Structurally and chemically compatible BiInSe₃ substrate for topological insulator thin films

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ABSTRACT

Quality of epitaxial films strongly depends on their structural and chemical match with the substrates: The more closely they match, the better the film quality is. Topological insulators (TI) such as Bi₂Se₃ thin films are of no exception. However, there do not exist commercial substrates that match with TI films both structurally and chemically, at the level commonly available for other electronic materials. Here, we introduce BiInSe₃ bulk crystal as the best substrate for Bi₂Se₃ thin films. These films exhibit superior surface morphology, lower defect density and higher Hall mobility than those on other substrates, due to structural and chemical match provided by the BiInSe₃ substrate. BiInSe₃ substrate could accelerate the advance of TI research and applications.

KEYWORDS

topological insulator, substrate, match, epitaxy, Bi₂Se₃, BiInSe₃

1 Introduction

Over the past few years, topological insulator (TI) thin films prompted the discovery of numerous novel quantum phenomena, such as quantum anomalous Hall effect [1–3], non-conventional quantum Hall effects [4–11], axion insulator state [12–14] and quantized Faraday and Kerr rotation [15]. All these quantum effects are sensitive to disorders and require either extremely low temperatures to freeze the disorder effect or ultralow defect densities. As demonstrated before [7–10], substrate is a significant source of disorder and existing commercial substrates always lead to high level of interfacial defects due to combination of structural and chemical mismatch. Figure 1(a) shows commonly used commercial substrates and their in-plane lattice parameters in comparison with TI materials. These substrates have either entirely different crystal structures and ionic configurations (such as InP(111) and SrTiO₃(111)) or vastly different lattice parameters (such as Al₂O₃). These structural and/or chemical mismatch inevitably leads to high level of interfacial defects and residual carrier densities, making it difficult to access the quantum signatures of topological surface states. An ideal substrate for a TI film should have the same crystal structure with similar lattice parameter and chemical composition to the TI material.

The importance of matched substrate is well known in semiconductor devices. In general, the best substrate for any material should be the same material. For example, the best substrate for Si film should be Si substrate and the best for GaAs film should be GaAs substrate, etc. However, not every material has large enough bulk crystals that can work as substrates, and GaN, the key material for blue LED device, is a good example. Because GaN substrate does not exist, growth of GaN thin films is done on other commonly available substrates such as Al₂O₃ or SiC. However, due to significant lattice mismatch, GaN films always have high density of defects, and thick buffer layers of GaN and/or AlN are required to reduce these defects in the active region to an acceptable level [16–19]. TI films such as Bi₂Se₃ grown on commercial substrates have similar problems of high density of interfacial defects. To make matters worse, unlike GaN, interfacial defects on TI films cannot be buried because the topologically protected surface band drives these defects electronically active. Fortunately, we have previously demonstrated that chemically and structurally well matched BiInSe₃ buffer layers can drastically suppress these interfacial defects in Bi₂Se₃ thin films [7, 8]. However, this buffer layer scheme requires a time-consuming and complex fabrication process, hindering broad applications of TI materials. Here, we show that BiInSe₃ bulk crystals can negate the need for the complex buffer layer scheme and provide excellent platform for TI thin films.

2 Results and discussion

BiSe₃, In₆Se₃ and the solid solution BiInSe₃ all share the same layered hexagonal structure with the weak van der Waals bonding between quintuple layer (QL) (1 QL is approximately 1 nm thick). Owing to the large band gap of In₆Se₃ ~ 1.3 eV, compared with ~ 0.3 eV for Bi₂Se₃, the solid solution BiInSe₃ not only provides ideal structural and chemical compatibility for Bi₂Se₃ growth, but also preserves the large band gap which is prerequisite to be used as substrate.

We grew the BiInSe₃ bulk crystal substrates by a modified Bridgman method. Starting materials of Bi (99.997%, Alfa Aesar), In (99.99%, Alfa Aesar) and Se (99.999%, Alfa Aesar)
with the molar ratio of 1:1:3 were mixed together and then sealed into an evacuated conical-shaped quartz tube. The quartz tube was put into a furnace with vertical temperature gradient and held at 850 °C for 48 h, then cooled down to room temperature to get polycrystalline BiInSe3. Then the polycrystalline BiInSe3 together with the quartz tube was taken out, sealed into a larger quartz tube, then put into the same furnace and heated to 950 °C, with a subsequent slow cooling to 550 °C over 400 h, and cooled down to room temperature to get single crystal BiInSe3. The obtained single crystals exhibits a shiny ingot with sharp conical tip, as shown in Fig. 1(b). The crystal boule can be easily cleaved by a blade along the growth direction and further cleaved by Scotch tape. The cleaved fresh BiInSe3 substrate shows clean and flat surface as shown in Fig. 1(c).

We performed X-ray diffraction (XRD) measurement to check the crystal quality, the result is shown in Fig. 1(d). The sharp (00l) diffraction peaks indicate good single crystalline quality of the BiInSe3 substrates.

Surface flatness is one of the key parameters essential for high quality epitaxial growth [20]. Figure 1(e) shows the surface roughness on a cleaved BiInSe3 substrate, as measured by atomic force microscopy (AFM): its surface roughness is 59 pm. In comparison, a common commercial Al2O3 substrate in Fig. 1(f) exhibits a roughness of 132 pm. The much smoother surface of the cleaved BiInSe3 substrate is due to the van der Waals nature of the Se-Se bonding: It always cleaves between the atomically-defined Se-Se layer. On the other hand, without such natural cleavage plane, commercial substrates like Al2O3, SrTiO3 or GaAs cannot avoid a certain level of atomic-level roughness despite elaborated processes of chemical and mechanical polishing.

For film growth, we mounted the BiInSe3 substrate onto a dummy Al2O3 substrate, which acts as sample holder, using PELCO® high performance ceramic adhesive (Ted Pella), then cured the adhesive, cleaved a fresh surface and put it into the molecular beam epitaxy (MBE) chamber right away: More details are included in a previous report [21]. Figure 1(g) gives the reflection high-energy electron diffraction (RHEED) pattern of the BiInSe3 substrate, exhibiting sharp bright streaks, which is another signature of atomically flat surface. Both AFM and RHEED measurements confirm the atomic flatness of the cleaved BiInSe3 surface.

In order to get rid of any contaminants, we outgas the BiInSe3 substrate at 600 °C for 30 min with Se flux supplied in the MBE chamber. Then after the substrate is cooled to 350 °C, we grow Bi2Se3 films on the BiInSe3 substrate by co-evaporating high-purity Bi and Se using standard effusion cells. Figure 2(a) shows the RHEED pattern after deposition of 10 QL Bi2Se3 on a BiInSe3 substrate. The bright and sharp RHEED pattern indicates high quality epitaxial growth of the Bi2Se3 film.

![Figure 1](image1.png) High quality single crystal substrate BiInSe3. (a) Schematic diagram of in-plane lattice parameters for some representative commercial substrates and 3D TI materials (Bi2Se3, Bi2Te3 and Sb2Te3). (b) Image of the as-grown shiny BiInSe3 ingot with conical tip. (c) Optical microscope image of cleaved fresh surface of a BiInSe3 single crystal, exhibiting clean flat surface. (d) XRD result of a typical BiInSe3 substrate. (e) and (f) AFM images (5 μm × 5 μm) of a BiInSe3 and commercial Al2O3 substrate surface, respectively. Inset words indicate the root mean square roughness of the surface. Units in the AFM scale bars are nm. (g) In situ RHEED pattern of the cleaved BiInSe3 substrate surface.

![Figure 2](image2.png) Characterizations of Bi2Se3 thin films grown on different substrates. (a) Sharp streaky RHEED pattern of the epitaxial Bi2Se3 film grown on BiInSe3 substrate. (b) AFM image of a 10 QL Bi2Se3 film grown on BiInSe3 substrate, exhibiting large area flat terraces. (c) AFM image of a 10 QL Bi2Se3 thin film directly grown on Al2O3. (d) AFM image of a 10 QL Bi2Se3 thin film grown on InSe2-BiInSe3 buffer layer using the method in Ref. [7]. Units in all the AFM scale bars are nm.
Surface morphology is an important indicator of the quality of a film. Figure 2(b) gives the AFM image of a 10 QL Bi2Se3 film surface grown on a BiInSe3 substrate. The most noticeable feature is the large flat terraces, which are much larger than those of previous Bi2Se3 thin films [22–28]. For comparison, we present morphologies of two control samples in Figs. 2(c) and 2(d). Figure 2(c) shows the AFM image of a 10 QL Bi2Se3 film directly grown on Al2O3 substrate. The surface shows characteristic triangular shaped terraces: Bi2Se3 films grown on InP(111) or Si(111) substrates exhibit even smaller terraces [26, 29]. Figure 2(d) shows the surface morphology of a 10 QL Bi2Se3 film grown on InSe-InSe-BiInSe3 buffer layer [7], which exhibits slightly larger terraces with sharper edges than Fig. 2(c) (Al2O3 substrate), but still much smaller than Fig. 2(b) (BiInSe3 substrate). Through this comparison, we can see that the BiInSe3 substrate is clearly better than both Al2O3 substrate and InSe-InSe-BiInSe3 buffer layer in terms of surface morphology. The lower Bi2Se3 nucleation density (thus larger terrace size) on BiInSe3 suggests lower defect density in the film, which provides an evidence for the higher crystalline quality. Moreover, because the InSe-InSe-BiInSe3 buffer layer is itself grown on ill-matched Al2O3 substrate, it cannot avoid these relatively small triangular terraces on its own. On the other hand, BiInSe3 substrate is a single crystal grown by Bridgeman method, and can be, after cleavage, atomically flat, free of terraces over a macroscopic scale as shown in Fig. 1(e). This large flat surface of well-matched substrate provides the ideal platform for Bi2Se3 thin film growth as shown in Fig. 2(b). As we can see from the following part, the superior surface morphology of Bi2Se3 film grown on BiInSe3 substrate also plays a very critical role in improving the electrical transport performance.

Electrical transport property is another tool to evaluate the quality of a TI thin film, especially for characterizing the level of defects. We grew 20 QL Bi2Se3 on BiInSe3 substrate with 100 nm Se capping on top, as shown in Fig. 3(a). Before investigating the transport properties of Bi2Se3 film, we rule out the shunting effect from the substrate by measuring the temperature dependent sheet resistance of the BiInSe3 substrate alone, as shown in Fig. 3(b). Here the BiInSe3 substrate was treated exactly the same way as the ones used for Bi2Se3 growth (mounted on Al2O3 substrate, cured with the adhesive, cleaved for a fresh surface and in-situ annealed at 600 °C in the MBE chamber). The sheet resistance of BiInSe3 substrate shows typical insulating behavior, rising sharply with decreasing temperature. On the other hand, as shown in Fig. 3(c), the sheet resistance of Bi2Se3 grown on BiInSe3 substrate exhibits typical metallic behavior [30]. The fact that BiInSe3 is several orders more insulating than Bi2Se3 film0m at low temperature undoubtedly excludes the shunting effect from the BiInSe3.

Figure 3(d) shows the Hall effect data, which gives the 2D carrier density of 7.8 × 1012 cm−2 at 8.6 K. Combining the results of Hall effect and sheet resistance gives the Hall mobility of 4,206 cm2/V·s. The same Bi2Se3 film sample was sitting in air for 15 months and then remeasured again. As shown in Fig. 3(c), the temperature dependent sheet resistance almost remains the same as the as-grown data. Figure 3(e) presents the magnetoresistance (MR) of the aged Bi2Se3 sample measured at 2 K and up to 9 T. The inset shows the enlarged plot at low field range, exhibiting an obvious resistance cusp feature, which is the typical signature of weak antilocalization (WAL). Figure 3(f) shows the Hall resistance of the aged Bi2Se3 sample, giving a higher 2D carrier density of 1.1 × 1013 cm−2 than the as-grown sample, which is the result of aging effect. The Shubnikov-de Haas (SdH) oscillation is absent in both MR and Hall resistance data, similar to the situation of Bi2Se3 films grown on InSe-InSe-BiInSe3 buffer layer, even though they possess record-low 2D carrier density and highest mobility [7, 8]. In Bi2Se3, the presence of quantum oscillations is not directly related to the quality of films. Those Bi2Se3 films that exhibit quantum oscillations have high carrier densities typically on the order of 1013 cm−2 with intermediate mobilities [31, 32]. Although the underlying reason for the absence of SdH oscillations in these low-carrier-density, high-mobility films still requires further exploration, one possibility is due to the carrier density inhomogeneity, which has been reported to significantly suppress the SdH oscillation in GaN/AlGaN heterostructures [33]. When the carrier density is low, the carrier density inhomogeneity could have more severe effect and result in the absence of SdH oscillation [34].

Figure 4 compares the 2D carrier density and Hall mobility of 20 QL Bi2Se3 films grown on various substrates: BiInSe3...
substrate clearly outperforms other substrates in both the residual carrier density and mobility. Among the substrates shown in Fig. 4, BiInSe3 is the only one with the 2D carrier density below $10^{13} \text{cm}^{-2}$ for 20 QL BiSe film. Meanwhile, the Hall mobility of Se capped BiSe grown on BiInSe3 substrate achieves 4,206 cm$^2$/V·s, significantly higher than on other substrates. It is worth mentioning that this value even outpaces the In$_x$Se$_{3-x}$BiInSe$_3$ buffer layer scheme [7]. There could be multiple factors contributing to the superior transport properties of BiInSe$_3$ films grown on the BiInSe$_3$ substrate. First, the structural match should minimize structural defects at the interface. Second, the chemical match eliminates unintended doping effect at the interface [22]. Lastly, the much larger terraces imply correspondingly longer mean free path, leading to the larger Hall mobility.

3 Conclusion

In recent years, TI thin films have been extensively investigated for both fundamental studies and spintronic applications such as spin-orbit torque devices [35–38]. Nonetheless, the existing commercial substrates lead to large residual carrier densities and low mobilities and hamper the progress of TI research. The newly introduced BiInSe$_3$ substrate, which is ideally matched both structurally and chemically with BiSe$_3$ films and can easily achieve atomically flat surfaces, will accelerate the advance of TI studies beyond the current limit.

4 Method

Transport measurement: The resistance and Hall resistance measurements were performed with the standard van der Pauw geometry in both a closed-cycle cryostat (8.6 K, 0.6 T) and a Quantum Design Physical Property Measurement System (PPMS; 2 K, 9 T). Electrical electrodes were made by manually pressing four indium wires on the corners of each sample. All the samples were carefully cut into square shape to minimize the deviation from van der Pauw geometry. Raw data of $R_{xx}$ and $R_{xy}$ were properly symmetrized and antisymmetrized respectively. 2D carrier density was extracted from $n_{2D} = \frac{1}{eB} \left( \frac{dR_{xx}/dB}{dR_{xy}/dB} \right)^{-1}$ where $e$ is the electronic charge and $dB/dB$ is the slope of the Hall resistance vs. magnetic field $B$, measured at the origin. The zero-field sheet resistance was calculated from $R_{\text{net}} = R_{xx} (B = 0) - \pi \ln(2)$ for the van der Pauw geometry. Hall mobility $\mu$ was calculated by using $\mu = \frac{eR_{\text{net}}n_{2D}}{2}$. 

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