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Synthesis and Properties of (BiSe)_{0.97}MoSe₂: A Heterostructure Containing Both 2H-MoSe₂ and 1T-MoSe₂

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ABSTRACT: The metastable heterostructure, (BiSe)_{0.97}MoSe₂, containing alternating bilayers of BiSe and MoSe2 trilayers was synthesized using the modulated elemental reactant method to determine if charge transfer from BiSe to MoSe₂ would stabilize the metallic 1T polymorph of MoSe₂. Optimum synthesis conditions were determined by following the structural evolution as a function of temperature. The structure of the product contained distorted rock salt-structured BiSe layers alternating with hexagonal MoSe₂ layers. High-angle annular dark field scanning transmission electron microscopy images revealed that two different polymorphs of MoSe₂ coexisted in (BiSe)_{0.97}MoSe₂. Raman spectroscopy confirmed the presence



of 1T MoSe₂ layers. X-ray photoelectron spectroscopy (XPS) indicated that there were two different electronic states for both Mo and Bi. The Mo states are consistent with having octahedral and trigonal prismatic coordination of molybdenum as found in the 1T and 2H polymorphs of MoSe₂. The two different electronic states for Bi are consistent with the presence of antiphase boundaries in the BiSe layers. Estimating the relative amount of each electronic state from the XPS spectra indicates that the percentage of 1T MoSe₂ is about 40%, whereas the amount of Bi^{3+} in the BiSe is approximately 60%. The measured resistivity increases as temperature is decreased, consistent with an activated conduction mechanism with a small activation energy (~0.05 eV). The temperature stability and low resistivity of $(BiSe)_{0.97}MoSe_2$ make it potentially interesting as a means of improving electrical contacts to MoSe₂.

roup 6 transition-metal dichalcogenides (MoS₂, MoSe₂, \mathbf{J} WS₂, and WSe₂) have attracted tremendous research interest because they change from indirect to direct band gap semiconductors at the monolayer limit.¹⁻⁵ This makes them attractive candidates for integration into a variety of ultrathin electronic and optoelectronic devices,^{6,7} such as field-effect transistors,⁸ light-emitting diodes,^{9,10} and photovoltaics.^{11,12} Their naturally occurring layered structure, with strong covalent bonding in the xy plane and weak van der Waals forces along the z axis, results in monolayer surfaces that are free of dangling bonds that commonly give rise to deep-gap trap states in tetrahedral semiconductors, such as silicon.¹ There has also been a growing body of literature on van der Waals heterostructures, in which 2D components are stacked on top of or alongside one another to impart or tune properties.¹⁴ Heterostructures containing group 6 dichalcogenides have been used to extend exciton lifetimes,¹⁵ tune band gaps,¹⁶ and improve carrier collection efficiencies.¹⁷

A significant challenge in device fabrication has been the difficulty of making Ohmic contacts to semiconducting dichalcogenides.¹⁸ Low-resistance Ohmic contacts are required for TMDs and TMD heterostructures to reach theoretically predicted intrinsic transport and optimal device performances. Common strategies used in bulk semiconductors such as degenerately doping source/drain regions are not possible in 2D material systems because of their extremely thin

dimensions.¹⁹ A novel strategy around this problem uses the metallic 1T phase of the group 6 TMDs with octahedral coordination of the metal to make electrical contact to the semiconducting 2H phase with trigonal prismatic coordination. A 2H-MoS₂ transistor with 1T-MoS₂ source/drain contacts significantly improved contact performance (low contact resistance) with zero gate bias.^{18,20} This strategy has also been used successfully in MoTe₂²¹ and WSe₂ systems.²²

Although significantly improved contact performance has been realized, there are several challenges. The synthesis of the 1T phase is commonly achieved by intercalation of the thermodynamically stable 2H phase,^{13,23} and lithium is not ideal due to its high mobility and volatility. The 1T phase is kinetically stable after deintercalation, and the phase transition from the 1T phase back to the thermodynamically stable 2H structure is reversible at low temperatures (~200 °C). This presents challenges in further processing of devices and limits higher temperature applications.²⁴ It is recognized that further investigation into stabilizing the metallic 1T phase is needed if the 2H to 1T phase engineering is to be a viable contact engineering strategy.²⁵

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In this study, we synthesized the metastable layered compound (BiSe)_{0.97}MoSe₂ containing alternating bilayers of BiSe and MoSe₂ trilayers. As BiSe donates charge to adjacent dichalcogenide layers in heterostructures containing NbSe₂ and TiSe₂, our goal was to determine if the BiSe layer donates charge to the MoSe₂ layer resulting in octahedral coordination of Mo or if BiSe creates antiphase boundaries creating a mix of Bi³⁺ and Bi^{0, 26-28} Our synthesis approach was to sequentially deposit elemental layers to form a precursor that has a composition modulation that mimics that of the targeted compound.²⁹ During low-temperature annealing, the precursor self-assembled forming a heterostructure. The heterostructure is stable to at least 350 °C. To the best of our knowledge, this is the first report of a ternary Bi-Mo-Se compound, and the first report of a misfit layer compound forming between BiSe and MoSe₂. High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images showed that the heterostructure consists of a mixture of 2H and 1T phases. X-ray photoelectron spectroscopy (XPS) showed that the compound contains ~50% of each MoSe₂ polymorph and that Bi also exists in two different oxidation states. Ohmic contacts were formed using indium metal, and temperaturedependent resistivity measurements showed that (Bi- $Se_{0.97}MoSe_2$ has an activated conductivity with a small activation energy (~0.05 eV).

EXPERIMENTAL SECTION

Heterostructure precursors were prepared by the modulated elemental reactants (MERs) method, which is a modified physical vapor deposition technique described in detail elsewhere. 29,30 Commercially obtained elements were evaporated in a custom-built deposition chamber while maintaining a vacuum of less than 1×10^{-6} Torr throughout the deposition. Electron beam guns were used to evaporate bismuth and molybdenum and an effusion cell was used to evaporate selenium. Evaporation rates were controlled and monitored by a set of piezoelectric quartz crystal microbalances. Rates of 0.03, 0.02, and 0.05 nm/s were used for bismuth, molybdenum, and selenium, respectively. Si(100) substrates were used for structural characterization and fused silica substrates were used for electrical measurements. During deposition, the substrates were mounted on a motorized carousel that moved above each elemental source. A LabVIEW software package controlled the sequence of elemental layers and opened and closed pneumatically controlled shutters. The time required to obtain the desired thicknesses of the elemental layers was determined by integrating the deposition rates sent from the quartz crystal microbalances. Samples were prepared with different numbers of repeating layers of SelMolSelBi. After deposition, the precursors were annealed for 10 min at temperatures between 50 and 450 °C on a hot plate in a dry nitrogen atmosphere with oxygen concentration <1 ppm. X-ray fluorescence (XRF) intensities were measured, and X-ray diffraction (XRD) scans were collected after annealing at each temperature.

A variety of different characterization techniques was used to characterize the precursor and the final compound. Atomic composition was evaluated using a Rigaku ZSX Primus II wave dispersive XRF spectrometer with a rhodium source, using the procedure described by Hamann et al.³¹ Low-angle X-ray reflectivity (XRR) and high angle XRD measurements for both the as-deposited and thermally treated films were obtained using a Bruker D8 Discover diffractometer, equipped with Cu K α radiation and a Göbel mirror. Out-of-plane structural refinement of the high-angle scans by Rietveld analysis used the FullProf software package^{32,33} to determine the position of atomic planes along the *c*-axis. A Rigaku SmartLab (Cu K α radiation) was used to collect grazing incidence in-plane XRD (GIXRD) scans. In-plane diffraction data was also obtained at the Advanced Photon Source on beamline 33-BMC using 0.0652533 nm radiation. The in-plane diffraction data obtained as a function of annealing conditions was analyzed by LeBail fitting using FullProf to determine the *a*- and *b*-axis lattice parameters. Electron transparent lamellae for electron microscopy investigation were made by a wedgeprep method³⁴ with a Ga⁺ focused ion beam on a Thermo Scientific Helios Nanolab 600i. HAADF-STEM images were collected using an aberration-corrected Thermo Scientific Titan (300 kV electron beam) TEM at the Pacific Northwest National Laboratory. Temperature-dependent resistivity measurements were taken between 150 and 295 K using the van der Pauw method³⁵ using a home-built system. The samples for resistivity measurements were deposited on fused silica substrates through a cross-shaped mask. Pressing indium on the ends of the cross resulted in Ohmic contacts. Raman measurements were carried out under ambient conditions on a LabRam HR800 Raman system with 514.7 nm wavelength excitation and a 2400 grooves per mm grating.

XPS measurements were carried out at room temperature in a UHV chamber at a pressure of approximately 3×10^{-10} mbar. A SPECS XR50M X-ray source and SPECS FOCUS 500 crystal monochromator provided Al K α radiation for excitation of the photoelectrons, which were analyzed by a SPECS Phoibos 150 MCD-9 hemispherical analyzer with nine channeltrons. The XPS measurements were carried out in normal emission detection geometry, and the X-ray source was oriented at an angle of about 45° relative to the c-axis of the crystal. All binding energies are referenced to the Au 4f 7/ 2 core level at 84.0 eV. To obtain clean surfaces by cleaving, we modified a method described previously.³⁶ In brief, the sample was mounted between two steel plates using low-degassing EPO TEK H72 epoxy resin on the sample plane and silver-filled EPO TEK H22 epoxy to make electrical contacts at the sample edges. The top plate was then broken off in the load lock of the system under dry N₂ flow. After rapidly transferring the sample into UHV, the absence of contaminants such as oxygen or carbon was shown by XPS survey spectra. The cleaving process on a given sample could be repeated by attaching another steel plate to the cleaved surface. High-resolution core level spectra were analyzed by fitting multiple convolved Gaussian-Lorentzian peak shapes (Voigt profiles) to the experimental data. The Lorentzian lifetime peak widths used in the fitted spectra were determined by fitting the Mo 3d, Se 3d, and Bi 5d spectra of commercially available MoS2 and Bi2Se3 single crystals. A Shirley background was used for all shown spectra.

RESULTS AND DISCUSSION

Precursors were prepared by repeatedly depositing a sequence of BilSelMolSe elemental layers. The thickness of each elemental layer was adjusted to mimic the atomic composition profile of the targeted (BiSe)_{0.97}MoSe₂ structure. The initial target number of atoms per Å² for each element in the BilSel MolSe sequence was estimated using the structure of bulk $MoSe_2$ and previously prepared compounds containing a rock salt-structured BiSe layer.^{26–28} The number of atoms per unit area from this estimate was close enough to that found in the prepared compounds that no additional precursors were required. The actual number of atoms per Å² for each element in the precursor was within five percent of the values calculated from the in-plane lattice parameters of (BiSe)_{0.97}MoSe₂. The period of the repeating sequence of BilSelMolSe layers in the precursor was measured using XRR and found to be 1.331(7) nm, which is slightly larger than the simple sum of the lattice parameters of the constituents. This larger value results from the inefficient packing arrangements of atoms in the noncrystalline precursor and the slight excess of Se deposited, which was found to facilitate self-assembly.

An annealing study was conducted to determine if the target BiSe/MoSe₂ structure formed and to identify the optimal thermal treatment for the self-assembly, if it did. XRF intensity for all elements remains constant at the target stoichiometry after annealing up to and including 350 °C. Decreases in the

XRF intensity of Se and Bi were observed after the 450 $^{\circ}$ C anneal. The specular XRD patterns collected during the annealing study are shown in Figure 1. The as-deposited scan



Figure 1. Specular XRD patterns collected after annealing at the indicated temperatures. The indices of the reflections are provided above the top diffraction pattern. The reflections from Bi₂Se₃ in the scan after annealing at 450 °C are identified by the asterisks (*). The small feature at $2\theta \approx 62$ is from the diffractometer stage.

contains several broad reflections. The broad reflection at low angle is due to the elemental layering, and the weaker broader reflections at higher angles are the coherent scattering from the beginning of the self-assembly process that occurs during the deposition. The position of the lowest angle maximum is shifted to slightly higher angles relative to the position calculated from the position of the higher angle reflections. The *c*-axis lattice parameter determined from the higher angle reflections increases monotonically with annealing temperature up to 350 °C. The first maxima in the diffraction pattern steadily shifts to higher angles and its shape evolves as the annealing temperature increases, becoming coherent with the higher angle reflections after the 350 °C anneal. After the 350 °C anneal, the reflections can all be indexed as 00l reflections, indicating preferred alignment. The c-lattice parameter after annealing at 350 °C (1.245(2) nm) is close to the c-axis lattice parameter reported previously for (BiSe)₁(MSe₂)₁ compounds, where M is Nb or Ti.^{26,37} This suggests that the sample is selfassembling to a compound with BiSe and MoSe2 sheets oriented parallel to the substrate. Although the position of the reflections does not change when annealed at 400 °C, the reflections increase in intensity and become narrower. Evidence for the formation of Bi2Se3 is observed after annealing at 450 °C, with maxima growing in at $2\theta \approx 19^{\circ}$ and 48.6°.38

Grazing-incidence in-plane (hk0) XRD scans were also collected as a function of annealing temperature (Figure 2). The as-deposited scan contains very weak and broad maxima, suggesting that crystalline BiSe and MoSe₂ have not formed during the deposition. The intensity of the broad reflections increases slightly after annealing at 200 °C and shifts to lower angles, but distinct reflections for BiSe and MoSe₂ only become evident after the film is heated at 300 °C.

The ratios of the intensity of the BiSe and MoSe₂ Bragg maxima change as a function of annealing temperature, reflecting the different rates at which the two layers self-assemble. At 450 °C, an additional reflection appears, which is consistent with the formation of Bi₂Se₃.³⁸ The XRF data and the diffraction data suggest that optimal annealing temperature is 350-400 °C.



Figure 2. In-plane XRD patterns collected after annealing at the indicated temperatures. The position of the reflections is consistent with those expected for BiSe and MoSe₂ at annealing temperatures of 400 °C or less. After annealing at 450 °C, a reflection appears at $2\theta \approx 24.5^{\circ}$, which can be assigned as the (100) reflection of Bi₂Se₃.

Low angle XRR scans were collected as a function of annealing time at a temperature of 350 °C to determine the optimal annealing conditions. The scans, shown in Figure 3,



Figure 3. Low-angle XRR patterns collected after annealing at 350 $^{\circ}\mathrm{C}$ for the times indicated above the scans.

contain two Bragg reflections from the targeted heterostructure and periodic oscillations resulting from the interference of scattered intensity off the top and bottom interfaces of the film (Kiessig fringes). As annealing time increases, the Kiessig fringes become more intense and can be observed to higher angles. The increase in the highest angle where Kiessig fringes are observed indicates that the top and bottom of the film are becoming more parallel, according to Parratt.³⁹ The number of minima between the critical angle and the first Bragg reflection in the sample annealed for 30 min matches the number of repeat units that were deposited (32). The consistency of the distance between Kiessig fringes and the systematic changes in their intensity indicate that the film formed a coherent structure. For a perfect sample, the thickness of the film should be equal to the *c*-lattice parameter determined from the highangle specular diffraction pattern (1.245(2) nm) multiplied by the number of unit cells deposited (32 layers). The calculated thickness (39.84(6) nm) is within error of the thickness of the film calculated from the position of each fringe maximum using Bragg's law corrected for refraction, 39.83(5) nm. The XRR scan after 30 min of annealing at 350 $^{\circ}\mathrm{C}$ is consistent with each repeat sequence of BilSelMolSe layers in the precursor self-assembling to form a single unit cell of (BiSe)_{0.97}MoSe₂. These data suggest that the optimal conditions for selfassembling the precursor to the targeted heterostructure are annealing at 350 °C for 30 min.

An in-plane XRD pattern of a precursor annealed at $350 \,^{\circ}$ C for 30 min collected at the Advanced Photon Source (beamline 33-BM-C) is shown in Figure 4. All of the reflections in the



Figure 4. In-plane XRD scan of an optimally annealed $(BiSe)_{0.97}(MoSe_2)_1$ sample. The *hk*0 indices for the MoSe₂ and BiSe sublattices are provided above each Bragg maxima. The lattice parameters resulting from a LeBail fit are summarized in Table 1.

pattern could be indexed as hk0 reflections arising from independent hexagonal and rectangular lattices. The lattice parameters of each were refined using a LeBail fit and are summarized in Table 1. The *a*-axis lattice parameter of the

Table 1. In-Plane Lattice Parameters for Each Sublattice from a LeBail Fit of the Diffraction Scan Shown in Figure 4

$MoSe_2 a (nm)$	BiSe a (nm)	BiSe b (nm)	misfit
0.332(1)	0.461(1)	0.426(1)	0.97

hexagonal sublattice (a = 0.332(1) nm) is consistent with that of MoSe2.40-44 The refinement of the lattice parameters of the rectangular basal plane unit cell yielded a = 0.461(1) nm and b = 0.426(1) nm. This is similar to the structure reported for BiSe in other BiSe heterostructures containing one layer of interleaved TMD (a = 0.447(1) nm, b = 0.428(1) nm for $(BiSe)_{1.11}NbSe_2^{26}$ and a = 0.456(1) nm, b = 0.424(1) nm for $(BiSe)_{1.15}TiSe_2^{35}$). The difference between the *a* and *b* lattice parameters, however, is slightly larger in (BiSe)_{0.97}(MoSe₂)₁. Mitchson et al. showed that the lattice parameters of the BiSe sublattice depended on the amount of charge that is transferred from the BiSe lattice into adjacent TX₂ layers based on changes observed in $(BiSe)_{1.16}(NbSe_2)_n$ compounds as n is increased.²⁷ Wood et al. also reported changes to the dimensions of the BiSe sublattice in the $(BiSe)_{1,14}[(TiSe_2)_n]$ system as *n* was increased from 2 to 4.²⁸ By analogy, the larger difference between the in-plane lattice parameters observed here may be rationalized on the basis of a larger charge transfer from BiSe to MoSe2. The misfit parameter, reflecting the difference in the atomic densities in the two substructures, was calculated from the in plane lattice parameters and is included in Table 1.

Figure 5 contains a specular XRD pattern of an optimally annealed sample along with a Rietveld refinement of the pattern. The positions of the atomic planes along the *c*-axis determined from the refinement are shown in the inset figure. The distance between the Mo and Se planes in the MoSe₂ layer refined to a value of 0.164(1) nm, which is 0.003 nm smaller than that reported for MoSe₂ itself.^{40–44} The refined distance between Se plane of the MoSe₂ layer and Bi plane in the BiSe layer is 0.297 nm, which is 0.004-0.013 nm larger than what is



Figure 5. Specular XRD scan of an optimally annealed precursor and its associated Rietveld refinement. The purple trace at the bottom of the figure is the residuals between the calculated and experimental patterns. The inset image contains the distance between the planes along the *c*-axis. All distances in the inset are given in nanometers.

reported in other ferecrystalline compounds containing BiSe adjacent to a dichalcogenide layer.^{26,27,37} Although Bi and Se in the BiSe layer would be expected to be in the same plane if it self-assembled into an ideal rock salt structure, the refinement converged with the Bi plane closer to the Se plane in MoSe₂ than the Se plane in BiSe by 0.037(1) nm. Similar puckering has been reported for other BiSe-containing systems.^{26,27,37} Wiegers suggested that the puckering results from an interlayer charge transfer between the BiSe layer and the dichalcogenide layer, which causes the cations in the MX layer to protrude into the interlayer gap toward the anion (X) atomic centers in the TX₂ layer.⁴⁵

Cross-sectional HAADF-STEM images provided further information about the structure of the two sublattices and their stacking. A representative image (Figure 6) contains



Figure 6. Cross-sectional HAADF-STEM image showing alternating layers of BiSe and $MoSe_2$. The $MoSe_2$ layers display two distinct atomic arrangements consistent with octahedrally (1T) and trigonal prismatically (2H) coordinated Mo.

alternating BiSe bilayers and MoSe₂ trilayers with flat, atomically sharp interfaces between them, consistent with the diffraction data discussed previously. The orientation of each layer varies from plane to plane throughout the image. This random rotational disorder is a common feature of compounds made from layered precursors.¹⁴ The layers in the image orientated along the low-index zone axes of the BiSe sublattice are consistent with a distorted rock salt structure. There were only limited areas where the sample was in the required



Figure 7. XPS data (black circles) of the (a) Mo 3d (b) Se 3d, and (c) Bi 5d core levels. The presence of two different types of Mo is evident in figure (a), consistent with trigonal prismatic (2H) and octahedral (1T) Mo in the $MoSe_2$ layers of $(BiSe)_{0.97}MoSe_2$. In the Se3d spectrum, three different types of Se are present; Se in 2H $MoSe_2$, Se in 1T $MoSe_2$, and an additional contribution from the Se atoms in BiSe. In the Bi 5d spectrum, two contributions are required to describe the data.

orientation to detect the antiphase boundaries, and we did not observe antiphase boundaries in the BiSe layers as seen previously in $(BiSe)_{1,16}(NbSe_2)_n^{27}$ Two distinct coordination environments were observed in the MoSe, layers aligned along the low-index zone axes. Chevrons were observed in some layers, consistent with a (110) orientation of a TX₂ compound in which the transition-metal atom has a trigonal prismatic coordination. This is the thermodynamically stable coordination of Mo in MoSe2. Diagonal slashes were observed in other layers, however, consistent with a (110) orientation of a TX₂ compound with the transition-metal atoms having octahedral coordination. Octahedral coordination of Mo in MoSe₂ layers was observed in LiMoSe₂ and other intercalated MoSe₂ compounds.^{13,23} This suggests that two different oxidation states for the Mo in $(BiSe)_{0.97}MoSe_2$ exist simultaneously. The different layers do not appear to form discrete, continuous layers, but instead nanoscale regions of both appear to be randomly distributed.

XPS spectra were collected to obtain information about the different electronic states of the different elements in (BiSe)_{0.97}MoSe₂. The spectra were collected from freshly cleaved, buried interfaces by cleaving the film along the van der Waals gaps to expose interior interfaces. This process was repeated on three different sample areas, and the representative spectra are presented in Figure 7. The Mo 3d core level spectrum (Figure 7a) was fitted using two Voigt doublets with identical peak shape, meaning identical Gaussian and Lorentzian peak width, spin-orbit separation, and intensity ratio of the 3d5/2 and 3/2 core levels. The positions of the doublets in energy are consistent with the different binding energies previously reported for octahedral and trigonal prismatic coordination of Mo in the 1T- and 2H-phase of MoSe₂.^{18,46,47} An additional signal is necessary to fit the spectrum, which stems from the coinciding Se 3s core level. The observed binding energies of the Mo $3d_{5/2}$ peak are 228.3 \pm 0.1 eV for the octahedral coordination and 228.9 \pm 0.1 eV for the trigonal prismatic coordination, consistent for all three samples investigated. Multiple components are also found in the Se 3d spectrum, shown in Figure 7b. Contributions from the 1T- and 2H-phase of MoSe, as well as the Se atoms bound in the BiSe layers have to be considered. The experimental data could be reproduced well by fitting three Voigt doublets with identical peak shape to the data. The chemical shift and intensity ratio between the two different coordinations of Mo were constrained to the values obtained from the fit of the Mo 3d core level. The core level position of $\text{Se3d}_{5/2}$ is 53.62(10), 53.89(10), and 54.47(10) for BiSe, 1T-MoSe₂, and 2H-MoSe₂, respectively. The Bi 5d core level spectrum, Figure 7c, also

requires multiple components. The peaks have a slight asymmetry toward lower binding energies, indicating the presence of two components. Fitting the spectrum with two Voigt doublets of identical peak shape gives binding energies of Bi $5d_{5/2} 25.00 \pm 0.10$ and 24.27 ± 0.10 eV. In a previous work on $(BiSe)_{1,16}(NbSe_2)_{n}$, these two components were assigned to Bi atoms being in either regular rock salt-type bonding (higher energy line) or at an antiphase boundary with Bi-Bi bonds between adjacent Bi atoms (lower energy line).²⁷ The component assigned to Bi atoms at the antiphase boundary appears at lower binding energy because of a smaller effective positive charge on these atoms due to electron localization. This suggests that antiphase boundaries are present in (BiSe)_{0.97}MoSe₂, even though none were directly observed in the HAADF-STEM images because of the limited sample size of areas with the correct orientation. The integrated intensity ratios of signals from octahedral and trigonal prismatic Mo in the 3 measured samples varied between 34 and 48% octahedral. We estimate that on average 40 \pm 10% of the MoSe₂ is present in the 1T-phase, which is consistent with the HAADF-STEM images. The intensity of the component at lower binding energy in the Bi 5d spectrum is approximately $40 \pm 10\%$ of the total peak intensity in (BiSe)_{0.97}MoSe₂. The energy difference and intensity ratio of the two components in the Bi spectrum is similar to those of the components assigned to the 1T- and 2H-polytype in the Mo 3d spectrum, suggesting that they are correlated. It is not possible to conclude from XPS alone, however, whether the lower binding energy component of the Bi 5d spectrum is a consequence of charge transfer, antiphase boundary formation, or a mixture of both.

Raman data collected on a (BiSe)_{0.97}MoSe₂ sample provides further evidence for the presence of 1T-MoSe₂ (Figure 8). The Raman spectra of a binary 2H-MoSe₂ thin film is also shown in Figure 8 as a reference, and all measured signals can be assigned to phonon modes of 2H-MoSe2.48 In BiSe0.97MoSe2, the A1g mode is shifted to lower wavenumbers, which is expected as the thickness of the MoSe₂ blocks are decreased to a monolayer.⁴⁹ Additional modes also appear at 106.3, 143.9, and 253.8 cm⁻¹. Gupta et al. observed similar modes at 106.4 and 150.7 cm⁻¹ in 1T-MoSe₂, along with a transition at 221.4 cm⁻¹, that are denoted as J_1 , J_2 , and J_3 , respectively.⁵⁰ These modes result from the reduction of in-plane symmetry from D_{3h} in the trigonal planar coordination of Mo in 2H-MoSe₂ to a lower in-plane symmetry in the 1T-phase, which has a distorted octahedral coordination of the Mo atoms. The J_3 mode is either not visible in BiSe_{0.97}MoSe₂ or is shifted to higher wavenumbers, presumably because of a strong ionic interaction between 1T-MoSe₂ with adjacent BiSe layers. The



Figure 8. Raman spectra of a binary $MoSe_2$ thin film with exclusively trigonal prismatic coordination (top) and $BiSe_{0.97}MoSe_2$ with both trigonal prismatic and octahedral coordination. The small peak marked with an asterisk at 300 cm⁻¹ originates from the silicon substrate.

strong ionic interaction is a consequence of the charge transfer between the BiSe layer and 1T-MoSe₂ that enables 1T-MoSe₂ to form.

Electrical resistivity data for a film of $(BiSe)_{0.97}MoSe_2$ is shown in Figure 9. The room-temperature resistivity is four



Figure 9. Temperature-dependent resistivity data for (Bi-Se) $_{0.97}$ MoSe₂.

orders of magnitude smaller than that measured for a binary MoSe₂ film also made by MER synthesis.⁵¹ The measured resistivity increases as temperature is decreased, indicating an activated conduction mechanism. At the lowest temperatures measured, the slope of the ln(resistivity) versus 1/T yields an activation energy of 0.05 eV for the carriers. For the higher temperatures measured, the slope increases, suggesting activation of additional carriers from an additional band with a larger activation energy. The activation energy is much smaller than the band gap of bulk 2H-MoSe₂ (\sim 1.53 eV)³ and a factor of 4 smaller than the activation energy for conduction measured for turbostratically disordered MoSe₂ (0.19 eV), both of which have trigonal prismatic Mo coordination. The magnitude and temperature dependence of the electrical resistivity of (BiSe)_{0.97}MoSe₂ is consistent with the STEM images, which indicates that the sample consists of nanoscale regions of MoSe₂ with trigonal prismatic coordination

randomly interspersed with nanoscale regions of $MoSe_2$ with octahedral coordination. The observed activated conductivity suggests that there is not a continuous network of metallic, octahedrally coordinated $MoSe_2$ regions, and we speculate that the carriers must need to hop from domain to domain. The small activation energy might also result from grain boundary depletion due to the small in-plane grain sizes.

CONCLUSIONS

The new metastable heterostructure (BiSe)_{0.97}MoSe₂ was prepared by self-assembling a precursor with a composition profile that matched that of the targeted compound. The structure of the compound consists of alternating bilayers of BiSe and MoSe₂ trilayers. Low index orientations in HAADF-STEM images show MoSe₂ layers with octahedral or trigonal prismatic coordination of Mo. XPS Mo 3d spectra show Mo in two different oxidation states, consistent with prior literature reports for 2H- and 1T-MoSe2. The Bi 5d spectrum shows that there are two different oxidation states for Bi as well, consistent with the presence of antiphase boundaries. This is consistent with electron donation from BiSe layers into MoSe₂ layers resulting in a mixed octahedral/trigonal prismatic coordination environment of the MoSe2 sublattice. The electrical data shows that the heterostructure is three orders of magnitude more conductive than binary 2H-MoSe₂ films, which is consistent with the inclusion of metallic 1T-phase domains. The temperature stability and low resistivity of this material make it potentially interesting as a means of improving contacts to MoSe₂ in device applications.

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The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

HAADF-STEM, high angle annular dark field scanning transmission electron microscopy; XRF, X-ray fluorescence; XRR, X-ray reflectivity; XRD, X-ray diffraction; GIXRD, grazing incidence in-plane X-ray diffraction; XPS, X-ray photoelectron spectroscopy

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