $\text{In}_x\text{Se}_y$  layers and also with respect to  $\epsilon$ -GaSe substrate are well suited to exploitation in electronics and optoelectronics.

## Results and discussion

The indium selenide layers reported here were grown on the cleaved surface of  $\epsilon$ -GaSe crystals by PVT. Details of the growth procedure are provided in the Methods section. The as-grown layers (Figure 2a and 3) have very different morphologies compared to those grown on  $\text{SiO}_2/\text{Si}$  (Figure 2b) [26] and have coverage over larger areas ( $> 10^3 \mu\text{m}^2$ ). The thinnest films that form on  $\epsilon$ -GaSe have a measured thickness,  $t \approx 4$  nm. Their regular triangular shape is strikingly distinct from our previous PVT-grown layers on  $\text{SiO}_2/\text{Si}$  substrates which were near-circular, slightly faceted films (Figure 2b) with lateral size of up to  $\sim 15 \times 15 \mu\text{m}^2$  and layer thickness down to 2.8 nm [26]. The AFM images in Figs. 2 and 3 suggest a common orientation and preferential alignment relative to the in-plane lattice vectors of the  $\epsilon$ -GaSe hexagonal lattice. This is confirmed in the large area optical micrograph in Fig 3a where the common alignment of triangular islands is clearly seen over a length scale  $\sim 100 \mu\text{m}$ ; this implies that the lattice vectors of the grown layer and the substrate are either aligned, or misaligned by  $30^\circ$ ; other misalignment angles would lead to multiple island orientations.

The chemical composition of the  $\text{In}_x\text{Se}_y$  layers grown on  $\epsilon$ -GaSe was assessed by electron dispersive X-ray (EDX) and X-ray photoelectron spectroscopy (XPS). Analysis of the EDX (Figure 3d and Supporting Information S1) and XPS spectra (Supporting Information S2) reveal a stoichiometric composition  $[\text{In}]:[\text{Se}] = 2:3$ , consistent with the formation of  $\text{In}_2\text{Se}_3$ . Identifying the specific crystalline phase of the  $\text{In}_2\text{Se}_3$  layers is generally difficult: different phases ( $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ , and  $\kappa$ ) may co-exist and some may share similar properties [30]. In particular, whereas the

crystal structures of  $\gamma$ - and  $\delta$ - $\text{In}_2\text{Se}_3$  are hexagonal and trigonal respectively, the rhombohedral crystal structures of  $\alpha$ - and  $\beta$ - $\text{In}_2\text{Se}_3$  phases are very similar to each other [41].

In general, Raman spectroscopy can help identify the crystalline phase of  $\text{In}_2\text{Se}_3$  due to the presence of distinct vibrational modes for the different phases [41,42]. However, in our case, due to the high background optical signal from the bulk  $\epsilon$ -GaSe substrate (thickness  $\sim 1$  mm), we were unable to detect distinct Raman modes from the thin  $\text{In}_2\text{Se}_3$  layers. In order to identify different crystalline phases, we have adopted a different approach to growth and have investigated the growth on thin  $\epsilon$ -GaSe exfoliated flakes (thickness ranging from 10 nm to 200 nm) on a  $\text{SiO}_2/\text{Si}$  substrate. The Raman background signal from these substrates is sufficiently weak (see below) to identify the phases of the grown  $\text{In}_x\text{Se}_y$  materials.

Figure 4a shows images of the growth of  $\text{In}_x\text{Se}_y$  on an  $\epsilon$ -GaSe flake. Interestingly, we find that growth occurs exclusively on the  $\epsilon$ -GaSe flakes with no deposition on the surrounding exposed  $\text{SiO}_2/\text{Si}$  substrate (Figure 4a). Figure 4b shows EDX elemental maps of indium selenide layers grown on an exfoliated  $\epsilon$ -GaSe flake at a substrate temperature,  $T_s = 560 \pm 10$  °C. The EDX analysis for this flake confirmed that the stoichiometric composition of the grown layers is  $\text{In}_2\text{Se}_3$  (see Supporting Information S3). A typical room temperature ( $T = 300$  K) micro-Raman spectrum of the  $\text{In}_2\text{Se}_3$  layers is shown in Figure 4c. The Raman modes are centred at  $\sim 105, 159, 182, 187$  and  $203 \text{ cm}^{-1}$  corresponding to the  $A_1$ -modes ( $105, 159, 182$  and  $203 \text{ cm}^{-1}$ ) and  $E_g$ -mode ( $187 \text{ cm}^{-1}$ ) of  $\alpha$ - $\text{In}_2\text{Se}_3$  [43]. A colour plot of the intensity of the Raman peaks observed in this  $\alpha$ - $\text{In}_2\text{Se}_3$  layer (inset of Figure 4c) indicates that the  $\alpha$ -phase does not coexist with other crystalline phases of  $\text{In}_2\text{Se}_3$ . In contrast, for the case of  $\text{In}_2\text{Se}_3$  layers grown on a  $\text{SiO}_2/\text{Si}$  substrate at a similar substrate position and temperature in the furnace during previous growth runs [26], we find that the Raman peaks are centred at  $\sim 110, 175$ , and  $205 \text{ cm}^{-1}$ , corresponding to the

intralayer vibrational  $A_1$ -modes (110 and 205  $\text{cm}^{-1}$ ) and the  $E_g$ -mode (175  $\text{cm}^{-1}$ ) of  $\beta\text{-In}_2\text{Se}_3$  [26,27].

Due to the temperature gradient within the tube furnace, we can grow different phases and stoichiometries of indium selenide during a single growth run depending on the position of each substrate within the quartz tube (Figure 1). We have grown four different types of indium selenide in this way including the layered phases  $\gamma\text{-InSe}$ ,  $\alpha\text{-In}_2\text{Se}_3$ ,  $\beta\text{-In}_2\text{Se}_3$ , and also  $\gamma\text{-In}_2\text{Se}_3$  which has a three dimensional crystal structure (see Figure 1e). In common with Fig. 4, for all of these phases we observe that growth occurs exclusively on the  $\epsilon\text{-GaSe}$  flakes and no material is deposited on the exposed  $\text{SiO}_2$  surface. The four different indium selenide phases were grown on exfoliated flakes of  $\epsilon\text{-GaSe}$  at different substrate temperatures,  $T_s$ , ranging between 500 °C and 580 °C (corresponding to 15 cm to 4 cm from the source material in our PVT furnace). The appearance of these phases in the observed sequence of decreasing temperatures is well matched with the temperature range over which they have been predicted to be stable in the phase diagram for the growth of  $\text{In}_x\text{Se}_y$  reported in ref [30].

Our as-grown  $\text{In}_x\text{Se}_y$  layers are chemically stable and optically active in air at room temperature over periods of several months. Distinct Raman modes are identified for the different phases of  $\text{In}_x\text{Se}_y$  (Figure 5a). The Raman maps in Figure 5b confirm that each crystalline phase is pure, with no mixing of phases. For  $\gamma\text{-InSe}$ , the Raman peaks are centred at  $\sim 117$ , 179, and 228  $\text{cm}^{-1}$ , corresponding to the intralayer vibrational  $A_1$ -modes (117 and 228  $\text{cm}^{-1}$ ) and the  $E_g$ -mode (179  $\text{cm}^{-1}$ ), previously identified in ref. [33]. The Raman modes of  $\alpha\text{-In}_2\text{Se}_3$  and  $\beta\text{-In}_2\text{Se}_3$  phases are described earlier in this section. For  $\gamma\text{-In}_2\text{Se}_3$  layers, the Raman peaks are centred at 152, 205, 221 and 230  $\text{cm}^{-1}$  and agree well with previously reported values for bulk  $\gamma\text{-In}_2\text{Se}_3$  [42,44]. The full width at half maximum (FWHM) of the main Raman mode in  $\gamma\text{-InSe}$

(FWHM  $\approx 3 \text{ cm}^{-1}$ ),  $\alpha\text{-In}_2\text{Se}_3$  (FWHM  $\approx 4 \text{ cm}^{-1}$ ) and  $\gamma\text{-In}_2\text{Se}_3$  (FWHM  $\approx 9 \text{ cm}^{-1}$ ) are significantly narrower than for  $\beta\text{-In}_2\text{Se}_3$  (FWHM  $\approx 16 \text{ cm}^{-1}$ ), see Figure 5a.

Whereas the growth by PVT of 2D indium selenide layers has been demonstrated only recently for  $\alpha\text{-In}_2\text{Se}_3$  [22,24] and  $\beta\text{-In}_2\text{Se}_3$  [26,27], the epitaxial growth of  $\gamma\text{-InSe}$  and  $\gamma\text{-In}_2\text{Se}_3$  has proven more difficult to achieve. There have been recent reports of the growth of  $\gamma\text{-InSe}$ , a material of particular interest due to its attractive optical and electrical properties, using pulsed layer deposition (PLD) and atomic layer deposition (ALD). A comparison of our results shows similar Raman peak positions and widths for material grown by PLD [37] and the results shown here; however, the Raman peaks for the material grown by ALD [38] are much broader and their position is closer to that expected for  $\beta\text{-In}_2\text{Se}_3$  [27].

The room temperature ( $T = 300 \text{ K}$ ) and low temperature ( $T = 10 \text{ K}$ ) normalized photoluminescence (PL) spectra of as-grown  $\gamma\text{-InSe}$ ,  $\alpha\text{-In}_2\text{Se}_3$ ,  $\beta\text{-In}_2\text{Se}_3$  and  $\gamma\text{-In}_2\text{Se}_3$  layers with thickness  $t > 20 \text{ nm}$  are compared in Figure 6a. For  $\gamma\text{-InSe}$ , the room temperature PL emission is centred at an energy  $E = 1.26 \text{ eV}$  and has a FWHM of  $\sim 80 \text{ meV}$ , similar to that measured previously for our bulk crystals grown by the Bridgman-method [33,45]. Similarly, the room temperature PL emission of as-grown  $\alpha\text{-In}_2\text{Se}_3$  has a peak at  $E = 1.41 \text{ eV}$ , as measured for our bulk Bridgman-grown crystals. The PL emission of  $\alpha\text{-In}_2\text{Se}_3$  is narrower (FWHM  $\approx 140 \text{ meV}$ ) and peaked at slightly lower energy than for as-grown  $\beta\text{-In}_2\text{Se}_3$  ( $E = 1.43 \text{ eV}$  and FWHM  $\approx 170 \text{ meV}$ ). The room temperature PL spectrum of  $\gamma\text{-In}_2\text{Se}_3$  is peaked at  $E = 1.95 \text{ eV}$  and shows three much weaker bands at lower energies ( $E = 1.44 \text{ eV}$ ,  $1.56 \text{ eV}$  and  $1.70 \text{ eV}$ ). We attribute the presence of these weaker bands to the recombination of carriers at localized states within the bandgap. For all the crystals, the low temperature ( $T = 10 \text{ K}$ ) PL emission peaks are centred at higher energies compared to those at  $T = 300 \text{ K}$ , with the largest thermal shift ( $\sim 200 \text{ meV}$ ) observed in  $\gamma\text{-In}_2\text{Se}_3$ .



The energy shift is accompanied by a monotonic increase of the PL intensity by up to a factor 200 when the temperature is decreased from 300K to 10K. These PL results confirm that our epitaxially grown layered phases are comparable in quality to bulk crystals grown by the Bridgman-method [33,45] and material grown by PLD [37] highlighting the promise of this approach to growing metal chalcogenides.

The electronic and vibrational properties of the as-grown  $\text{In}_x\text{Se}_y$  layers can be influenced by the presence of crystal defects, such as In- and Se-vacancies [30]. Vacancies can modify atomic orbitals and band gap energies due to ordering and bond relaxation [46]. These defects can also influence the position and linewidth of the Raman and PL lines due to disorder, lattice distortion and phonon scattering around the defects. As shown in Figure 5, the Raman modes for  $\beta\text{-In}_2\text{Se}_3$  and  $\gamma\text{-In}_2\text{Se}_3$  tend to be broader than for  $\alpha\text{-In}_2\text{Se}_3$  and  $\gamma\text{-InSe}$ , suggesting that the latter phases have better crystalline quality. In particular, the low temperature PL spectra of the  $\beta\text{-In}_2\text{Se}_3$  layers reveal a dominant carrier recombination from defects and/or impurity levels that is weakly dependent on the layer thickness (Supplementary Information S4). This behaviour contrasts with that of the other phases ( $\gamma\text{-InSe}$ ,  $\alpha\text{-In}_2\text{Se}_3$  and  $\gamma\text{-In}_2\text{Se}_3$ ) where narrow PL emissions are observed at low temperature due to recombination of excitons and/or carriers localized on shallow impurities (Figure 6). In particular, the narrow PL-line in  $\gamma\text{-In}_2\text{Se}_3$  reveals a structured PL spectrum, see Figure 7. The apparently ‘anomalous’ and asymmetric line-shape of the PL band can be modelled by fitting it to two ( $P = 120 \mu\text{W}$ ) or three ( $P = 1 \text{ mW}$ ) Gaussian components, as shown in Figure 7a. The high-energy line (X) is attributed to excitonic emission: it persists in the spectrum even at low power densities (Figure 7a) and at high temperatures (Figure 7b). The lower-energy tail of the spectrum is significantly reduced with respect to the X-line as the power decreases and/or the temperature increases. This behaviour is consistent with a

contribution to the spectrum from charged exciton and/or biexcitons with binding energies larger than 20 meV.

Finally, using the electron affinity for bulk  $\text{In}_x\text{Se}_y$  and  $\epsilon\text{-GaSe}$  [47,48] and the band gap energies deduced from the measured PL spectra at RT, we plot in Figure 6b the band alignments for different stoichiometries and phases. It can be seen that heterostructures based on these materials could offer several potential advantages over to existing semiconductor heterojunctions by enabling a diverse range of component layers even when the lattice mismatch is large, tuneable optical response over an extended NIR-VIS wavelength range, and a range of interesting band alignments and potential profiles.

## Conclusions

In summary, we have demonstrated that the uniform cleaved surface of the vdW crystal  $\epsilon\text{-GaSe}$  can be used as a substrate for the epitaxial growth of large-area ( $> 10^3 \mu\text{m}^2$ )  $\text{In}_x\text{Se}_y$  layers. We have successfully grown four well-defined crystalline phases of  $\text{In}_x\text{Se}_y$ . The  $\text{In}_x\text{Se}_y$  compounds have a larger unit cell than  $\epsilon\text{-GaSe}$  with an in-plane lattice mismatch ranging between 6% and 47%. The successful growth of  $\gamma\text{-InSe}$ ,  $\alpha\text{-In}_2\text{Se}_3$ ,  $\beta\text{-In}_2\text{Se}_3$  and  $\gamma\text{-In}_2\text{Se}_3$  on exfoliated  $\epsilon\text{-GaSe}$  nanolayers offers the prospect for large-area device fabrication and junction devices that exploit the distinctive optical absorption and luminescent emission of the component layers. Due to the absence of dangling bonds, different vdW crystals can be grown one upon another without any restriction on the lattice mismatch, a major obstacle with traditional all-covalent multicomponent semiconductor structures where the presence of strain relaxation and crystalline defects can quench the room temperature photoluminescence. The optical spectra and the temperature dependence indicate distinct electronic properties for the different stoichiometric

phases of indium selenide and demonstrate a wide spectral range of photoluminescence from the visible ( $\gamma$ - $\text{In}_2\text{Se}_3$ ) to the near-infrared ( $\gamma$ - $\text{InSe}$ ,  $\beta$ - $\text{In}_2\text{Se}_3$  and  $\alpha$ - $\text{In}_2\text{Se}_3$ ). In addition to different combinations of bandgaps and band alignments, the  $\text{In}_x\text{Se}_y$  polytypes and  $\epsilon$ -GaSe offer additional attractive features, including lightweight and compatibility with different substrates, well suited for a range of novel applications, including ferroelectricity in  $\alpha$ - $\text{In}_2\text{Se}_3$  [49] and high-sensitivity broad-band  $\text{In}_x\text{Se}_y/\epsilon$ -GaSe photodiodes [50].

## Methods

*Synthesis of  $\text{In}_x\text{Se}_y$  layers.* For the growth of  $\text{In}_x\text{Se}_y$  layers by physical vapour deposition, we used Bridgman-grown high-quality  $\gamma$ -polytype InSe crystals ground into powder and placed in a tube furnace. The tube furnace comprised a 45 cm long Carbolite furnace, 1 m long both open ended quartz tube (tube diameter,  $d = 3.2$  cm), a rotary pump and an Ar flow controller. The InSe powder was heated from  $T = 25$  °C to 600 °C at a rate of 3 °C per minute and kept at 600 °C for 4 to 9 hours. An Ar flow of 150 sccm was used to provide a pressure of 1.6 mbar and to transport the vapour for deposition on a substrate, placed downstream at 4 to 15 cm away from the source material, which provides a substrate temperature range between  $T_s \approx 580$  °C to 500 °C. The system was then allowed to cool slowly to room temperature over a period of 10 hours.

*Chemical and topographic characterization.* The XPS measurements were performed using a Kratos AXIS ULTRA with a monochromatic Al  $K\alpha$  X-ray source ( $h\nu = 1486.6$  eV) operated at 10 mA emission current and 12 kV anode potential ( $P = 120$  W), and the data processing was performed using CASAXPS version 2.3.17PR1.1 software with Kratos sensitivity factors (RSFs) to determine atomic % values from the peak areas. The electron collection spot size is  $\sim 700 \times 300 \mu\text{m}^2$ . All XPS binding energies were calibrated with respect to the C 1s peak at a binding

energy of 284.8 eV. The scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) analysis were performed at 20kV in high vacuum ( $\sim 10^{-6}$  mbar) with an FEI Quanta 650 ESEM equipped with an Oxford Instruments X-Max<sup>N</sup> 150 EDX detector. The topography images were acquired by an Asylum Research MFP-3D atomic force microscope (AFM) in tapping mode under ambient conditions.

*Optical studies.* The experimental set-up for  $\mu$ PL and Raman measurements comprised a He-Ne laser ( $\lambda = 633$  nm) and a frequency-doubled Nd:YVO<sub>4</sub> laser ( $\lambda = 532$  nm), an XY linear positioning stage or a cold-finger cryostat, an optical confocal microscope system, a spectrometer with 150 and 1200 groves/mm gratings, equipped with a charge-coupled device and a liquid-nitrogen cooled (InGa)As array photodetector. For the room temperature studies, the laser beam was focused to a diameter  $d \approx 1$   $\mu$ m using a 100 $\times$  objective and the  $\mu$ PL spectra were measured at low power ( $P \sim 0.1$  mW) to avoid lattice heating. For the low  $T$  studies the laser beam ( $P$  up to 12 mW) was focused through the window of an optical cryostat to a diameter  $d \approx 3$   $\mu$ m using a 50 $\times$  objective.

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### **Supplementary data**

Supporting Information available: EDX and XPS spectra of  $\text{In}_2\text{Se}_3$  films grown on a bulk  $\epsilon$ -GaSe substrate; EDX maps and spectrum of  $\text{In}_2\text{Se}_3$  grown on an exfoliated  $\epsilon$ -GaSe flake; and low temperature PL spectra of  $\beta$ - $\text{In}_2\text{Se}_3$  layers grown on a  $\text{SiO}_2/\text{Si}$  substrate. This material is available free of charge via the internet at <http://iopsciences.iop.org/>. The data, including images and spectroscopic measurements, on which this manuscript was based is available as an online resource with digital object identifier 10.17639/nott.xx.

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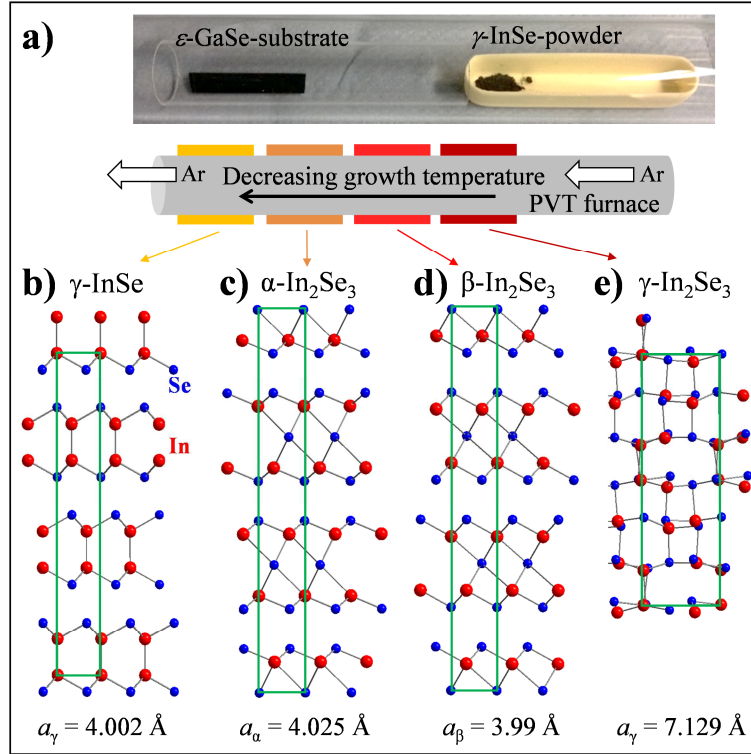
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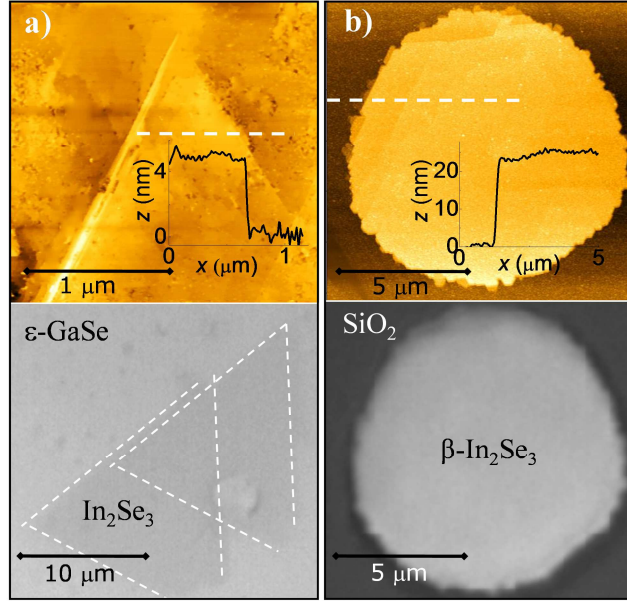
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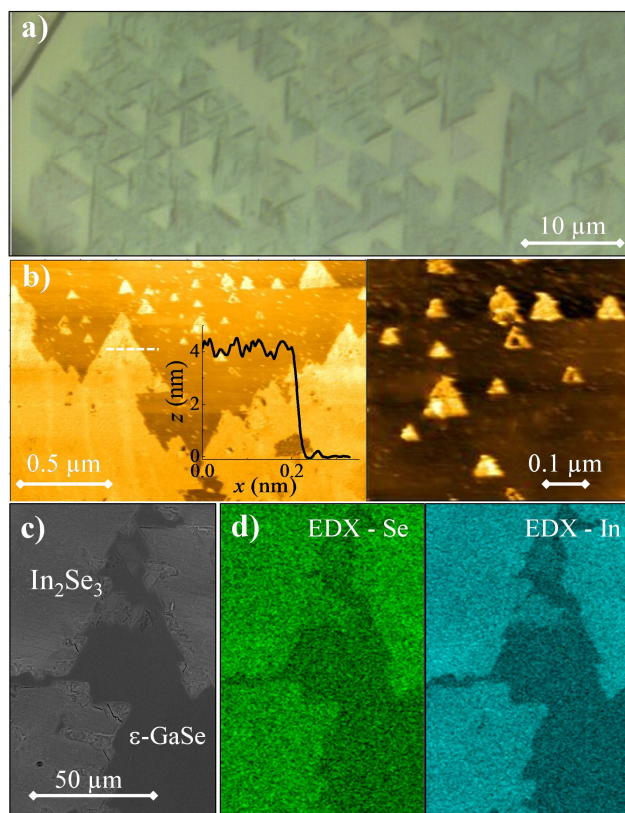
## Figures



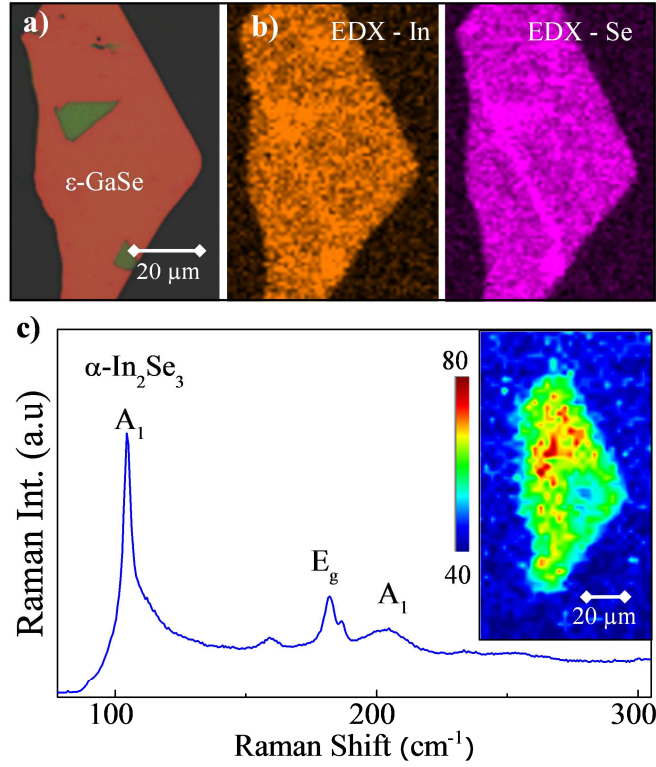
**Figure 1:** **a)** Image and schematic diagram of the quartz tube for the PVT growth of  $\text{In}_x\text{Se}_y$  on  $\epsilon$ -GaSe. The temperature gradient in the quartz tube enables the growth of different phases of  $\text{In}_x\text{Se}_y$ . **(b-c-d-e)** Side view of the crystal lattice and unit cell of  $\gamma$ -InSe (b),  $\alpha$ -In<sub>2</sub>Se<sub>3</sub> (c),  $\beta$ -In<sub>2</sub>Se<sub>3</sub> (d) and  $\gamma$ -In<sub>2</sub>Se<sub>3</sub> (e). The in-plane lattice constants are also shown for each phase.  $\gamma$ -InSe has rhombohedral crystal structure and the primitive unit cell contains three layers, each consisting of four closely-packed, covalently bonded, atomic sheets in the sequence Se-In-In-Se [33]. The  $\alpha$ -In<sub>2</sub>Se<sub>3</sub> and  $\beta$ -In<sub>2</sub>Se<sub>3</sub> phases have the same rhombohedral crystal structure and the primitive unit cell contains three layers, each consisting of five covalently bonded, monoatomic sheets in the sequence Se-In-Se-In-Se. For  $\alpha$ -In<sub>2</sub>Se<sub>3</sub> the outer Se-atoms in each vdW layer are aligned, whereas in  $\beta$ -In<sub>2</sub>Se<sub>3</sub> they are located into the interstitial sites of the Se-atoms in the neighbouring layers [41]. The  $\gamma$ -In<sub>2</sub>Se<sub>3</sub> phase has hexagonal crystal structure with distorted wurtzite-type-like atomic arrangement [51].



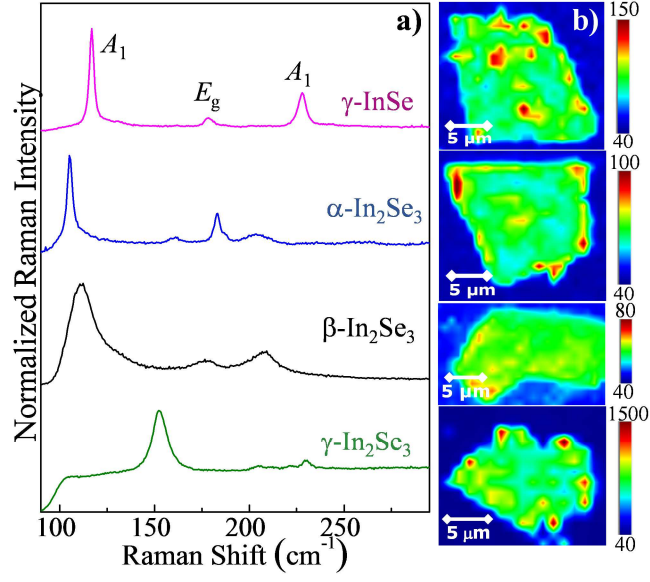
**Figure 2. (a-b)** Topographic AFM image and z-profile (top), and optical micrographs (bottom) of In<sub>2</sub>Se<sub>3</sub> layers grown on (a) the cleaved surface of a bulk ε-GaSe substrate and (b) a SiO<sub>2</sub>/Si substrate. The AFM z-profiles were obtained along the dashed lines shown in the AFM images.



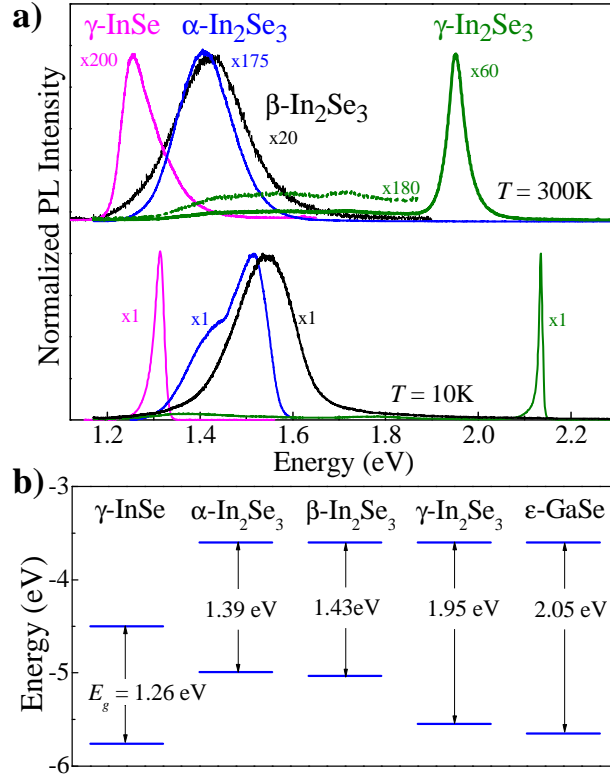
**Figure 3.** (a) Optical micrograph, (b) topographic AFM images and z-profile, (c) backscattered electron SEM image and (d) EDX elemental maps of In<sub>2</sub>Se<sub>3</sub> grown on the cleaved surface of a bulk ε-GaSe substrate. The AFM z-profile was obtained along the dashed line shown in the AFM image.



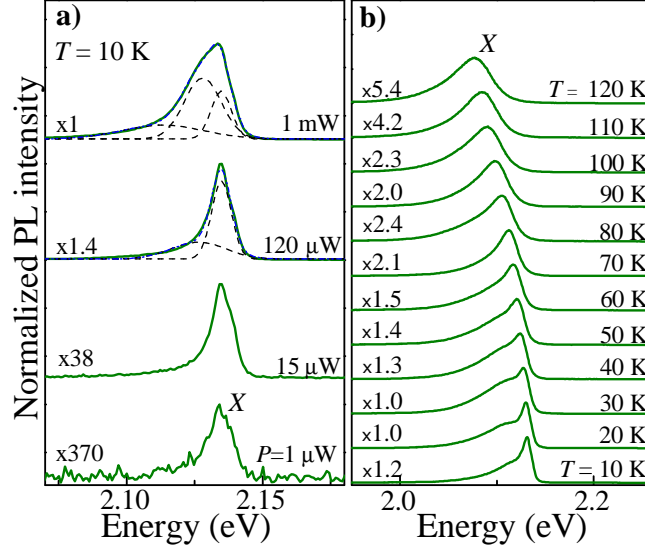
**Figure 4.** (a) Optical micrograph of an exfoliated  $\epsilon$ -GaSe flake on a  $\text{SiO}_2/\text{Si}$  substrate before the growth. (b) EDX elemental maps and (c) Raman spectrum and map for  $\alpha$ - $\text{In}_2\text{Se}_3$  grown on the exfoliated  $\epsilon$ -GaSe flake shown in part (a). The Raman map was obtained by plotting the micro-Raman intensity at 105  $\text{cm}^{-1}$  corresponding to the main  $A_1$ -mode of  $\alpha$ - $\text{In}_2\text{Se}_3$  ( $\lambda = 633 \text{ nm}$  and  $P = 0.1 \text{ mW}$ ).



**Figure 5:** (a) Room temperature ( $T = 300$  K) Raman spectra and (b) maps for In<sub>x</sub>Se<sub>y</sub> layers grown on exfoliated  $\epsilon$ -GaSe flakes. The Raman maps were obtained by plotting the Raman intensity of the main  $A_1$ -mode in each In<sub>x</sub>Se<sub>y</sub> layer ( $\lambda = 633$  nm and  $P = 0.1$  mW).



**Figure 6.** (a) Room temperature ( $T = 300\text{ K}$ ) and low temperature ( $T = 10\text{ K}$ )  $\mu\text{PL}$  spectra of  $\gamma\text{-InSe}$ ,  $\alpha\text{-In}_2\text{Se}_3$ ,  $\beta\text{-In}_2\text{Se}_3$  and  $\gamma\text{-In}_2\text{Se}_3$  layers grown on exfoliated  $\epsilon\text{-GaSe}$  flakes. All optical measurements were conducted on films with thickness  $t > 20\text{ nm}$ . Layers of thickness  $t < 20\text{ nm}$  are required to observe a measurable increase of the direct band gap with decreasing  $t$ . (b) Schematic showing the band alignments [47,48] of the materials which can be grown on  $\epsilon\text{-GaSe}$ ; the bandgaps of the different phases of  $\text{In}_x\text{Se}_y$  which we have grown are very close to the literature values.



**Figure 7.**  $\mu$ PL spectra of  $\gamma$ - $\text{In}_2\text{Se}_3$  layers grown on exfoliated  $\varepsilon$ -GaSe flakes for **(a)** different excitation laser powers  $P$  ( $T = 10\text{K}$ ,  $\lambda = 532\text{ nm}$ ) and **(b)** different temperatures ( $\lambda = 532\text{ nm}$  and  $P = 3\text{ mW}$ ). The dashed-curves in (a) are the multi-peak Gaussian fits to the data.