Molecular beam epitaxy growth and structure of self-assembled Bi$_2$Se$_3$/Bi$_2$MnSe$_4$ multilayer heterostructures

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1. Introduction

Extensive research in modern nanoelectronics has been aimed at understanding the growth, characterization, and physical properties of a wide range of two-dimensional materials, including graphene [1–4], two-dimensional transition metal dichalcogenides [5, 6], and topological insulators (TIs) [7–10], in which, in the case of TIs, recent advancements in condensed matter theory have predicted systems with nontrivial topological classifications that exhibit unique electronic properties, particularly at their interface with a topologically trivial system or with the vacuum [11–15]. These materials support topological surface states characterized by spin that is locked to the momentum and is protected from backscattering. A great deal of recent interest has been directed at exploring phase transitions in such materials that exhibit certain symmetry-breaking properties, such as superconductivity [16, 17], magnetism [18], or a combination of both [19].

One of the most widely-studied TIs is Bi$_2$Se$_3$ [16, 20, 21], which demonstrates both topological insulating properties [10, 22] and excellent thermoelectric transport properties [23], and is formed of stacks of repeating...
quintuple layers (QLs) of Se–Bi–Se–Bi–Se lamellae weakly bound by van der Waals forces (figure 1(a)). Breaking time reversal symmetry by incorporating a magnetic component in the TI system, such as by introducing magnetic dopants to the material, has been shown to produce such intriguing phenomena as surface state mediated ferromagnetism [24], and has been both predicted [7, 25] and shown [26] to produce a quantum anomalous Hall effect, where a Hall conductivity of $\frac{e^2}{h}$ is observed when the Fermi level is tuned to the gap in the Dirac cone without the application of a magnetic field. Engineering exotic topological states is the topic of much of the contemporary research in TIs, including research of magnetic TIs as a materials platform for the study of interactions between topological surface states and symmetry-breaking magnetic states.

Motivated to study the physics of magnetically doped TIs, numerous studies have been published on the physics of materials produced by molecular beam epitaxy (MBE) grown with fluxes of elemental Bi, Se, and Mn [27–30]. This growth procedure is expected to produce a dilute magnetic alloy of Bi$_2$Se$_3$, with Mn entering the system at Bi-substitutional sites randomly throughout the thin film, with Mn concentration determined by the relative arrival rate of Mn ions to Bi and Se ions during growth. We propose here that, instead of the Mn atoms arranging themselves as randomly dispersed dopants in the Bi$_2$Se$_3$ lattice, this growth produces an until-now unstudied material, Bi$_2$MnSe$_4$, in the form of a self-assembled layered heterostructure with Bi$_2$Se$_3$ in a near-periodic self-assembled heterostructure consisting of layers of Bi$_2$Se$_3$ separated by single-layer Bi$_2$MnSe$_4$ crystals. Bi$_2$MnSe$_4$ is formed by the intergrowth of [111] planes of rock-salt MnSe with QLs of Bi$_2$Se$_3$, analogous to the growth of homologous compound Bi$_2$MnTe$_4$ [31].

Here we report the compositional and structural properties of Bi$_2$Se$_3$/Bi$_2$MnSe$_4$ heterostructures, and we propose an epitaxial growth mechanism by which Bi$_2$MnSe$_4$ naturally forms a heterostructure with the TI Bi$_2$Se$_3$. Greater concentrations of Mn result in an increase in the number of Bi$_2$MnSe$_4$ septuple layers (SLs) in the crystal. We support the proposed growth chemistry with theoretically-derived energetics obtained from density functional theory (DFT) calculations, and we present a series of calculated band structures that reveal that Bi$_2$MnSe$_4$/Bi$_2$Se$_3$ is a magnetic TI in which Bi$_2$MnSe$_4$ is a materials system characterized by a distinctive blend of magnetic and topological insulating quantum matter components.
2. Experimental section

The epitaxial growth of Bi$_2$Se$_3$/Bi$_2$MnSe$_4$ is achieved by following the MBE growth method for binary alloy Bi$_2$Se$_3$ described by Liu et al. with the additional inclusion of a Mn beam from a standard evaporation cell. Samples with different Mn concentrations were produced by varying the temperature of the Mn effusion cell between 675 °C and 720 °C to adjust the Mn flux incident on the substrate. The growth was monitored by in situ reflection high-energy electron diffraction to measure growth rate and to ensure high quality layer-by-layer growth. Samples were grown on both GaAs(001) and GaAs(111) substrates. For the purpose of this study, differences at the substrate–sample interface of Bi$_2$Se$_3$ and the Mn-rich Bi$_2$Se$_3$ grown on GaAs(001) as compared with growing on GaAs(111) are ignored. Liu et al. presents strong evidence that Bi$_2$Se$_3$ grows with a sufficiently sharp interface on GaAs(001), as it has been shown to do on GaAs(111) [32] due to immediate strain relaxation between the substrate and the TI film due to the weak van der Waals coupling between the substrate and the TI film [33–35].

X-ray photoelectron spectroscopy (XPS) measurements were performed in a commercial instrument equipped with a hemispherical electron analyzer with monochromatized Al Kα or non-monochromatized Mg Kα x-rays as the excitation source. XPS measurements were performed in a base pressure of $6.7 \times 10^{-7}$ Pa ($5 \times 10^{-9}$ Torr) or less, and photoelectrons were collected at normal emission. The XPS spectra were fit using a Voigt lineshape and either a linear background (for Bi 5d) or a Shirley background (for Se 3d). For a given photoelectron core level, the spectra were fit simultaneously where the Gaussian components were coupled, Lorentzian components coupled for the same chemical state, and the spin–orbit doublet ratios of $d_{5/2}$/$d_{3/2}$ as 3:2 were used. For Se 3d, the spin–orbit separation of 0.85 eV was used for the fits.

Samples were prepared for transmission electron microscopy (TEM) by standard mechanical polishing and argon-ion-milling using a FEI Helios dual beam focused ion beam, with the sample held at liquid-nitrogen temperature during the latter process in order to avoid unintentional ion-milling artifacts. TEM images were produced using an FEI Titan 80-300 TEM capable of operating in both transmission (TEM) and scanning transmission electron microscopy (STEM) modes. The FEI Titan 80-300 system is capable of detecting all elements with atomic number 5 and higher using energy dispersive x-ray (EDX) spectroscopy with a spatial resolution of 0.14 nm. X-ray diffraction for binary Bi$_2$Se$_3$ and Bi$_2$Se$_3$/Bi$_2$MnSe$_4$ heterostructures samples of varying Mn concentrations, as well as the peak locations for pure Bi$_2$Se$_3$ and pure Bi$_2$MnSe$_4$ for reference, was measured using the Cu Kα radiation line.

Calculated crystal structure, optimized by minimizing the energy of the structure, total energy, and electronic structure calculations were performed in the framework of DFT using the Quantum ESPRESSO [36] code. The generalized gradient approximation (GGA) of the Perdew–Burke–Ernzerhof-type [37] is used for the exchange and correlation potential. We have used norm-conserving, optimized, designed nonlocal pseudopotentials for all atoms [38, 39]. Pseudopotentials were constructed with (full relativistic) and without (scalar relativistic) spin–orbit coupling. To guarantee convergence, all calculations are performed with a plane-wave cutoff of 70 Ry on an $8 \times 8 \times 8$ Monkhorst–Pack [40] $k$-point mesh for bulk geometries and $8 \times 8 \times 1$ $k$-point grid for the slab geometries.

Commercial materials, instruments and equipment are identified in this paper to specify the experimental procedure as completely as possible. In no case does such identification imply a recommendation or endorsement by the National Institute of Standards and Technology.

3. Results and discussion

3.1. General composition and structure

The described MBE growth resulted in self-assembly of single-layer Bi$_2$MnSe$_4$ crystals separated by layers of Bi$_2$Se$_3$ in a near-periodic self-assembled heterostructure. Samples grown for this study had total atomic concentrations of Mn$_{0.025}$Bi$_{0.375}$Se$_{0.600}$ (2.5% Mn), Mn$_{0.042}$Bi$_{0.375}$Se$_{0.683}$ (4.2% Mn), Mn$_{0.076}$Bi$_{0.346}$Se$_{0.584}$ (7.6% Mn), and Mn$_{0.098}$Bi$_{0.330}$Se$_{0.580}$ (9.0% Mn), as measured by particle-induced x-ray emission (PIXE) and confirmed by Rutherford backscattering (RBS), and had respective thicknesses of 80 nm, 92 nm, 90 nm, and 95 nm. Note that the total Mn concentrations determine the observed number of Bi$_2$Mn$_x$Se$_{3-x}$ layers relative to Bi$_2$Se$_3$ layers. We propose a structure of composition Bi$_2$Mn$_x$Se$_{3-x}$ that we predict by DFT calculations to have a lower absolute energy than Mn-doped Bi$_2$Se$_3$ with Mn distributed randomly at Bi-substitutional sites. Bi$_2$Mn$_x$Se$_{3-x}$ is isostructural to binary alloy Bi$_2$Se$_3$ and is a homologous compound of Bi$_2$Se$_3$, the QL structure of which is shown in figure 1(a), with R3m space group. The Bi$_2$Mn$_x$Se$_{3-x}$ SL shown in figure 1(b), is a 2D layer consisting of seven monoatomic layers with stacking sequence of Se–Bi–Se–Mn–Se–Bi–Se along the a-axis, with individual 2D layers weakly bound to each other by van der Waals forces. SL thickness determined by DFT calculations is about 1.26 nm, which is confirmed by TEM measurements (to be discussed later). Lattice parameters, bond
lengths, and energies were calculated for both Bi2Se3 and the proposed system Bi2MnSe4, as well as for Bi3Se4 and Bi2\(_{1-x}\)Mn\(_x\)Se3 for completeness, allowing us to fully compare the structures that may have grown due to incidence of Bi, Se, and Mn beams on the growth surface during MBE growth.

The lattice parameters and inter-lamellar distances indicated in figure 1(b) are given in table 1. Bi–Se bond lengths, given for the distance between the Bi atoms and both the Se1 and the Se2 atoms, were calculated for all structures; for structures containing Mn, Mn to nearest-neighbor Se bond lengths were calculated. DFT-calcualted bond length values are presented in table 2. Calculated Bi–Se bond lengths for Bi2Se3 are in good agreement with experimentally measured values, 2.85 Å and 3.07 Å for Se1 and Se2, respectively [41]. We performed extended x-ray absorption fine structure (EXAFS) measurements at the Argonne National Laboratory Advanced Photon Source near the x-ray absorption K-edge of elemental Mn—6539.0 eV—to ascertain the average Mn–Se bond lengths on samples with 2.5%, 4.2%, and 9.0% Mn content. The Mn incorporation model considers Mn at sites with photoelectron scattering paths to six nearest neighbor Se atoms. The simulated fits created from these models were done on the real space Fourier transform \(\chi(R)\) of the response \(k^2\chi(k)\), the data for which is shown in figure 2 in black. The simulated fits, shown in red, are consistent with measured data. We both predict and measure that Mn–Se bonds are lower than Bi–Se bonds in Bi2Se3, which is expected in the case of Mn substitutionally incorporating at a Bi site in Bi2Se3. The EXAFS-measured bond lengths (table 3), however, are in much closer agreement to the Mn–Se distance that we compute for Bi2MnSe4 than they are for those for Mn at Bi sites in Bi2Se3. This suggests that Mn is more likely to incorporate in Bi2MnSe4 layers during growth via the intergrowth of \{111\} planes of MnSe with Bi2Se3 layers than at Bi-substitutional sites in a Bi2Se3 lattice. Crystalline MnSe has a measured Mn–Se bond length of 2.71 Å [43], which is within 2% of our calculated Mn–Se bond length values in Bi2MnSe4 and is in very close agreement with our EXAFS-measured Mn–Se bond length values for all samples.

DFT calculations in the GGA approximation were performed to evaluate the total energies of the four different systems with equivalent elemental composition, 3Bi + 4Se + Mn. The energy for each system is calculated for the four crystal structures plus the energy of free atoms of elements necessary to preserve overall elemental composition. The four structures are Bi2Se3, Bi2MnSe4, Bi3Se4, and Bi2\(_{1-x}\)Mn\(_x\)Se3 with half of the Bi atoms substituted with a Mn atoms (BiMnSe3), all corresponding to a BiMnSe system with a total Mn concentration of 12.5%. These elemental single atoms represent free adatoms on the growth surface. The energies for each composition are given as the energy difference from that of binary Bi2Se3 plus single atoms of

| Table 1. Lattice parameters and inter-lamellar distances. |
|---|
| (a) Lattice parameters (Å) |
| | Bi2Se3, this work | Bi2Se3, experiment [41] | Bi2MnSe4 |
| | | | |
| a | 4.097 | 4.138 | 4.197 |
| c | 28.804 | 28.64 | 37.797 |
| (b) Lamella spacing (Å) |
| | Bi2Se3, this work | Bi2Se3, experiment (average) [41, 42] | Bi2MnSe4 |
| | | | |
| d_{12} | 1.543 | 1.572 | 1.543 |
| d_{23} | 1.982 | 1.934 | 1.934 |
| d_{34} | 1.983 | 1.934 | 1.934 |
| d_{45} | 1.546 | 1.572 | 1.546 |
| d_{56} | — | — | 1.451 |
| d_{67} | — | — | 1.454 |
| d_{vdW} | 2.547 | 2.536 | 2.537 |

| Table 2. DFT-calculated bond lengths. |
|---|
| | Bi–Se bond length (Å) | Mn–Se bond length (Å) |
| Crystal structure | Se1 | Se2 | Se1 | Se2 |
| Bi2Se3 | 2.87 | 3.01 | — | — |
| Bi2MnSe4 | 2.84 | 3.11 | — | 2.76 |
| Bi3Se4 | 3.03 | 3.10 | — | — |
| BiMnSe3 | 2.64 | 2.74 | 2.62 | 2.69 |
elemental Mn, Bi, and Se and are presented in Table 4. The results suggest that elemental beams of Bi, Se, and Mn incident on the growth surface present thermodynamically favorable conditions for the growth of binary Bi\(_2\)Se\(_3\) despite the presence of a beam of Mn. PIXE and RBS measurements, however, prove that Mn has incorporated into the material, suggesting that Mn that is not incorporated during the formation of Bi\(_2\)Se\(_3\) layers during growth, instead remaining diffuse on the growth surface as Bi\(_2\)Se\(_3\) layers form, is incorporated through the formation of the compound with the next lowest energy: Bi\(_2\)MnSe\(_4\).

A simple epitaxial growth mechanism for the self-assembly of Bi\(_2\)Se\(_3\) layers interspersed with septuple Bi\(_2\)MnSe\(_4\) is proposed as follows. As the compositional elements Bi, Se, and Mn are incident on the growth surface present thermodynamically favorable conditions for the growth of binary Bi\(_2\)Se\(_3\) despite the presence of a beam of Mn. PIXE and RBS measurements, however, prove that Mn has incorporated into the material, suggesting that Mn that is not incorporated during the formation of Bi\(_2\)Se\(_3\) layers during growth, instead remaining diffuse on the growth surface as Bi\(_2\)Se\(_3\) layers form, is incorporated through the formation of the compound with the next lowest energy: Bi\(_2\)MnSe\(_4\).

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Table 3. EXAFS-measured bond lengths.

| Mn %     | Average Mn–Se bond length (Å) |
|----------|-------------------------------|
| 2.5% Mn  | 2.74 ± 0.01                   |
| 4.2% Mn  | 2.73 ± 0.01                   |
| 9.0% Mn  | 2.72 ± 0.01                   |

Table 4. Energy of formation for various Bi, Mn, Se compositions.

| Composition                  | Energy difference from Bi\(_2\)Se\(_3\) + Mn + Bi + Se |
|------------------------------|---------------------------------------------------------|
| Bi\(_2\)Se\(_3\) + Mn + Bi + Se | 0 eV                                                   |
| Bi\(_2\)MnSe\(_4\) + Bi      | 1.14 eV                                                |
| Bi\(_2\)Se\(_3\) + Mn        | 4.65 eV                                                |
| BiMnSe\(_4\) + 2Bi + Se      | 10.0 eV                                                |

Figure 2. X-ray absorption fine structure for 2.5% Mn, 4.2% Mn, and 9.0% Mn. The black curves are EXAFS from measured x-ray absorption data; the red curves are simulated fits from a Bi-substitutional Mn incorporation model.
Bi$_2$MnSe$_4$, like Bi$_2$Se$_3$, is a layered material. Bright field TEM images reveal the conspicuous layered growth pattern of the Bi$_2$Se$_3$/Bi$_2$MnSe$_4$ layered structure described by our growth model and presented for 2.5% Mn-Bi$_2$Se$_3$ in figure 5(a). Regions of different contrast indicate different crystal structure domains. Striations of lighter contrast represent layers where the Mn incorporated into the sample is concentrated. Differences in the cross-sectional structure of these layers are visible in the STEM images shown in the figures 5(b) and (c). The total Mn concentration can be approximated from the STEM images as the fraction of the Bi$_2$MnSe$_4$ layers multiplied by the assumed Mn atomic fraction in these layers of 1/7, giving estimated Mn values of 2.5 ± 0.3% and 4.3 ± 0.6% for Mn$_{0.025}$Bi$_{0.375}$Se$_{0.600}$ and Mn$_{0.042}$Bi$_{0.375}$Se$_{0.583}$, respectively, in good agreement with values measured by PIXE. Representative STEM images are shown in figures 6(a) and (b) for samples with 2.5% and 4.2% total Mn concentration, respectively. This supports the hypothesis that the SLs are primarily Bi$_2$MnSe$_4$ as opposed to a mixed (Bi$_{1-x}$Mn$_x$)$_2$Se$_3$ alloy, and that almost all of the Mn is incorporated in these layers. This is further supported by EDX spectroscopy, where Mn is shown to primarily occupy the septuple-lamellae layers.

Figure 3. (a) Compositional elements Bi, Se, and Mn are incident on the growth surface. (b) Thermodynamic conditions favor the growth of binary Bi$_2$Se$_3$, with Mn$^{2+}$ adatoms remaining diffuse on the growth surface. (c) At a critical Mn adatom surface density, a single Bi$_2$Mn$_x$Se$_{3-y}$ layer forms to ‘clear’ the growth surface of Mn, thus permitting further uninterrupted Bi$_2$Se$_3$ growth. This mode of growth results in an approximately periodic repetition of single Bi$_2$MnSe$_4$ layers separated by a number of Bi$_2$Se$_3$ layers defined by the relative arrival rate of Mn ions to Bi and Se ions during growth.

Figure 4. XRD of Bi$_2$Se$_3$ and Bi$_2$Se$_3$ grown with Mn of varying concentrations, with GaAs peaks labeled. {0 0 3} -type Bi$_2$Se$_3$ and Bi$_2$MnSe$_4$ peaks are shown below for reference.
and is largely absent in the quintuple-lamellae layers, indicating the septuple-lamellae layers, or SLs, are Bi$_2$MnSe$_4$ and the quintuple-lamellae layers, or QLs, are Bi$_2$Se$_3$. (Representative EDX-measured chemical composition along a 5.2 nm path that includes two Bi$_2$MnSe$_4$ SL’s is shown in the supplementary materials available online at stacks.iop.org/NJP/19/085002/mmedia.)

3.2. XPS measurements

The proposed Bi$_2$Se$_3$/Bi$_2$MnSe$_4$ heterostructure composition in these MBE-grown materials is supported by identifying Mn, Se, and Bi chemical states in binary Bi$_2$Se$_3$ and Bi$_2$Se$_3$/Bi$_2$MnSe$_4$ samples using XPS. XPS is a surface spectroscopy measurement, and due to the significant oxidation at the surface of samples, considerable analysis of the spectra is necessary to deduce compositional information of the bulk material. By examining the Mn oxidation states and differences in the amount that Se and Bi precipitate out of the material as a function of Mn inclusion or exclusion, we can identify signatures of sample composition. Specifically, we identify Mn oxidation states corresponding to Bi$_2$MnSe$_4$ and not to Bi-substitutional Mn in (Bi$_{1−x}$Mn$_x$)$_2$Se$_3$. In addition, the incorporation of Mn in Bi$_2$Se$_3$ induces observable physical changes in the growth of the native oxide at the surface due to differing amounts of Se and Bi precipitating out of the material as a function of Mn inclusion or exclusion, we can identify signatures of sample composition. Specifically, we identify Mn oxidation states corresponding to Bi$_2$MnSe$_4$ and not to Bi-substitutional Mn in (Bi$_{1−x}$Mn$_x$)$_2$Se$_3$. In addition, the incorporation of Mn in Bi$_2$Se$_3$ induces observable physical changes in the growth of the native oxide at the surface due to differing amounts of Se and Bi precipitating out of the samples during growth as compared to growth of pure Bi$_2$Se$_3$. Air-exposed samples are of relevance as they realistically link the physical properties to adatom transport and incorporation during epitaxial growth. XPS was used to measure the surface composition of air-exposed Bi$_2$Se$_3$ and Bi$_2$MnSe$_4$ surfaces in samples composed of 0% and 7.6% Mn.

Details of the XPS analysis are presented in the supplementary materials. The Mn 2p peaks shown in figure 7(a) reveal a shake-up feature between 644 and 648 eV that is a distinct indication of Mn$^{2+}$ [44–46], which persists even after about 5 nm of oxidized surface is removed by Ar plasma. These data suggest that when Mn is incorporated into a bismuth chalcogenide crystal during epitaxial growth, it is likely to incorporate in its most stable oxidation state, Mn$^{2+}$, at a Bi$^{2+}$-substitutional site in a Bi$_2$Se$_3$-structural arrangement; or, equivalently, as MnSe intergrown with a QL of Bi$_2$Se$_3$. This chemistry leads to the incorporation of Mn in this material in Bi$_2$MnSe$_4$ layers.
Further insight on the impact of Mn-inclusion in Bi$_2$Se$_3$ growth is gained from the Se and Bi XPS spectra, shown in figures 7(b) and (c) for the Se 3d spectra and the Bi 5d spectra, respectively, of both the air-exposed Bi$_2$Se$_3$ and Bi$_2$MnSe$_4$. The Se 3d spectra contains evidence for the existence of selenide (Se$^{2-}$), elemental selenium (Se$^0$), and oxidized selenium (SeO$_x$), where the presence of Se$^0$ is indicative of Se precipitation out the bulk film by diffusion during growth [47, 48]. The Bi 5d spectra shows the presence of two different Bi chemical states: Bi$^{3+}$ in Bi$_2$Se$_3$, and oxidized Bi. From the deconvolution of the Se 3d and the Bi 5d spectra, the fractional composition of the selenide (Se$^{2-}$), elemental selenium (Se$^0$), and oxidized selenium (SeO$_x$), and the fractional composition of Bi in Bi$_2$Se$_3$ and BiO$_x$ can be estimated from the spectral fits, shown in figure 7(d) for binary Bi$_2$Se$_3$ and Mn:Bi$_2$Se$_3$ with 7.6% Mn and 9.0% Mn. The results suggest that, with the inclusion of Mn, more Se precipitates out of the crystal, which corresponds to a decrease in the selenide component as the oxidized component remains constant. Similarly, the inclusion of Mn into the Bi$_2$Se$_3$ system correlates with an increase in the fraction of oxidized Bi in a fashion consistent with our observation of increasing Se$^0$, the precipitation of which results in the presence of non-bonded Bi atoms susceptible to oxidation. Analysis of the Se 3d and Bi 5d spectra suggests that the Mn ion, due to its preference for a different coordination environment than that of Bi in Bi$_2$Se$_3$, disrupts the thermodynamic equilibrium of Bi$_2$Se$_3$ growth, as it favors the alternative structural and compositional arrangement of the Bi$_2$MnSe$_4$ layers in which the Mn incorporates. A corresponding increase in strain to the system accelerates Se diffusion and precipitation out of the system, resulting in a higher incidence of oxidized Bi at the surface.

### 3.3. Electronic structure

To explore the electronic properties of this newly synthesized material, band structure was calculated along the high symmetry lines in the two-dimensional Brillouin zone (BZ) using optimized lattice geometries (see supplementary materials). Calculations include full relativistic corrections associated with the strong spin–orbit coupling in these systems. The topological ordering is evident in the band structure calculated for Bi$_2$MnSe$_4$ in a slab geometry with 6 SLs when the magnetic moments of Mn are not included in the calculation (figure 8(a)). A single gapless Dirac-like mode with a Dirac point at $k = 0$, shown clearly in the zoomed in region of the Dirac...
point (figure 8(b)), signifies topologically nontrivial ordering. A gap is produced at the Dirac point $\Delta$ (figure 8(c)) when the magnetic moments of the Mn ions are introduced as part of the calculation for 6 SL Bi$_2$MnSe$_4$. The band structure for this structure is shown in figure 8(d), indicating that the surface states of this material behave as a massive Dirac fermion [7], which would signify the existence of a topologically-protected quantum anomalous Hall state [7]. The evolution of the surface states is shown for the increasing number of Bi$_2$MnSe$_4$ SLs with magnetization considered in the calculation. The states that ultimately evolve into surface states are emphasized with overlaid circles at calculated $E(k)$ values of those states. The band structure of a single Bi$_2$MnSe$_4$ SL (figure 8(e)) shows weak spin–orbit coupling reminiscent of the bulk band structure calculated with spin–orbit coupling absent (see supporting information). As additional layers are incorporated, the band gap begins to progressively close for the two-SL (figure 8(f)) and four-SL (figure 8(g)) systems, and eventually undergoes a band inversion such that massive Dirac-like band-crossing surface states are observable in the six-SL Bi$_2$MnSe$_4$ system, indicative of topologically non-trivial behavior [7]. In the six-SL case, the valence band near the $K$ point crosses the Fermi level, signifying an insulator-to-metal transition, and implying that Bi$_2$MnSe$_4$ with a thickness greater than six SL is a topologically non-trivial metal. Consequently, parallel transport of p-type bulk carriers and massive Dirac fermions in the topological surface state is expected in pure Bi$_2$MnSe$_4$. A Bi$_2$Se$_3$/Bi$_2$MnSe$_4$ heterostructure of sufficient thickness is theoretically predicted to be a topologically non-trivial system. Furthermore, such a system has the potential to be tuned to eliminate Fermi level crossing of the valence band by modifying the Mn content—and thus the number of Bi$_2$Se$_3$ layers separating single Bi$_2$MnSe$_4$ layers—to produce a stoichiometric TI material that would support measurable novel topological surface states.

This material is predicted to demonstrate similar electronic behavior to what is predicted for (Bi$_{1-x}$Mn$_x$)$_2$Se$_3$, suggesting that many of the studies asserted to have been performed on MBE-grown
Bi$_{2-x}$Mn$_x$Se$_3$ [27–30] may have been, and likely were, in fact, performed on Bi$_2$Se$_3$/Bi$_2$MnSe$_4$ heterostructures. Producing a growth method that achieves precise Bi$_2$Se$_3$/Bi$_2$MnSe$_4$ heterostructure layer control or pure Bi$_2$MnSe$_4$ growth is highly challenging. Samples grown with Mn concentrations of 9.0% and above were observed to have increasingly high crystalline disorder and high instances of MnSe cluster formation, necessitating further study of the growth parameterization.

### 4. Conclusions

This study lays the groundwork for further investigation of the MBE growth of Bi$_2$Se$_3$/Bi$_2$MnSe$_4$ multilayer heterostructures, and is the first investigation of any kind on topologically non-trivial magnetic bismuth-chalcogenide compound Bi$_2$MnSe$_4$. Here we have presented structural, compositional, and electronic characteristics of this new material, along with a model for its epitaxial growth. We undertook rigorous characterization of the crystal structure and chemical composition of this material by a broad range of complementary studies. We computed structural arrangements and determined energies of formation by DFT calculations. We further applied DFT calculations to obtain the electronic band structure for Bi$_2$MnSe$_4$, demonstrating the topological non-triviality of this system and, by extension, Bi$_2$Se$_3$/Bi$_2$MnSe$_4$ multilayer heterostructures. Additionally, the mechanism by which this material naturally forms a heterostructure with the TI Bi$_2$Se$_3$ presents the opportunity for studying the interaction between the topological surface states hosted by Bi$_2$Se$_3$ and the magnetically-ordered states hosted by Bi$_2$MnSe$_4$ suitable to engineering a magnetic topological material with stoichiometric composition in pursuit of a magnetic topological system free from the introduction of disorder arising from the random incorporation of magnetic dopants in an otherwise ordered system. The Bi$_2$Se$_3$/Bi$_2$MnSe$_4$ multilayer heterostructure discussed here is a remarkable example of a multicomponent quantum matter system, one at the crossroads of research in the fields of magnetism, TIs, and two-dimensional layered materials.
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Competing financial interests
The authors declare no competing financial interests.

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