Formation of β-In₂Se₃ Layers Grown via Selenium Passivation of InP(111)B Substrate

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ABSTRACT

Indium selenide, In₂Se₃, has recently attracted growing interest due to its novel properties, including room temperature ferroelectricity, outstanding photoresponsivity, and exotic in-plane ferroelectricity, which open up new regimes for next generation electronics. In₂Se₃ also provides the important advantage of tuning the electrical properties of ultra-thin layers with an external electrical and magnetic field, making it a potential platform to study novel two-dimensional physics. Yet, In₂Se₃ has many different polymorphs, and it has been challenging to synthesize single-phase material, especially using scalable growth methods, as needed for technological applications. In this paper, we use aberration-corrected scanning transmission electron microscopy to characterize the microstructure of twin-free single-phase ultra-thin layers of β -In₂Se₃, prepared by a unique molecular beam epitaxy approach. We emphasize features of the In₂Se₃ layer and In₂Se₃/InP interface which provide evidence for understanding the growth mechanism of the single-phase In₂Se₃. This novel approach for forming high-quality twin-free single phase two-dimensional crystals on InP substrates is likely to be applicable to other technologically important substrates.

Two-dimensional (2D) van der Waals (vdW) materials have garnered much interest over the past decade because of the large variety of 2D compounds having potential applications for next generation electronic and optoelectronic devices^{1,2}. The class of 2D vdW materials began to evolve two decades ago, with the discovery of graphene^{3,4} which is a semimetal. Since then, the list of 2D materials has been rapidly expanding, and includes insulators such as hexagonal boron nitride (h-BN), transition metal dichalcogenides (TMDCs), such as MoS₂, materials from group III-VI family (e.g. In₂Se₃, GaSe), and the black phosphorus family (e.g. P, SnS)⁵. Unlike 3D materials, it is easy to engineer the band gap using quantum confinement simply by changing the number of layers in the 2D material⁶. Since these compounds are layered with strong in-plane covalent bonds, while planar layers are held together by weak out-of-plane vdW forces, the layers are easily separable via mechanical exfoliation and can be stacked up with different 2D materials to create novel heterostructures⁵. Either by quantum confinement or by making heterostructures, many interesting physics topics can be studied, for example, superconductivity, magnetism, and charge density waves. Furthermore, the properties the 2D material can be changed by applying an external electrical and magnetic field so that the material can be tuned into a different phase. For example, experiments showed that TiSe₂, a semimetal, can be tuned into a superconducting phase by applying an external electric field⁷.

Indium selenide, In_xSe_y has recently attracted renewed interest not only due to applications in thermoelectric devices to harness green energy⁸ but also owing to some of its novel properties such as room temperature ferroelectricity in the α -In₂Se₃ phase⁹, outstanding photoresponsivity in β -In₂Se₃¹⁰, and exotic in-plane ferroelectricity in β '-In₂Se₃^{11,12}. Thus, In₂Se₃ has potential applications in energy harvesting, such as solar cells and photodetectors¹⁰, as well as in electronic applications, such as ferroelectric semiconductor field effect transistors⁹ and phase change materials for data storage¹³. However, In₂Se₃ is a complex material with many different polymorphs, known as α , β , β ', γ , δ , and $\kappa^{14,15}$. Hence, it has been challenging to synthesize single-phase In₂Se₃. There are a few reports of In₂Se₃ growth using physical vapor transport (PVT)¹⁴ which limits the crystal size, while chemical vapor deposition (CVD)¹⁶ and metalorganic chemical vapor deposition (MOCVD)¹⁷ are employed for scalable synthesis. Yet the overall quality of the material is not good. Among all scalable crystal growth methods, molecular beam epitaxy (MBE) is the preferred technique since it can provide high crystalline quality and controllability of thickness down to the few Ångstrom level. However, there is only one report of In₂Se₃ grown on sapphire substrates using MBE¹⁸. Thus, epitaxial growth of scalable In₂Se₃ is still in its infancy. Hence, it is important to develop a scalable growth method that provides high quality and single-phase In₂Se₃, especially on substrates that are currently in use for technological applications.

In this study, we have used aberration-corrected scanning transmission electron microscopy (STEM) to conduct an in-depth analysis of twin-free single phase β -In₂Se₃ as-grown on smooth non-vicinal InP(111)B substrate using a non-conventional MBE growth method developed in our laboratory¹⁹. Based on this analysis, we also discuss the possible growth mechanism that resulted in the untwinned nature of the material. Understanding and controlling the mechanism at play should enable application of the same approach to growth of other heteroepitaxial structures involving layered, vdW materials on 3D crystalline substrates. It may also enable the possibility of stabilizing the In₂Se₃ α -phase which is of important technological interest owing to its ferroelectric properties.

Previously, we have presented extensive evidence for the twin-free nature of In₂Se₃ grown on smooth non-vicinal InP(111)B substrates using high resolution X-ray diffraction (HR-XRD) measurements¹⁹ which was then used as a template to achieve twin-free Bi_2Se_3 . In this paper, we characterize the structural properties of this twin-free Bi_2Se_3 and In_2Se_3 using cross-sectional STEM with special emphasis on features of the In_2Se_3 layer and its interfaces, which provide the evidence needed to understand the growth mechanism of the twin-free In_2Se_3 layer grown by the unique non-conventional technique¹⁹.

A cross-sectional high -angle annular -dark-field (HAADF) STEM image of the sample, which consists of two distinct layers, Bi₂Se₃ and In₂Se₃, with thicknesses of 65 nm and 7 nm, respectively, is shown in Figure 1a. The Bi₂Se₃ layer displays a defect-free nature without antiphase domains and no indication of twin boundaries or dislocations. Further cross-sectional HAADF-STEM images taken at widely separated locations on the same sample, confirm the excellent crystal quality (see Supplementary Material). In contrast, reports of twin-free Bi₂Se₃ grown on rough non-vicinal InP(111)B substrates have previously shown the presence of antiphase domains due to variations in substrate height²⁰ and Bi₂Se₃ grown on flat InP(111)B has shown twin boundaries as well as dislocations²¹. Figure 1b shows well-ordered Bi₂Se₃ quintuple layers with an overlay of an atomistic model (Figure 1c), which confirms the presence of the rhombohedral crystal structure with the space group $R\bar{3}m$. Additional HAADF-STEM images focusing on the In₂Se₃ layer of the sample are shown in Figures 1d and 2a again depicting a wellordered highly crystalline material which seems free of any structural defects.

Previously, we found by using HR-XRD¹⁹ that these In₂Se₃ layers had a rhombohedral crystal structure with the space group $R\overline{3}m$. It is well known that In₂Se₃ with this space group has two principal polymorphs, namely the α and β phases^{15,14,22}. Since the lattice parameters of α -In₂Se₃ and β -In₂Se₃ are very similar, using HR-XRD, we were unable to determine the identity of the In₂Se₃ phase i.e., whether it was α , β or a mixture of the two. Attempts to determine the In₂Se₃

phase using Raman spectroscopy and photoluminescence spectroscopy also failed because the In₂Se₃ layer was too thin and the background signal from the InP wafer completely masked the signal from the layer.



Figure 1. Cross-sectional HAADF-STEM images of Bi₂Se₃ (65-nm thick) grown on In₂Se₃/InP(111)B. (a) Highly ordered Bi₂Se₃ layer having an abrupt interface with the In₂Se₃ layer; (b) Enlarged image of Bi₂Se₃ layer with overlay of the atomistic model of Bi₂Se₃ quintuple layer. (c) Atomic model of B₂Se₃ quintuple layer consisting of 5 atoms. (d) Cross-sectional HAADF-STEM image showing well-ordered In₂Se₃ layer and interfaces with Bi₂Se₃ and InP.

Using cross-sectional HAADF-STEM images, as shown in Figure 2a, we established that the In₂Se₃ layer consists of a single phase. Furthermore, by using atomic-resolution HAADF-STEM images, such as shown in Figure 2b, and by overlaying atomistic models of α -In₂Se₃ and β -In₂Se₃ (see Figure 2c), we can conclude that the In₂Se₃ layer grown here is the β phase. The different phases of In₂Se₃ which can be formed readily, make it very difficult to achieve single phase material²³. However, these results indicate that the In₂Se₃ layers grown using our newly developed technique¹⁹ is capable of forming single-phase β -In₂Se₃.

Figure 2d shows an enlarged image of Figure 2a highlighting the interface between the In₂Se₃ and Bi₂Se₃ layers. In the image, we see evidence for indium diffusion into the Bi₂Se₃ layer as well as the formation of a single crystalline quintuple layer (1QL) with a mixture of both In₂Se₃ and Bi₂Se₃. In this intermixed layer, the 5-atom quintuple chain highlighted inside the red box is similar in size and shade to the In₂Se₃ region whereas those in the blue box have larger atoms at the In atomic column positions, which indicates these are Bi atoms that form Bi₂Se₃ layer above then makes an abrupt interface with this layer. We do not observe any interfacial layer of poor crystalline quality, neither diatomic steps nor Bi₂Se₄ clusters as seen at the interface that forms when Bi₂Se₃ is grown on flat InP or on rough non-vicinal InP substrates, as reported elsewhere^{20,21}.



Figure 2. (a) Cross-sectional HAADF-STEM image of the sample taken at higher magnification than the image in Figure 1(d) showing the high crystallinity of β phase In₂Se₃ layer. (b) Enlarged image showing the atomic resolution of the β phase In₂Se₃ layer. An overlay of indium atoms in α and β phases of In₂Se₃ quintuple layer with indium atoms in InP lattice are also shown. Atomic model of InP(111)B lattice is shown next to the β -In₂Se₃ atomic model. (c) Atomic model of α and β phases of In₂Se₃ quintuple layer which consists of 5 atoms. (d) Enlarged image of Figure 2(a) showing In diffusion into Bi₂Se₃ layer at Bi₂Se₃/In₂Se₃ interface. The quintuple layer highlighted in the red box shows 5-atom chain In₂Se₃ whereas 5-atom chain Bi₂Se₃ is shown in the blue box. Orange and yellow lines are for guiding the eyes.

The interface between the In₂Se₃ layer and the InP substrate has several notable features. As visible in the HAADF-STEM image shown in Figure 1a and the higher magnification image, Figure 1d, the interface has dark regions alongside the clear and sharp interface, suggesting the presence of some possibly defective regions. A significant contrast feature visible in some higher magnification cross-sectional bright field (BF) STEM images (Figures 3a and b) of the sample suggests significant Se diffusion into the substrate beyond the In₂Se₃/InP interface. The presence of excess Se, as evident from the contrast difference near the interface, does not however alter the crystal structure of the InP substrate, which remains zinc blende. This observation suggests that the In atoms remain fixed in their lattice sites during the In₂Se₃ formation process while Se diffuses into the substrate, displacing P. Then, with the special annealing step during the growth process, the Se atoms re-arrange to form In₂Se₃ quintuple layers. Figure 3c is a schematic illustrating the In₂Se₃ formation steps during oxide desorption from the InP(111)B substrate surface in the unique MBE-based growth approach used here¹⁹.



Progression of oxide desorption with time

Figure 3. (a) Cross-sectional BF-STEM images highlighting diffusion of Se atoms into InP substrate during the In₂Se₃ growth process. (b) Cross-sectional BF-STEM image at higher magnification showing that the presence of excess Se atoms does not alter the crystal structure of the InP, which remains zinc blende. (c) Simple schematic showing Se atoms diffuse into InP substrate while P atoms diffuse out during the oxide desorption process and the formation of In₂Se₃ as the oxide desorption process is completed.

If this proposed mechanism, in which In atoms remain "anchored" through the process, is valid, then the preference to form the single β -In₂Se₃ phase over the α -In₂Se₃ phase can be understood. In Figure 2b, we have overlayed the In atoms in the α and β phases of In₂Se₃ quintuple layers on top of the In atoms in the InP(111)B lattice. We observe that the 4 In atoms in the red oblique square of the β -In₂Se₃ are well superimposed on top of the In atoms in the InP lattice whereas only the top two In atoms out of the four In atoms are superimposed in the red oblique square of the α -In₂Se₃, while the bottom two are shifted away from the In atoms in the InP lattice. This careful observation also leads to the conclusion that the In atoms remain anchored during the In₂Se₃ formation process Based on these observations of cross-section STEM images as discussed above, the proposed growth mechanism for the formation of the twin-free and single-phase β -In₂Se₃ is illustrated using a cartoon atomic model in Figure 4 where the transformation of the 3D InP lattice into 2D β -In₂Se₃, via an intermediate Se substituted zinc blende structure, is apparent in this growth process.



Figure 4. Proposed growth mechanism demonstrated using a cartoon atomic model for the formation of untwinned single-phase In_2Se_3 layer based on the STEM image analysis. Orange arrows and green arrows represent desorption of P atoms from the substrate, and diffusion of Se atoms into the substrate, respectively.

In Summary, we have shown that high quality In₂Se₃ and Bi₂Se₃ crystalline layers that are fully twin-free and largely free of defects, can be achieved. STEM observations also show that the sample consists primarily of single phase β -In₂Se₃. Close observation of the InP/In₂Se₃ interface provides evidence for an exchange mechanism in which Se first substitutes for P in the zinc blende InP, followed by a crystal structure transformation to the rhombohedral In₂Se₃ structure. This result implies that In atoms are not mobile during the transformation, thus resulting in twin-free In₂Se₃. This unique growth mechanism for In₂Se₃ also results in pure β -phase In₂Se₃. Controlling the mechanism at play would enable the application of this approach to other heteroepitaxial structures involving layered, vdW materials on 3D crystalline substrates. It may also enable the possibility of stabilizing the different phases of In₂Se₃ which are of important technological interest owing to their exotic properties.

DATA AVAILABILITY

All data are available from the corresponding author upon reasonable request.

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AUTHOR CONTRIBUTIONS

K.S.W. conceived and executed the research and MBE growth. K.S.W. and M.C.T. wrote and reviewed the manuscript. M.R.M and D.J.S were responsible for the relevant sample preparation and STEM imaging and reviewed the manuscript. All authors contributed to interpretation of the data and discussions.

NOTES

The authors declare no competing interests.

ACKNOWLEDGMENTS

This work was supported by NSF grant number HRD-2112550 (NSF CREST Center IDEALS). Partial support is also acknowledged from NSF grant number DMR-2011738 (PAQM). The authors acknowledge use of facilities in the John M. Cowley Center for High Resolution Electron Microscopy at Arizona State University, supported in part by NNCI-ECCS-1542160.

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Electronic Supplementary Information

1. Materials and Instrumentation

Samples were grown on smooth, non-vicinal Fe-doped InP(111)B \pm 0.5° substrates with a phosphorus-terminated surface. A Riber 2300P molecular beam epitaxy (MBE) system with a base pressure of $5x10^{11}$ Torr was used to grow the material. The system was equipped with *in situ* reflection high-energy electron diffraction (RHEED) to facilitate monitoring of material growth in real time. High-purity (99.9999%) bismuth (Bi) and selenium (Se) were used as source materials. The Bi and Se fluxes were provided by a RIBER dual-zone effusion cell and a RIBER valved cracker cell for corrosive materiel (VCOR), respectively. An ultra-high vacuum (UHV) nude ion gauge positioned to intercept the path of the fluxes was used to measure beam equivalent pressures (BEP).

The samples were characterized using high-angle annular-dark-field (HAADF) and brightfield (BF) scanning transmission electron microscopy (STEM) imaging using a probe-corrected JEOL ARM200F operated at 200kV. Cross-section samples suitable for TEM observation were prepared using a dual-beam Thermo Fisher Helios 5G UX gallium ion milling system, initially at 30keV with subsequent thinning at 5keV and 2keV to reduce the amount of surface damage.

2. Synthesis

A Bi₂Se₃ layer was grown on an In₂Se₃ layer, which was formed using a unique and nonconventional Se self-passivation technique developed in our group¹. The In₂Se₃ layer was formed at a substrate temperature of $T_{sub} = 505$ °C with an Se overpressure of 1×10^{-5} Torr during the oxide desorption process without an indium (In) source cell. The Bi₂Se₃ growth temperature (T_{sub}), growth rate and BEP ratio of Se to Bi were $T_{sub} = 270 \text{ °C}$, ~0.5 nm/minute and ~100:1 respectively. A 1x1 RHEED pattern was observed after Bi₂Se₃ growth with increased intensity relative to the In₂Se₃ layer. The newly developed growth procedure for the formation of the In₂Se₃ layer and the twin-free nature of In₂Se₃ as well as Bi₂Se₃, were previously discussed in detail by Wickramasinghe et al¹. The substrate temperature was measured using a thermocouple mounted behind the substrate holder. The sample analyzed here consisted of a 65-nm-thick Bi₂Se₃ layer on top of a ~ 7-nm-thick In₂Se₃ layer, both of which are twin-free¹.

3. HAADF images



Supplemental Figure 1. Cross-sectional HAADF-STEM images of Bi₂Se₃ (65-nm thick) grown on In₂Se₃/InP(111)B taken from a region several microns away from the area shown in Figure 1.a.

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