

Synthesis and Characterization of $[(\text{PbSe})_{1+\delta}]_4[\text{TiSe}_2]_4$ Isomers

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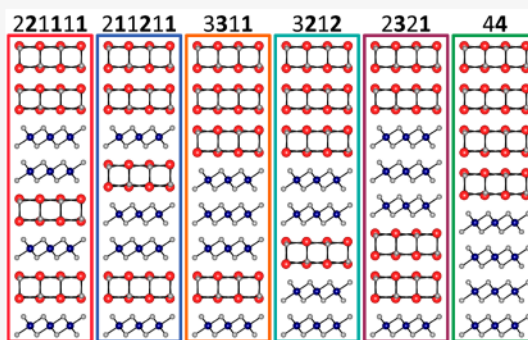
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ABSTRACT: This work presents the preparation of a series of $[(\text{PbSe})_{1+\delta}]_4[\text{TiSe}_2]_4$ isomers via a low temperature synthesis approach that exploits precursor nanoarchitecture to direct formation of specific isomers. The targeted isomers formed even when the precursors did not have the correct amount of each element to make a unit cell from each repeating sequence of elemental layers deposited. This suggests that the exact composition of the precursors is less important than the nanoarchitecture in directing the formation of the compounds. The as-deposited diffraction data show that the isomers begin to form during the deposition, and Ti_2Se_3 , in addition to PbSe and TiSe_2 , are present in the specular diffraction patterns. HAADF-STEM images reveal impurity layers above and below an integer number of targeted isomer unit cells. The structural data suggest that Ti_2Se_3 forms as Se is deposited on the initial Ti layers and remains throughout isomer self-assembly. During growth, the isomers deplete the local supply of Ti and Pb , creating diffusion gradients that drive additional cations toward the growth front, which leaves surface impurity layers of TiSe_2 and TiO_2 after the supply of Pb is exhausted. The deposited stacking sequences direct formation of the targeted isomers, but fewer repeating units form than intended due to the lack of material per layer in the precursor and formation of impurity layers. All isomers have negative Hall and Seebeck coefficients, indicating that electrons are the majority carrier. The carrier concentration and conductivity of the isomers increase with the number of interfaces in the unit cell, resulting from charge donation between adjacent layers. The opposite variation of the carrier concentration and mobility with temperature result in minima in the resistivity between 50 and 100 K. The very weak temperature dependence of the carrier concentration likely results from changes in the amount of charge transfer between the layers with temperature.



INTRODUCTION

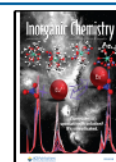
Molecular chemists have developed synthetic methods to prepare kinetically stable compounds with designed structures. This permits them to prepare multiple compounds containing the same number and type of elements connected in various arrangements.^{1–3} The local arrangement of atoms in a compound determines the physical, electronic, and biological properties it exhibits.^{4–11} For example, the five different structural isomers of hexane (hexane, 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane, and 2,3-dimethylbutane) all have different melting and boiling points as a consequence of their varying local arrangements.^{12–15} The ability to predict metastable–stable compounds via simple bonding rules (i.e., each carbon must have four bonds, each oxygen two bonds, and each hydrogen one bond) combined with an understanding of how to control the kinetics by manipulating reaction conditions (solvents, protecting groups, catalysts) enables molecular chemists to propose and test structure–property relationships toward optimizing desired properties.^{2,16–18}

It is more challenging to prepare structural isomers of inorganic compounds with extended structures, known as

polymorphs.¹⁹ Some well-known examples of polymorphs are vaterite, calcite, and aragonite. These compounds are different structural forms of calcium carbonate which exhibit different properties and free energies of formation.^{20–23} Typically, polymorphs are prepared by changing the reaction conditions (temperature, pressure, composition of the reacting system, etc.) so that the desired product is the most thermodynamically stable product in that reacting system. The structure of the product cannot be predicted from simple bonding rules or reaction conditions but is instead determined experimentally. For compounds only stable at high temperature or pressure, quenching the system to room temperature and pressure often traps the now metastable polymorph. The lack of knowledge of how to control reaction kinetics to obtain targeted inorganic, extended, structures severely limits the number of polymorphs

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that can be prepared.^{24–27} The holy grail in the synthesis of compounds with extended structures is a *design and mechanism-based approach to the synthesis of metastable compounds with targeted structure*.²⁸

Presented here is the synthesis and characterization of six different structural isomers of the compound $[(\text{PbSe})_{1+\delta}]_4[\text{TiSe}_2]_4$, which have the same composition and unit cell sizes, but the sequence of PbSe bilayers and TiSe_2 trilayers vary between isomers. The different isomers were prepared from precursors with sequences of an elemental layer designed to mimic the nanoarchitecture of the targeted isomer. While the amount of Pb and Ti in the deposited precursors was insufficient to make the desired number of repeating units, the artificial layering pattern of deposited layers still directed the self-assembly of the desired isomers. X-ray diffraction and HAADF-STEM data support the formation of the desired isomer nanoarchitectures with a decreased number of unit cells and additional impurity phases present on the top and bottom of the sample. As-deposited structural characterization indicated that TiSe_2 and PbSe crystallized during the deposition and were organized in stacking sequences consistent with the targeted isomer. Unexpectedly, Ti_2Se also crystallized during deposition at the interface with the substrate. The HAADF-STEM images suggest that the sample crystallizes from the bottom to the top, with the concentration gradients created at the growth front driving diffusion of Pb and Ti to the growing isomers. The measured electrical transport properties systematically vary as a consequence of changes in the nanoarchitecture, with lower resistivity and higher carrier concentrations found in compounds with a higher density of PbSe/ TiSe_2 interfaces within the isomer's unit cell. This is likely the result of charge transfer from PbSe to TiSe_2 being dependent on interfacial interactions. This work indicates that the self-assembly process begins during the deposition itself, driven by the heat of formation of the constituent layers. The nanoarchitecture of the precursor is sufficient to direct the formation of the targeted structure isomers, even if the composition of the precursor deviates significantly from that of the product, suggesting that the compounds are significant local energy minima in the free energy landscape.

MATERIALS AND METHODS

The $[(\text{PbSe})_{1+\delta}]_4[\text{TiSe}_2]_4$ heterostructure isomer precursors were prepared from physical vapor deposition of elemental layers onto silicon and fused silica substrates. Elemental Pb and Ti were evaporated from electron beam guns operating at 6 kV. Elemental Se was deposited from a Knudsen effusion cell. All elements were purchased from Alfa Aesar and were greater than 99.95% purity. Shutters above each evaporating source were programmed to sequentially open for the period of time required to deposit the appropriate thickness of each element to form either bilayers of PbSe or trilayers of TiSe_2 . The thickness of the elemental layers deposited was monitored by quartz crystal microbalances. PbSe bilayers were deposited with a Pb|Se shutter sequence and TiSe_2 trilayers with a Ti|Se shutter sequence. The sequence of Pb|Se and Ti|Se layers was controlled such that the nanoarchitecture of the precursor resembled the structure of the targeted isomer.²⁹ The sequence of Pb|Se and Ti|Se layers for each isomer was repeated 11 times to build a film that was approximately 550 Å thick. The elemental precursors were annealed at 350 °C for 30 min in an N_2 atmosphere to promote self-assembly into a crystalline heterostructure.^{30–35}

Amount of material per unit area was determined for each heterostructure using wavelength dispersed X-ray fluorescence (XRF) data. The data were analyzed using a previously published method in

which the raw intensity of each sample is determined by integrating under the signal curve and subtracting the background signal.³⁶ Calibration curves for each element were used to relate the measured signal to the number of atoms per unit area in each film.

Locked-coupled θ – 2θ and grazing-incidence in-plane X-ray diffraction (XRD) data were both collected using laboratory Cu–K α radiation with parallel beam optics on Bruker D8 Discover and Rigaku Smartlab instrumentation, respectively. Grazing-incidence scans were carried out with an incident angle of 1.0° and the detector 4.0° above the sample plane. Ab-initio X-ray reflectivity (XRR) patterns from the idealized targeted structures were generated with the Bede REFS modeling software assuming bulk densities.

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were collected using a probe aberration corrected FEI Titan 80–300 (300 kV, 120 mm camera length, $C_s < 1 \mu\text{m}$). Energy dispersive X-ray spectroscopy (EDS) data were acquired with a 2.3 ms dwell time per pixel and summed over several drift-corrected frames. Cross-sectional lamellae for STEM imaging were made using an FEI Helios 600 Nanolab dual-beam FIB.³⁷

Electrical measurements were carried out on a house-built closed-cycle He cryostat using a 1.5 T magnet. Van der Pauw resistivities and Hall resistivities both were collected on cross-pattern films through Cu wires and In contacts. Reported values were calculated using thicknesses from reflectivity measurements of the annealed films. Seebeck coefficients were also measured using a house-built system. One edge of the film was cooled slightly, and both S and ΔT were measured between two type-T thermocouples.

RESULTS AND DISCUSSION

XRR and XRD data indicate that the as-deposited precursors have a more complex structure than elemental layers in a particular pattern. Figure 1 contains a representative XRR pattern of an as-deposited $[(\text{PbSe})_{1+\delta}]_4(\text{TiSe}_2)_4$ isomer precursor (the 211211 isomer is shown). The pattern contains Kiessig fringes consistent with the 11 layers deposited, the first several Bragg reflections from the element layering, and Laue oscillations between the Bragg maxima. A film composed of 11

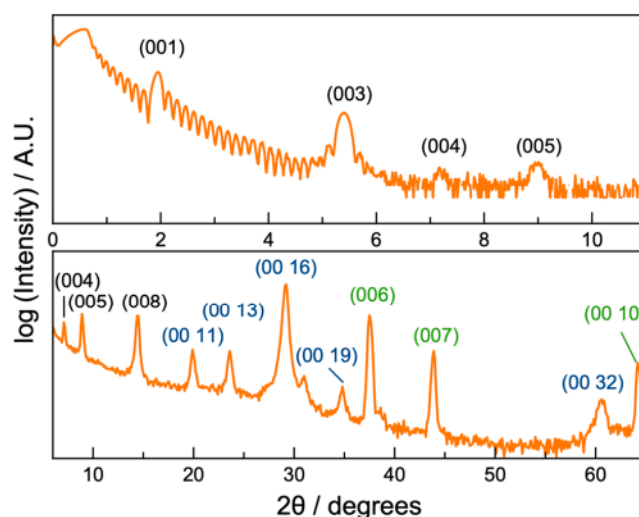


Figure 1. Representative as-deposited XRR and XRD for a 211211 isomer demonstrating behavior observed in all of the $[(\text{PbSe})_{1+\delta}]_4(\text{TiSe}_2)_4$ isomer heterostructures. The 00l reflections, corresponding to the artificial layering, the crystallized $[(\text{PbSe})_{1+\delta}]_4(\text{TiSe}_2)_4$ isomer heterostructure, and the impurity Ti_2S phase, are indexed in black, blue, and green, respectively. Additional as-deposited XRR patterns can be found in the Supporting Information, Figure S1.

repeat units of a $[(\text{PbSe})_{1+\delta}]_4(\text{TiSe}_2)_4$ isomer is expected to have a total film thickness of ~ 535 Å, slightly lower than the observed film thickness for the as-deposited isomers which range from 544 to 557 Å. The thickness of the elemental layering determined from the position of the first-order Bragg reflection is slightly higher than the targeted value expected for a $[(\text{PbSe})_{1+\delta}]_4(\text{TiSe}_2)_4$ repeat unit, 48.68 Å, in all of the samples (ranging from 49.19 to 50.81 Å). However, the observed Laue oscillations indicate that there are only 10 layers present in the repeating elemental modulation, requiring that one of the as-deposited layers differs from what was intended. Representative XRD patterns, Figures 1 and S1, for as-deposited $[(\text{PbSe})_{1+\delta}]_4(\text{TiSe}_2)_4$ isomer precursors indicate that PbSe and TiSe_2 have nucleated during deposition and that there are already coherent blocks of the $[(\text{PbSe})_{1+\delta}]_4(\text{TiSe}_2)_4$ isomer heterostructure before annealing. Surprisingly, there are also reflections consistent with the formation of a crystallographically aligned Ti_2Se impurity phase which has a *c*-axis lattice parameter of 15.6 Å. XRR, XRD, and HAADF-STEM images (discussed in subsequent paragraphs) all show that annealing the precursors at 350 °C for 30 min in an N_2 atmosphere provides enough energy for the self-assembly of the elemental precursors into the desired $[(\text{PbSe})_{1+\delta}]_4(\text{TiSe}_2)_4$ isomer structure, although only 8–9 layers of the intended isomers form and the presence of the Ti_2Se impurity phase remains.

The annealed heterostructures were analyzed by XRF to quantify the amount of material present in each film, and the results are summarized in Table 1. While the targeted isomer

Table 1. Total Atoms/Å² in Each of the Annealed $[(\text{PbSe})_{1+\delta}]_4(\text{TiSe}_2)_4$ Isomer Films^a

isomer	atoms/Å ²		
	Pb	Ti	Se
221111	3.61(1)	3.65(1)	9.82(2)
211211	3.64(1)	3.74(1)	10.28(2)
3311	3.71(1)	3.61(1)	9.78(2)
3212	3.65(1)	3.59(1)	10.02(2)
2321	3.60 (1)	3.87(1)	10.33(2)
44	3.38 (1)	4.02(1)	10.47(2)

^aThe error in the conversion factor between XRF intensity and number of atoms per unit area is 2–3%.

structures all had the same number of total atoms/Å² for each element (see Table 2), there is a large variation in the actual amount of material measured in the films after deposition, reflecting the challenges of reproducibly depositing monolayer amounts of various elements ($\sim 10^{-7}$ grams/cm²). We use quartz crystal microbalances (QCMs) to monitor the amount of material incident upon the substrate, which have about a 5%

Table 2. Calculated Number of Atoms/Å² for Each Element in the $[(\text{PbSe})_{1+\delta}]_4(\text{TiSe}_2)_4$ Isomers for Different Film Thicknesses

no. of $[(\text{PbSe})_{1+\delta}]_4(\text{TiSe}_2)_4$ repeating units	atoms/Å ²		
	Pb	Ti	Se
8	3.39	2.91	9.19
9	3.82	3.28	10.34
10	4.24	3.64	11.49
11	4.37	4.00	12.64

measurement error for the nanogram sensitivities required. However, the QCMs need to be located adjacent to the sample substrates, making this an indirect measurement that is sensitive to deviations in the flux within the plume of vaporized atoms. The spatial distribution of fluxes within the plume typically remains constant within a set of samples, resulting in a constant proportionality between the amount of material incident on the QCM to the amount incident on the substrate. Unfortunately, the spatial distribution of fluxes within the plume changes with time as the source size decreases and with a number of experimental parameters (beam raster area and raster rates, impurities on source surfaces, etc.). Pb is the limiting element in all of the films, and there is not enough Pb, Ti, or Se in any of the films to form 11 unit cells of any of the targeted isomers (see Table 2). Insufficient Pb, Ti, and Se in the precursors explains why fewer unit cells formed compared to what was targeted. To form, the intended isomers required diffusion within and between deposited layers to provide Pb to the nucleation sites. This results in less than 11 repeating units forming. Surprisingly, the deposited nanoarchitecture and initial layer growth in the precursors was sufficient to direct the formation of the targeted isomers despite atoms diffusing between deposited layers and fewer than the targeted number of isomer layers forming.

XRR patterns of the annealed films provide insight into the complex structure of the products that formed during annealing. Information contained in the XRR patterns is detailed in Figure 2, using the 3212 isomer pattern as a

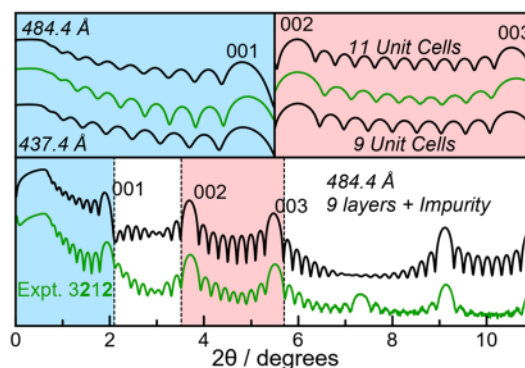


Figure 2. Experimental and simulated XRR patterns for the 3212 structural isomer. The upper left panel focuses on the Kiessig fringes, indicating that the total film thickness is 491.4 Å. The upper right panel emphasizes the Laue oscillations, showing that 9 unit cells are present, not the 11 expected from the deposition sequence. The bottom panel compares the simulated and experimental patterns based on the complete model described in the text.

representative example. The 3212 isomer has a layer sequence of aaabbb, where the thicknesses of the PbSe component in the unit cell (a) has a normal typeface and the TiSe_2 (b) is bold in the 3212 abbreviation. Bragg maxima from the self-assembled product are observed in the XRR pattern, and the position of these maxima yield a *c*-axis lattice parameter of 48.60(1) Å, which is consistent with the expected unit cell of a $[(\text{PbSe})_{1+\delta}]_4(\text{TiSe}_2)_4$ isomer composed of four layers of TiSe_2 and four layers of PbSe. The XRR pattern also has smaller maxima, which come from two different effects. Near the critical angle, these smaller maxima are called Kiessig fringes, and they are a consequence of the X-ray interference reflecting from the top and the bottom of the film. At higher angles, the

smaller maxima between the Bragg reflections, called Laue oscillations, result from incomplete destructive interference from the finite number of unit cells in the film. The number of Laue oscillations between consecutive Bragg reflections depend on the number of complete unit cells contributing to the interference effect. The top left panel of Figure 2 shows that a film thickness of 484.4 Å results in Kiessig fringes that match those observed for the 3212 isomer. A film that is composed of nine unit cells contributing to the total thickness does not match the experimental low angle data between the critical angle and the first Bragg reflection. The top right panel of Figure 2 compares simulations of the Laue fringes for a heterostructure with the targeted 11 unit cells and a heterostructure with nine unit cells contributing to the interference effect with the experimental data for the 3212 isomer. Simulations for a film composed of 9 repeating unit cells matches the observed experimental data, while simulations for 11 repeating unit cells do not.

Since Kiessig fringes are extremely sensitive to the quality of interfaces (roughness) while the Laue oscillations are sensitive to the number of unit cells interfering in the sample and the extent of their disorder, the experimental low angle patterns reflect the changing contributions of both diffraction effects throughout the presented angular range. The discrepancy between the total film thickness and the number of repeating units indicates that there is extra material present in the films. This extra material can exist either above and/or below the nine unit cells of the 3212 isomer. The relative thickness of the top and bottom impurity layers influences the rate of decay of the intensity above the critical angle. The roughness of the layer on top of the 3212 block determines the angular dependence of the relative contributions of the Kiessig and Laue interference effects. The bottom panel in Figure 2 shows a simulated pattern containing nine unit cells of the 3212 isomer with 47 Å of extra thickness divided between a 35 Å layer underneath and a 12 Å layer with a roughness of 5 Å on top. The positions of the maxima line are consistent between the simulated and experimental patterns. The magnitude of the Laue oscillations is larger in the simulated pattern because the 3212 block was modeled as an ideal film. The intensity of the Laue oscillations can be suppressed and the intensity of the fourth-order Bragg reflection can be increased by adding roughness to one or more of the unit cells. The 35 Å layer underneath the 3212 isomer block is likely the Ti_2Se impurity phase observed in the as-deposited XRD and is likely responsible for the as-deposited XRR patterns containing Laue fringes for only 10 layers.

Similar models were created for all of the targeted $[(\text{PbSe})_{1+\delta}]_4[\text{TiSe}_2]_4$ heterostructure isomers. The stacking sequence of the 8-layer blocks within the repeating unit were varied and we assumed atomically sharp interfaces between the constituent structures. Also assuming a constant electron density within each constituent results in a square-wave function for the electron density as shown in Figure 3. This simple model assumed the c -lattice parameters for the heterostructures were equal and the interfaces between the eight constituent unit cells occurred at intervals of 1/8th of a unit cell. Within the unit cell, 221111 and 211211 compounds have five interfaces, the 3311, 3212, and 2321 compounds have three interfaces, and the 44 profile has one interface. The Fourier transform of the electron density of each $[(\text{PbSe})_{1+\delta}]_4[\text{TiSe}_2]_4$ heterostructure isomer is different due to the distinctive placement of the eight constituent layers

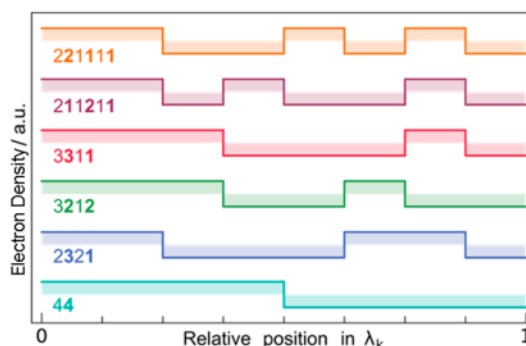


Figure 3. Schematic representation of the variation of electron density through a unit cell for each of the $[(\text{PbSe})_{1+\delta}]_4[\text{TiSe}_2]_4$ isomers.

within the unit cell. Consequently, the pattern of intensities of the 00 l reflections in the specular diffraction will be unique for each structural isomer.

Experimental XRR patterns for each of the $[(\text{PbSe})_{1+\delta}]_4[\text{TiSe}_2]_4$ isomers are shown in Figure 4 along with simulated patterns using both the electron density profiles

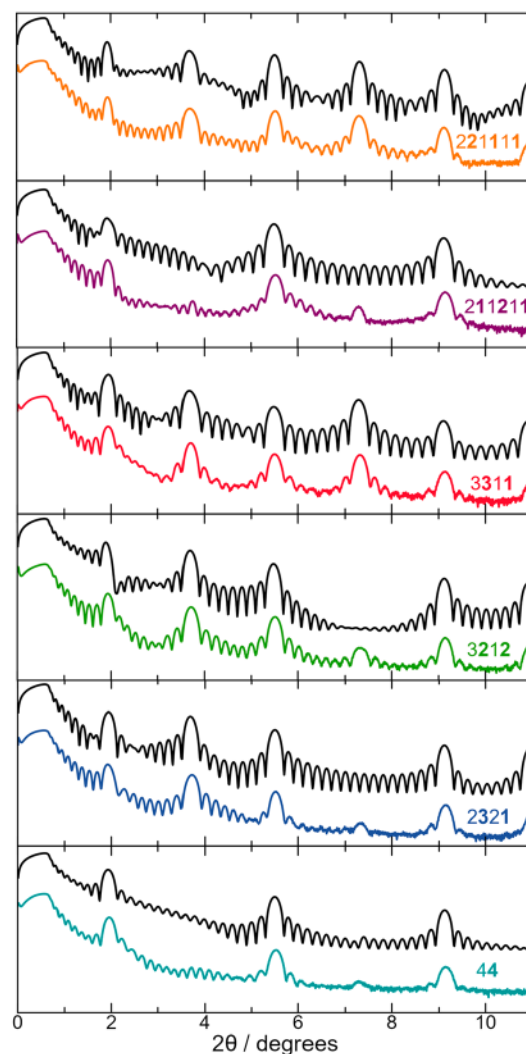


Figure 4. X-ray reflectivity patterns (in color) shown against simulated patterns created using models of the targeted isomers (in black) described in Figure 3.

Table 3. Parameters Extracted from the XRR Patterns as Described in the Text^a

sample	number of unit cells in isomer block	total thickness (Å)	thickness of isomer block	bottom impurity thickness (Å) (±5)	top impurity thickness (Å) (±5)	bottom impurity roughness (Å)
221111	9	514	438	40	36	1.0
211211	8	498	389	48	34	5.0
3311	8	482	389	60	40	5.0
3212	9	484	437	35	12	5.0
2321	9	481	437	14	30	8.0
44	9	491	437	27	27	5.0

^aNot shown in the table are parameters that do not vary the model significantly. These parameters (the bottom impurity roughness (5 Å) and the roughness of the Si substrate (5 Å)) were held constant in all of the models.

determined from Figure 3 and the parameters gathered using the method described for the 3212 isomer. Bragg reflections observed in the XRR patterns occur at nominally the same 2θ angle for all of the $[(\text{PbSe})_{1+\delta}]_4[\text{TiSe}_2]_4$ isomers, indicating that the repeating unit is similar. Relative patterns of the Bragg reflection intensities correlate well between the models and experimental data. Small intensities experimentally observed when the models predict zero intensity result from approximations made for the models shown in Figure 3. For the model it was assumed the interfaces were located at exactly 1/8th intervals of the unit cell, but experimentally the Se–Ti–Se trilayer and a Pb–Se bilayer thicknesses are not equal. Another assumption used in the model is that the layers are perfectly smooth, when in reality some roughness is observed. The positions of the Laue oscillations in the models were adjusted by varying the number of unit cells of each isomer to match the experimental data. Positions of Kiessig fringes in the model were manipulated to match the experimental data by varying the total sample thickness via the excess material on the top or bottom of the film. STEM images of each isomer were used as a guide to approximate the amount of extra material present. The patterns are somewhat insensitive to the exact ratio of thickness of the top/bottom impurity layers, so the decay of the intensity from the critical angle to the first Bragg maxima was adjusted by varying the exact thicknesses of the top and bottom impurity layers. Roughness of the layer on top of the isomer block was adjusted to match the observed change from Kiessig fringes to Laue oscillations, which differs based on impurity thicknesses and number of unit cells. Parameters from the models for each isomer are summarized in Table 3. All of the $[(\text{PbSe})_{1+\delta}]_4[\text{TiSe}_2]_4$ isomers have fewer unit cells in the isomer blocks than the targeted number. The total thicknesses of the isomers are all less than what was measured for the as-deposited samples as a result of Se loss during annealing in an open system. It was determined, via XRR simulations and HAADF-STEM, that all $[(\text{PbSe})_{1+\delta}]_4[\text{TiSe}_2]_4$ isomers have impurity layers above and below the block of repeating units.

Specular and in-plane XRD patterns of the crystallized isomer heterostructures are shown in Figure 5. Lattice parameters were determined for each of the $[(\text{PbSe})_{1+\delta}]_4[\text{TiSe}_2]_4$ isomers and are summarized in Table 4. All but three of the maxima in the specular X-ray diffraction patterns can be indexed as 00 l reflections corresponding to the nanoarchitecture of the targeted isomers. The c -axis lattice parameters, determined from the position of the 00 l reflections, are similar for all of the isomers and are consistent with a repeating unit composed of four layers of PbSe and four layers of TiSe_2 , as was observed in the as-deposited data. The three reflections not belonging to the isomer's unit cell can be

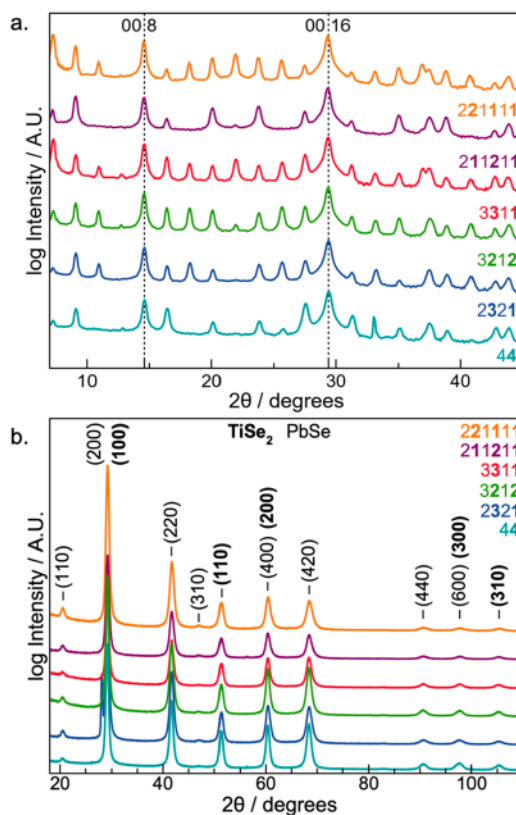


Figure 5. Specular (a.) and in-plane (b.) XRD patterns of the $[(\text{PbSe})_{1+\delta}]_4[\text{TiSe}_2]_4$ structural isomers. The indices of the observed reflections are shown above each reflection in the in-plane pattern and representative indices are indicated in the specular pattern.

Table 4. Lattice Parameters for the $[(\text{PbSe})_{1+\delta}]_4[\text{TiSe}_2]_4$ Structural Isomers Determined from the Annealed Diffraction Patterns

sample	c -axis lattice parameter (Å)	PbSe a -axis lattice parameter (Å)	TiSe_2 a -axis lattice parameter (Å)	impurity phase
221111	48.66(1)	6.121(1)	3.560(1)	14.41(4)
211211	48.64(1)	6.132(1)	3.566(1)	14.54(1)
3311	48.62(1)	6.131(1)	3.561(1)	14.53(3)
3212	48.60(1)	6.134(1)	3.563(1)	14.55(2)
2321	48.56(1)	6.128(2)	3.561(2)	14.54(1)
44	48.52(2)	6.132(1)	3.560(1)	14.55(1)

indexed as 00 l reflections from Ti_2Se . The lattice parameter obtained, 14.52(5) Å, matches that expected for Ti_2Se .³⁸ This is consistent with the excess Ti observed in the number of atoms/Å² determined from the XRF data for the annealed

compounds and the impurity phase observed in the representative as-deposited diffraction. All of the reflections in the in-plane diffraction scan can be indexed as $hk0$ reflections from either a hexagonal or square unit cell, whose lattice parameters correspond to either TiSe_2 or PbSe , respectively (Table 4). Relative intensities of the reflections from each constituent are constant between isomers, indicating that there are similar relative amounts of PbSe and TiSe_2 in each heterostructure. Both the PbSe and TiSe_2 in-plane lattice parameters remain constant as the isomer nanoarchitecture is varied, indicating that there is no structural change as a function of layer sequence. There are no observed reflections corresponding to the Ti_2Se impurity phase in the in-plane diffraction. The (110) and (310) reflections observed in the square unit cell indicate that PbSe does not have the bulk rock salt structure, because these reflections are forbidden in the $Fm\bar{3}m$ rock-salt space group. This indicates that the PbSe structure has distorted with either Pb or Se no longer on special position sites, which is not unexpected for these ultrathin layers. A similar distortion was observed in $(\text{PbSe})_m(\text{MoSe}_2)_n$ compounds, where atoms moved ~ 20 pm from ideal rock salt structure positions.³⁹ The structures of the PbSe-TiSe_2 isomers studied in this paper were not refined due to the large number of crystallographic parameters that would be required for these more complicated unit cells and the limited number of reflections observed.

HAADF-STEM images, collected for each of the $[(\text{PbSe})_{1+\delta}]_4(\text{TiSe}_2)_4$ isomers, provide local information about defects and overall sample structure. Figure 6 shows a

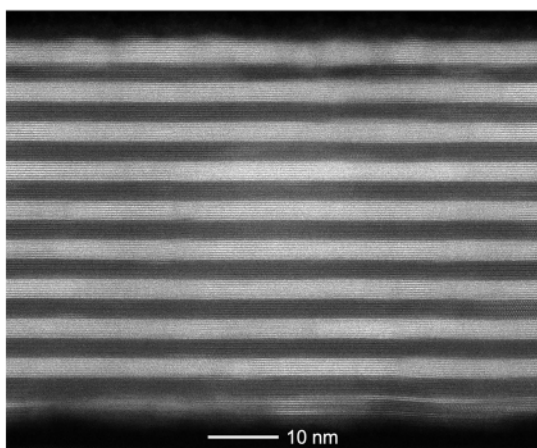


Figure 6. HAADF-STEM image of the 44 $[(\text{PbSe})_{1+\delta}]_4[\text{TiSe}_2]_4$ structural isomer showing the entire film from substrate to surface.

full film image of the 44 $[(\text{PbSe})_{1+\delta}]_4(\text{TiSe}_2)_4$ isomer. Rock-salt layers containing Pb show up as bright regions due to the higher average atomic number relative to TiSe_2 layers, which are darker. STEM-EDS data for the 2321 isomer, shown in the Supporting Information, confirms this assignment. Distinct bright atomic columns of atoms can be seen in regions where the electron beam aligns with a crystallite's zone axis. Different layers and regions within the same layer have different orientations, indicating both rotational disorder and some stacking defects. The majority of the film consists of nine unit cells of the isomer, which is consistent with the XRR data discussed previously. At the top and bottom of the film there is material that is not consistent with the repeating blocks of the isomer. In the layer closest to the substrate there are regions

where Ti_2Se grains can be found in addition to smaller regions of TiSe_2 and $(\text{PbSe})_1(\text{TiSe}_2)_1$. These observations are consistent with the analysis of the XRF, XRR, and XRD data discussed previously.

Figure 7 shows HAADF-STEM images of all $[(\text{PbSe})_{1+\delta}]_4[\text{TiSe}_2]_4$ structural isomers. These images dem-

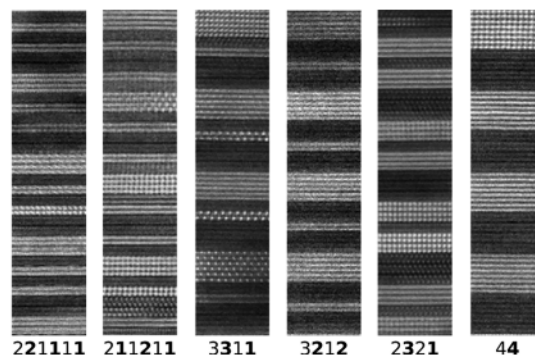


Figure 7. HAADF-STEM images of each isomer heterostructure highlighting the formation of the targeted nanoarchitecture, sharp interfaces between constituents, and rotational misregistration between layers.

onstrate that the films consist of different sequences of PbSe and TiSe_2 layers with sharp planar interfaces between them. The different layering schemes for each of the six isomers can be clearly identified and are further supported by the EDS profile shown in Figure S3. There is extensive rotational disorder occurring between the different constituent layers in each block, evident by zone axis orientations appearing in only some of the layers. As observed in the specular XRD patterns, the thickness of the repeating layer schemes are the same for all six isomers. The majority of the samples are composed of a central block of the targeted isomer and the number of unit cells in the blocks agrees with that determined from the Laue fringes in the XRR patterns. While there are stacking defects in all of the isomer domains, it is quite surprising that the imperfect 11 repeating sequences deposited in the precursors contain sufficient information to direct the self-assembly of 8–9 unit cells into the targeted isomer stacking sequences.

The structural data presented above provide insight into the isomers' growth from the deposited precursor. It suggests that Ti_2Se forms at the substrate surface when Se is deposited onto the initial Ti layer. We tested this in a separate experiment, showing that Ti_2Se forms when depositing Se on Ti in a Ti–Se precursor, even when the Ti to Se ratio is 1:2. Forming Ti_2Se as the initial layer results in an excess Se concentration since the amount of Ti and Se deposited was intended to form a TiSe_2 layer in the isomer samples. When Pb intended to form PbSe in the first repeat unit is deposited, it reacts with the excess Se from the first TiSe_2 layer to form a PbSe layer. When the next layer of Ti is deposited (intended for the second repeat unit), it is deposited on a Se rich layer which allows the formation of TiSe_2 to occur. The TiSe_2 grows out horizontally from its nucleation site. Since the repeating sequence is low on Ti, the formation of the growth stops when the Ti at the growth front has been depleted, leaving some amorphous material in the layer. Similar behavior occurs for the next PbSe layer, but the TiSe_2 basal plane surface results in the formation of crystallographically aligned PbSe at the interface. Since the repeating sequence is also low on Pb, the formation of the

growth stops when the Pb at the growth front has been depleted, leaving some amorphous material in the layer. This process continues, on average, for about four unit cells, which corresponds to a crystallite size of ~ 200 Å perpendicular to the substrate. Subsequent deposited layers are more disordered.

A schematic illustrating the as-deposited structure and how it evolves is shown in Figure 8. To simplify the image a

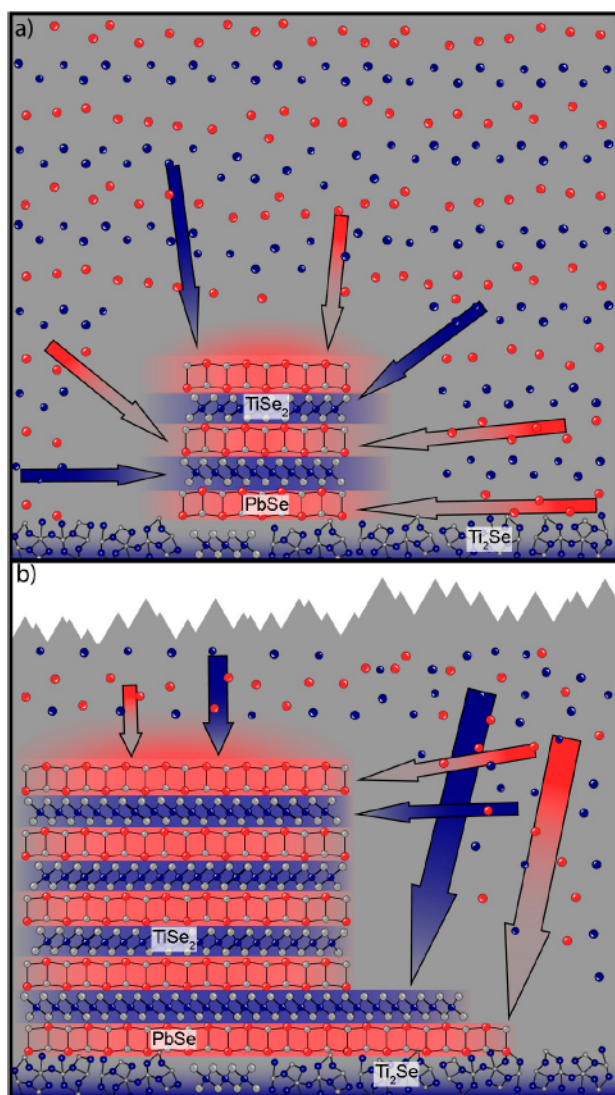


Figure 8. Atomistic picture demonstrating the initial crystallization in the isomers (a) and a snapshot showing the movement of atoms and further crystal growth upon annealing (b). The arrows demonstrate the concentration gradient of the metals and point to where the metals are diffusing. On deposition a layer of Ti_2Se forms and persists even after annealing. Pb atoms are shown in red, Ti atoms in blue, and Se atoms in gray.

$([\text{PbSe}]_{1+\delta})_1(\text{TiSe}_2)_1$ repeating unit structure was used in place of the more complex $([\text{PbSe}]_{1+\delta})_4(\text{TiSe}_2)_4$ isomer structure. When the temperature is increased during annealing, the concentration gradients drive diffusion of Pb and Ti to the growth front. In addition to growth parallel to the substrate, additional layers crystallize perpendicular to the substrate and facilitate further growth of the heterostructure. Around the crystallized structure is a region that is metal poor/Se rich as a result of the nucleation site stealing metal from the

surrounding area to form the structure. The requirement to steal material from the surrounding area is the result of the wrong atoms/Å² being deposited per layer in the precursor. Since all of the samples were most deficient in Pb, it is the species that will be depleted first, leaving a TiSe top layer which reacts with oxygen during annealing to form an amorphous oxide. We anneal our films in an N_2 environment with <1 ppm of O_2 , which is insufficient to prevent formation of a surface oxide during annealing. The thickness of the isomer layer therefore ends up being 2 or 3 unit cells less than the 11 that were targeted, consistent with the number of Laue oscillations seen in the XRR scans and the HAADF-STEM images. The ability to prepare the metastable isomers without being precisely on composition is an advantage in the quest to find new material phases, since it is challenging to precisely control the absolute amount of an element at the monolayer level. These metastable compounds have a broad enough energy minimum in the free energy landscape that the system still forms the targeted isomer even if the composition deviates from the target, as long as the nanoarchitecture resembles the targeted compound.

Temperature-dependent resistivity graphs for the six $([\text{PbSe}]_{1+\delta})_4[\text{TiSe}_2]_4$ isomers are shown in Figure 9. The

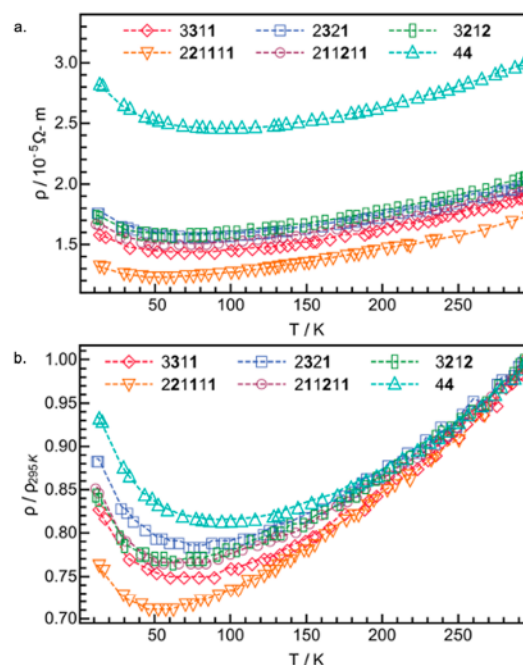


Figure 9. Temperature-dependent resistivity of six $([\text{PbSe}]_{1+\delta})_4(\text{TiSe}_2)_4$ isomer heterostructures, with both measured (a) and normalized (b) values.

isomer with the smallest number of interfaces per unit cell, the 44 isomer, has the highest resistivity, while the 221111 isomer, which has the most interfaces, has the lowest resistivity at all temperatures. The magnitude of the resistivity and the slow decrease in resistivity as temperature is decreased from room temperature suggest that these samples are metallic. At low temperatures, however, all the samples have an increase in resistivity similar to those observed in the previously reported $([\text{PbSe}]_{1+\delta})_m[\text{TiSe}_2]_n$ compounds.^{30,32,35,40} The similarity of the normalized resistivity versus temperature plots, Figure 9b, suggests that the same phenomena are occurring in all of the

isomers. Minima in the resistivity for the isomers occur between 50 and 100 K, with the 44 isomer, having the highest temperature minima, and the 221111 isomer, the lowest.

Hall coefficients were measured as a function of temperature to provide more information about the increase in resistivity at low temperatures. The Hall coefficients were negative for all isomers over the entire temperature regime, indicating that electrons dominate the electrical transport. Carrier concentrations were calculated from the Hall data, assuming a single band model, and are plotted as a function of temperature in Figure 10a. The carrier concentrations slowly decrease as

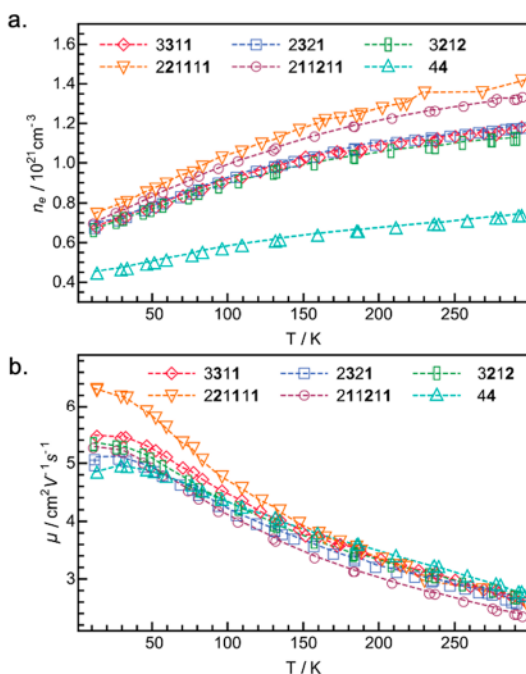


Figure 10. Temperature-dependent carrier concentration (a) and mobility (b) of six $[(\text{PbSe})_{1+\delta}]_4(\text{TiSe}_2)_4$ isomer heterostructures. Values are calculated assuming a single n-type band.

temperature is decreased in all of the samples. The decrease in carrier concentration has a very weak temperature dependence, suggesting that an activated process is not the source of the increasing carrier concentration with increasing temperature. Isomers with the same number of interfaces in the unit cell have similar carrier concentrations, with the 44 structure having the lowest and the 221111 and the 211211 isomers the highest. Carrier mobility, calculated from the resistivity and Hall data, is shown in Figure 10b. The mobility values and their temperature dependences are similar for all of the isomers, with mobility increasing with decreasing temperature before becoming constant below 50 K. At low temperatures, higher mobilities correlate with increasing buried interface density. This is somewhat surprising as more interfacial scattering from the layers, which should be relatively temperature independent, unlike other mechanisms (e.g., electron–electron or electron–phonon scattering), would be expected for structures with high interface density. The minima in the resistivity appears to be a consequence of the interplay between the decreasing carrier concentration and increasing mobility as temperature is decreased. As the temperature decreases the mobility increases at a faster rate than the carrier concentration decreases, resulting in observed resistivity

decrease. At low temperatures, the decreasing carrier concentration and plateau of the mobility result in the resistivity increase.

The room-temperature Seebeck coefficient was collected for each isomer compound, and the values are shown in Figure 11.

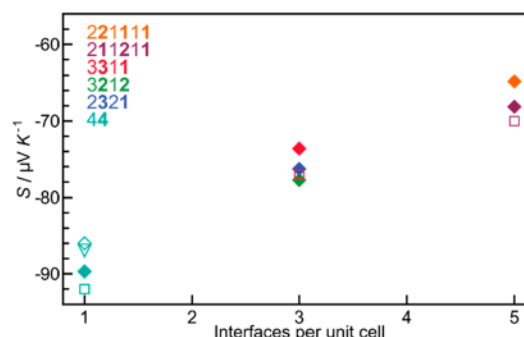


Figure 11. Room-temperature Seebeck coefficients for each of the $[(\text{PbSe})_{1+\delta}]_4(\text{TiSe}_2)_4$ isomer heterostructures. Colors correspond to the nanoarchitecture, and symbols correspond to the precursor parameters.

Several $[(\text{PbSe})_{1+\delta}]_4(\text{TiSe}_2)_4$ isomers were measured to explore how much the room temperature transport measurements varied between samples. There was a 5% variation of the Seebeck coefficient between the four samples measured. The negative Seebeck coefficients obtained for all of the isomers agree with the Hall measurements, indicating that electrons are the majority carrier type. The magnitude of the Seebeck coefficients systematically decrease as the interface density decreases in the $[(\text{PbSe})_{1+\delta}]_4(\text{TiSe}_2)_4$ isomers. This and the Hall data suggest that band alignments in $[(\text{PbSe})_{1+\delta}]_4(\text{TiSe}_2)_4$ isomers result in charge transfer from PbSe into TiSe_2 . The PbSe– TiSe_2 bilayers should be thought of as a conducting entity due to charge transfer between the constituents. The more PbSe– TiSe_2 interfaces there are, the higher the carrier concentration as charge transfer occurs at each interface, as shown schematically in Figure 12. The unusual decrease in the carrier concentration with temperature may be a consequence of the two structures changing independently with temperature, resulting in a change in the amount of charge transfer between the two constituents as a function temperature.

CONCLUSION

This work investigated the synthesis, formation, structure, and transport properties of $[(\text{PbSe})_{1+\delta}]_4(\text{TiSe}_2)_4$ isomers. While the correct amount of material deposited was not enough to form 11 repeat units of a $[(\text{PbSe})_{1+\delta}]_4(\text{TiSe}_2)_4$ isomers, the intended nanoarchitectures still formed albeit with fewer unit cells than targeted. During deposition, an impurity Ti_2Se phase formed at the substrate interface and there was initial crystallization of both TiSe_2 and PbSe in sequences that match the structure of the targeted isomers. Both the initial layering scheme and the heat of formation of the targeted isomers drives the formation of the resulting material. XRR, XRD, and HAADF-STEM analyses confirm the formation of approximately eight or nine repeating units with the correct nanoarchitecture, with thin impurity phases present on the top and bottom. Transport data collected for the isomers indicate that the resistivity and carrier concentration depend on the number of interfaces in the unit cell of the isomers. This suggests that charge transfer between the constituent layers is

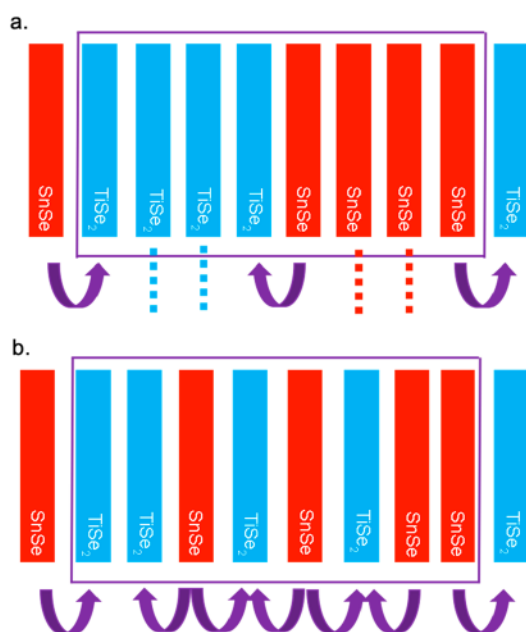


Figure 12. Schematic demonstrating charge donation occurring in isomers containing different numbers of buried interfaces, e.g., the 44 (a) and the 221111 (b). The SnSe layers are shown in red and the TiSe₂ in blue, and purple arrows depict the charge donation from the SnSe to the TiSe₂ layers. The purple boxes indicate a single isomer repeating unit.

the source of the electrons. The mobility and carrier concentration vary inversely with temperature, resulting in a minimum in the resistivity between 50 and 100 K. The ability to prepare metastable isomers provides a new handle for tuning properties in thin film materials, and the tolerance of the self-assembly process to deviations from stoichiometry facilitates the discovery of new compounds using this synthesis approach.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c01416>.

Representative XRR patterns before annealing that indicate the layering structure of the isomers upon deposition, table of as-deposited repeat unit thickness and total film thickness for the isomers, representative as-deposited in-plane diffraction indicating the initial crystallization that occurs before annealing, and STEM-EDS results for the 2321 isomer that indicate the fine layering structure of the heterostructures (PDF)

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Notes

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■ ABBREVIATIONS USED

XRF, X-ray fluorescence; XRR, X-ray reflectivity, XRD, X-ray diffraction; HAADF-STEM, high-angle annular dark field scanning transmission electron microscopy; EDS, energy dispersive X-ray spectroscopy

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