Two-Dimensional Bismuth-Rich Nanosheets through the Evaporative Thinning of Se-Doped Bi₂Te₃

Eve D. Hanson^a, Fengyuan Shi^a, Thomas C. Chasapis^b, Mercouri G. Kanatzidis^b, and Vinayak. P.

Dravid^{a*}

Abstract:

High bulk conductance obscures the behavior of surface states in the prototypical topological insulators Bi₂Te₃ and Bi₂Se₃. However, ternary phases of Bi₂Te_{3-y}Se_y with balanced donor and acceptor levels may lead to large bulk resistivity, allowing for the observation of the surface states. Additionally, the contribution of the bulk conductance may be further suppressed by nanostructuring, increasing the surface-to-volume ratio. Herein we report the synthesis of a ternary tetradymite newly confined to two dimensions. Ultra-thin large-area stable nanosheets were fabricated via evaporative thinning of a Bi₂Te_{2.9}Se_{0.1} original phase. Owing to vapor pressure differences, a compositional shift to a final Bi-rich phase is observed. The Se/Te ratio of the nanosheet increases tenfold, due to the higher stability of the Bi-Se bonds. Hexagonal crystal symmetry is maintained despite dramatic changes in thickness and stoichiometry. Given that small variations in stoichiometry of this ternary system can incur large changes in carrier concentration and switch majority carrier type, the large compositional shifts found in this case imply that

a. *Department of Materials Science and Engineering, Northwestern University, 2220 Campus Drive, Evanston, Illinois 60208, USA*

b. *Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, USA*

* Corresponding author: v-dravid@northwestern.edu (Prof. Vinayak P. Dravid)
Cook Hall, Room 1133 2220 Campus Drive Evanston, IL 60208-3108 USA
Phone: (847) 467-1363
Fax: (847) 467-6573

compositional analysis of similar CVD and PVD grown materials is critical to correctly interpret topological insulator performance. Further, the characterization techniques deployed, including STEM-EDS and ToF-SIMS, serve as a case study in determining such compositional shifts in two-dimensional form.

Keywords: A Evaporative Thinning; B Topological Insulator; A3 Physical Vapor Deposition processes; B1 Nanomaterials; A1 Solid Solutions; B2 Semiconducting ternary compounds

Introduction

Topological insulators are a novel form of matter: they are bulk insulators with metallic surface states that are topologically protected against scattering by time-reversal symmetry.¹ Bismuth selenide (Bi_2Se_3) and bismuth telluride (Bi_2Te_3) were some of the first 3D topological insulators to be experimentally realized.^{2, 3} However, both Bi_2Se_3 and Bi_2Te_3 suffer from high bulk carrier densities, obscuring the surface state conduction and frustrating efforts to properly study the transport properties of the surface states

Both Bi_2Se_3 and Bi_2Te_3 are narrow band gap semiconductors crystallizing in the primitive rhombohedral structure formed by the sequence of atomic layers Q(1)–Bi–Q(2)–Bi–Q(1) (Q = Te or Se) forming quintuple layer “slabs” (Fig. 1) with space group $R\bar{3}m$.⁴ Small deviations in stoichiometry and the small energy formation of native defects often results in relatively large carrier densities.⁵ Appropriate alloying of the binaries may result in bulk insulating behavior. It has been shown that ternary phases with suppressed bulk conductance due to balanced donor and acceptor level may lead to more measurable surface states.⁶ Various groups have been able to tune the bulk topological insulator Fermi level and Dirac cone surface by modifying the composition of the solid solutions.^{7,8} In addition, majority bismuth-rich compositions of the form $(\text{Bi}_2)_m(\text{Bi}_2\text{Te}_3)_n$ have been predicted to have bulk topological insulating behavior.⁹

Reducing sample size and increasing the surface-to-volume ratio may further suppress the contribution of bulk carriers. Two-dimensional (2D) nanosheets of the end-member compounds Bi_2Se_3 and Bi_2Te_3 have experimentally shown enhanced thermoelectric performance as well as more readily measurable topologically-protected surface states.¹⁰⁻¹² Nanostructures within the $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ series have displayed significantly enhanced contribution of the surface states relative to their bulk counterparts, indicating the promise of composition-tuned nanomaterials in transport studies of topological insulators.^{13, 14}

Several methods have been utilized for the size reduction of topological insulators.¹⁵⁻¹⁷ However, these synthesis methods often suffer from very low growth rates or poor quality. Among them, the evaporative thinning method was found successful in the fabrication of 2D binary materials.¹⁸ The evaporative thinning strategy comprises two steps: first, a physical vapor deposition that deposits micron-thick flakes, and second, an annealing step that evaporatively thins off material, leaving behind a single or bilayer 2D nanosheet.¹⁸

In this report, for the first time, we adapt the evaporative thinning technique to a ternary composition $\text{Bi}_2\text{Te}_{2.9}\text{Se}_{0.1}$. Utilizing Scanning Transmission Electron Microscopy Energy Dispersive Spectroscopy (STEM EDS) and Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS), we demonstrate that the final nanosheets undergo large compositional changes. The final thinned sheets are bismuth-rich with a tenfold-increased Se/Te ratio. The hexagonal symmetry of the resultant structure is confirmed despite the dramatic changes in thickness and stoichiometry. The observed compositional shifts are well explained through a thermodynamic vapor pressure driven mechanism.

The large interest in this class of 2D materials strongly demands the understanding of the underlying mechanisms dictating the final composition and thus the final properties. Therefore, our in-depth structural and compositional analyses of a phase never before reported in 2D form serves as a case study in the field of nanoscale compounds synthesized via vapor pressure or CVD means. With their predominantly bismuth character, the final nanosheets could be further explored for exotic electronic properties.^{9, 14}

Experimental

Bulk crystals growth methods were the same as in the previous report on evaporative thinning, with a growth temperature of 850 °C for both Bi_2Se_3 and Bi_2Te_3 .¹⁸ Following the synthesis of bulk

Bi_2Se_3 and Bi_2Te_3 , the crystals were crushed into powder with a mortar and pestle. The appropriate ratio of Bi_2Se_3 powder and Bi_2Te_3 powder were intimately mixed to reach the $\text{Bi}_2\text{Te}_{2.9}\text{Se}_{0.1}$ nominal composition. Sheets with $\text{Bi}_2\text{Te}_{2.9}\text{Se}_{0.1}$ nominal stoichiometry were deposited using a catalyst-free physical vapor deposition method. The source powder was placed in the center of the hot zone of a 12" Lindberg Blue tube furnace within a 1" silica tube. Si substrates with a 300 nm SiO_2 layer were placed downstream in a colder zone within the furnace (approx. 3 cm from source material), suspended on alumina boats. The chamber pressure was maintained at approximately 20 Torr with an ultra-high purity Ar flowing in at 25 sccm. The furnace was heated to 490 °C over the course of 15 min and held at that temperature for 25 min before quenching by opening up the furnace.

After the initial deposition of $\text{Bi}_2\text{Te}_{2.9}\text{Se}_{0.1}$, the substrates covered with crystalline plates were positioned in the hot center of the tube furnace and held at 450 °C for 15 min for evaporative thinning. The furnace was opened after the prescribed time in order to quench the samples. Similar to the deposition step, the chamber was held at 20 Torr with 20 sccm of flowing Ar during evaporative thinning.

STEM EDS measurements were taken using a Hitachi HD-2300 Dual EDS STEM to determine pre-thinning stoichiometry. The beam size for STEM imaging and STEM EDS is 0.4 nm with probe current 700 pA using 200 kV. Thirty frames and 10s acquisition time for each spectrum were used to obtain the STEM EDS mapping with good quality. Quantification was calculated with the Cliff-Lorimer with absorbance algorithm, and the atomic percent error represents +/- one standard deviation. TEM was carried out using JEOL 2100F microscope operating at 200 kV. For S/TEM sample preparation, $\text{Bi}_2\text{Te}_{2.9}\text{Se}_{0.1}$ plates were first deposited onto single crystal NaCl substrates using the same growth conditions described above. The NaCl substrates were then dissolved in a small amount of deionized water, and the flakes were scooped out using a TEM grid with 5 nm Si_3N_4 window. The grid was then air-dried on filter paper in a sealed container. A graphite cap was used

to reduce interfering signal from the cap. The TEM samples were then subjected to the same thinning conditions as the samples on 300 SiO₂/Si substrates, and similar EDS measurements were taken.

ToF-SIMS was also deployed for 2D compositional analysis. SIMS consists of mass spectroscopy of secondary ionized particles that are emitted from a sample after being bombarded with energetic primary particles.¹⁹ These ionized secondary particles can be both elemental ions and ionized clusters. By analyzing the time of flight, ToF-SIMS can distinguish between different mass complexes in the sample. Static SIMS uses a low current density primary ion beam in order to maintain monolayer surface integrity for long analysis periods (into several hours).²⁰ SIMS measurements were taken on a PHI TRIFT III ToF-SIMS with a Gallium ion gun. Static SIMS conditions were used to prevent damage to the sample. The primary ion beam was kept below 10¹³ ions/cm². Under these low dose conditions, the surface atomic layer is kept intact for several hours. Ga⁺ ions were sputtered over a 100 μm area for 10 seconds to remove surface contamination without destroying the underlying sample.

Results and Discussion

Evaporative thinning of the deposited flakes produces high-quality, ultra-thin nanosheets of the ternary compound. Figure 2 contains low magnification optical images of one such sheet pre (a) and post (b) evaporative thinning on a 300 nm SiO₂/Si substrate. The contrast between the nanosheet and the substrate decreases as the sheet height is reduced to nanometer scale. Figure 2c shows an SEM image of the same sheet. Both the optical and SEM images show that the sheet has retained its lateral dimensions, without any lateral shrinking during the evaporative thinning. Figure 3 is comprised of the corresponding AFM image and profile of the thinned nanosheet. The AFM image and profile show that the nanosheet is 1.2 nm in thickness with slight variation. Both

the AFM and SEM images indicate that the wide-area (15 micron) sheets are smooth and continuous, without holes or tears. However, the key question is how the composition of these large area nanosheets compares to their deposited, thick counterparts.

To probe this question, STEM EDS maps were taken on $\text{Bi}_2\text{Te}_{2.9}\text{Se}_{0.1}$ nominal composition flakes before and after evaporative thinning. Figure 4 shows the STEM HAADF image, as well as EDS mapping of the Bi L edge, Te K edge, and Se K edge of $\text{Bi}_2\text{Te}_{2.9}\text{Se}_{0.1}$ after initial deposition, in their thick, bulk-like state. Bi, Te, and Se signals are all consistent throughout the flake, suggesting homogeneous distribution of the elements without phase segregation. The EDS spectrum extracted from the mapping shows Bi, Te and Se peaks, and quantification from the spectrum shows stoichiometry close to the nominal composition as shown in Table 1. The edges for quantification were chosen based on carefully calibrated k-factors of Bi_2Se_3 and Bi_2Te_3 .²¹ These results show that after the initial deposition, the chemical composition aligns between the nominal and experimentally determined stoichiometries.

Similar STEM EDS maps were taken from the same flakes after evaporative thinning. In order to examine the flake composition's evolution, a partially thinned flake was obtained by carefully controlling the time and temperature. Figure 5(a) shows the STEM secondary electron image of the thinned flake, while Figure 5(b) through (d) shows the STEM EDS mapping of the thinned flake. The thick part of the flake continues to show consistent mixing of the three elements as shown in Figure 5 (b) to (d). Due to the ultra-thin nature of the thinned region, the EDS mapping does not show obvious Bi, Te, or Se signal. However, with longer collection times the EDS spectra from the thin region have better signal to noise ratios. The EDS spectrum in Figure 5 (e) from the thinned region shows all elements are present. Quantification from these EDS spectra shows that the evaporative thinning corresponds to significant changes in stoichiometry in the ternary compound, as indicated

in Table 1. Table 1 includes the ratios of the highest-intensity relevant x-ray peaks, and the corresponding estimated atomic percentage quantifications. The thinned flake is now predominately Bismuth, as calculated from the STEM-EDS spectra. Further, the atomic percentage ratio of Se/Te has increased by more than 10x. This methodology was employed across many samples with similar Bi-rich nanosheet outcomes.

As a further source of composition information, we characterized the compounds both before and after evaporative thinning with ToF-SIMS. Figure 6(a) shows SIMS profiles of a representative sheet before thinning. Given their respective electronegativities, a positive ion mode was used to measure the Bi ion signal, and negative ion mode to measure the Te and Se ion signal. Reference Bi_2Te_3 and Bi_2Se_3 compounds were used to determine the appropriate SIMS conditions and to determine the most appropriate isotopes to compare. The reference samples suggest that the Bi^{209} isotope, the Te^{128} isotope, and both the Se^{78} and Se^{80} isotopes have the most reliable signal intensities. The SIMS profiles confirm that Bi, Te, and Se are present in the composition on the surface of the deposited, thick $\text{Bi}_2\text{Te}_{2.9}\text{Se}_{0.1}$ sheet before thinning. After evaporative thinning, based on the SIMS spectra of the post-thinned flake in figure 6b, Bi, Te, and Se are all present. After the Ga^+ sputtering to clean the surface, no appreciable amounts of oxidized species (SeO^- , TeO^-) were detected. While quantitative SIMS analysis can be quite complex, the qualitative trends of the relative intensity ion ratios in the SIMS profiles parallel the EDS profiles for the chalcogenides. Before thinning, there is more Te present in the sample than Se. After thinning, the Te intensity has dropped precipitously while the Se intensity has remained relatively stable. Both EDS and SIMS indicate that the post-thinned nanosheet is Bismuth rich.

The evaporative thinning synthesis provides a facile way to make a nanosheet Bi-rich ternary compound not previously synthesized in 2D. Based on both compositional techniques, evaporative

thinning preferentially removes Te and Se from the structure. This can be understood via a thermodynamic vapor pressure mechanism.

Both Bi_2Se_3 and Bi_2Te_3 disassociate in the vapor phase into their constituent ions Bi^{3+} and $\text{Se}^{2-}/\text{Te}^{2-}$.²² Based on mass effusion experiments, these constituent ions form species that sublime from the Bi_2Q_3 structure at different rates as follows:

- $p(\text{Te}_2) > p(\text{BiTe}) \gg p(\text{Bi}_2)$
- $p(\text{Se}_2) > p(\text{BiSe}) > p(\text{Bi}_2)$

Of these various species Te_2 is the most volatile corresponding to Bi_2Te_3 being more volatile than Bi_2Se_3 .

Our proposed vapor pressure-driven mechanism describes both the original physical vapor deposition step as well as the later evaporative thinning step. In both cases, the Bismuth and Chalcogen ions dissociate. During the deposition phase, there are enough nucleation events and energy for re-association into the favorable stoichiometry during flake formation on the silicon substrate.

In the thinning step material is only vaporized and removed. There is no opportunity for re-association. As such, the vapor pressure differences dominate so that Te, and to a lesser degree Se, are driven from the structure, leaving behind a Bi-rich 2D sheet. Figure 7a shows pictorially this preferential evaporation process taking place, with more Te leaving the structure than the other elements. This corresponds to Te vacancies having a lower formation energy than Se vacancies in some intermediate compositions such as $\text{Bi}_2\text{Te}_2\text{Se}$.²³ As the Bi sheets inside the crystal structure retain their hexagonal symmetry, the final structure of the Bi-rich nanosheet is hexagonal as

indicated by the TEM diffraction pattern in Figure 7b. From the diffraction pattern, the lattice parameter of the thinned sheet is calculated to be 4.44 Å. This lattice parameter aligns nicely with those calculated for similar Bi-rich bulk compounds, Bi₇Se₃ (4.43 Å) and Bi₇Te₃ (4.47 Å), with differentiation between the two within the margin of error.^{24,25, 26} The lattice parameter data suggests that the nanosheet structure is similar to these layered Bi-rich Bi₇Q₃ compounds. The structure for bulk Bi₇Se₃ consists of the quintuple layer slabs characteristic of Bi₂Se₃, with additional Bi-Bi bilayer slabs. For the evaporatively thinned nanosheets, the structure is likely analogous to this one, with both Se and Te atoms incorporated in the Chalcogen atomic positions.

For bulk Bi-rich compounds, the density of states have been calculated to be semi-metallic, with both holes and electrons contributing to conductivity.²⁶ However, quantum confinement often opens up a bandgap, and interaction between the topological surface states has been observed in monolayer Bi₂Te₃ nanosheets.²⁷ Precise electronic characterization is warranted to probe these transport phenomena in the Bi-rich nanosheets.

By understanding this mechanism, we see that different sublimation conditions can cause large changes in nanoscale stoichiometry even while the symmetry remains the same. With extensive work being done on nanoscale members of the Bismuth-Chalcogenide compounds, compositional analysis is critical to determine the impact that different synthetic methods can have on the nature and properties of these materials.

Conclusions

A new 2D Bi-rich composition in the ternary Bi-Te-Se system has been fabricated via an evaporative thinning technique. Utilizing both STEM-EDS and SIMS, we have been able to determine the compositional shift from Bi₂Te_{2.9}Se_{0.1} to a Bi-rich nanosheet as a result of

chalcogen ions being preferentially driven out of the structure due to vapor pressure differences. The resultant structure shows single-crystal hexagonal symmetry, with a lattice parameter aligning with a Bi-rich phase. Based on analogous bulk Bi-rich Selenide and Telluride structures, the 2D Bi-rich nanosheet structure likely includes a Q(1)–Bi–Q(2)–Bi–Q(1) quintuple layer slab with Bismuth bilayers to accommodate the additional Bismuth atoms. With their predominantly Bismuth character and Chalcogen doping, these nanosheets should be further explored to probe their unique electronic properties.

Evaporative thinning could potentially be utilized as a unique method to create 2D Bismuth-rich Selenides $\text{Bi}_n(\text{Bi}_2\text{Se}_3)$ from the bulk Bismuth-Selenium series.

Further, the mechanism of Bi-rich nanosheet formation highlights that moderate temperature and pressure changes can cause large shifts in stoichiometry of these compounds. Within the Bi-Te-Se systems even small changes in composition can incur native defect formation, changing both carrier concentrations and majority carrier type. As such, detailed compositional analysis is vital to correctly probe the topological insulating and thermoelectric performance of similar compounds.

Acknowledgements

This material is partially based upon work supported by the Air Force Office of Scientific Research under Award No. FA9550-12-1-0280. This work made use of the EPIC facility (NUANCE Center-Northwestern University), which has received support from the MRSEC

program (NSF DMR-1121262) at the Materials Research Center; the International Institute for Nanotechnology (IIN); and the State of Illinois, through the IIN.

The authors would also like to acknowledge the aid of Dr. Costantinos Stoumpos in preparing the schematics, and Jeffrey Cain for instructive discussions.

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Figures:

Figure 1:

Caption: Schematic drawing of the $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ layered structure, which has the same symmetry as Bi_2Se_3 and Bi_2Te_3 . The dotted lines highlight the symmetry of the structure and do not represent bonds. The top quintuple slab shows the atomic positions within a single unit cell, while the bottom quintuple slab has been expanded to highlight the hexagonal symmetry of each atomic layer.

Figure 2:

Caption: (a) Optical image of $\text{Bi}_2\text{Te}_{2.9}\text{Se}_{0.1}$ sheet before thinning, (b) Optical image of the same sheet after evaporative thinning, (c) SEM image after evaporative thinning.

Figure 3:

Caption: (a) AFM image of thinned Bi-rich nanosheet, (b) AFM height profile after thinning.

Figure 4:

Caption: STEM EDS mapping of $\text{Bi}_2\text{Te}_{2.9}\text{Se}_{0.1}$ flake before thinning. (a) HAADF image of the flake. (b) to (d) are the mappings of Se K, Te K and Bi L edges, respectively. (e) is a spectrum from the area indicated by the red square box in (a). The Cu peaks arise from the brass sample holder. The inset of (e) is a zoomed-in spectrum of the Bi L and Se K edges.

Figure 5:

Caption: STEM EDS mapping of $\text{Bi}_2\text{Te}_{2.9}\text{Se}_{0.1}$ flake after thinning. (a) Secondary electron image of the partially thinned flake. (b) to (d) are the mappings of Se K, Te K and Bi L edges, respectively. (e) is a summed spectrum from the area indicated by the red square box in (a). The Cu and Fe peaks arise from the sample holder and microscope column respectively. The inset of (e) is a zoomed-in view to show Bi L and Se K edges.

Table 1:

	Bi L/ Te K	Bi L/ Se K	Te K / Se K	Bi L Atomic % (error)	Te K Atomic % (error)	Se K Atomic % (error)
Thick Sheet	7.8	20.2	2.6	44.9 (.34)	52.4 (1.8)	2.6 (.21)
Thin Nano- sheet	21.8	9.7	0.3	65.8 (2.9)	23.2 (17.9)	11.0 (1.7)

Caption: Comparison of EDS peak ratios and resultant EDS-derived stoichiometries before and after evaporative thinning.

Figure 6:

Caption: (a) Representative deposited $\text{Bi}_2\text{Te}_{2.9}\text{Se}_{0.1}$ thick sheet SIMS spectra, (b) Representative spectra from a collection of post-thinned Bi-rich nanosheets. Spectra are of the most common Bi, Te, and Se mass isotopes.

Figure 7:

Caption: (a) Schematic of evaporative thinning process within a single unit cell. Chalcogens are preferentially driven from the structure, leaving behind a predominantly Bismuth sheet. The dotted lines highlight hexagonal symmetry within the structure. The evaporative thinning process leads to a final hexagonal symmetry, shown in (b), the diffraction pattern of a Bi-rich nanosheet along the [001] orientation.