

The Instability of Monolayer-Thick PbSe on VSe₂

Dmitri Leo Mesoza Cordova, Shannon Sanaya Fender, Mohammad Shahriar Hooshmand, Mina R. Buchanan, Joshua Davis, Taryn Mieke Kam, Renae N. Gannon, Robert Fischer, Ping Lu, Benjamin E. Hanken, Mark Asta, and David C. Johnson*

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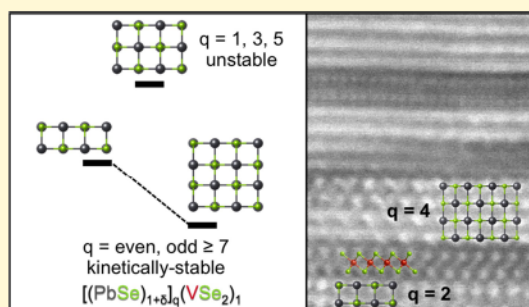
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ABSTRACT: Two-dimensional monolayers derived from 3D bulk structures remain a relatively unexplored class of materials because of the challenge of stabilizing nonepitaxial interfaces. Here, we report an unusual reconstruction during the deposition of precursors when targeting the synthesis of heterostructures with an odd number of PbSe monolayers. Multilayer elemental precursors of PbSe + VSe were deposited to have the correct number of atoms to form $[(\text{PbSe})_{1+q}(\text{VSe}_2)_1]$ where q is the number of PbSe monolayers in the heterostructure. Structural analysis of the self-assembled precursor via X-ray reflectivity, X-ray diffraction, and HAADF-STEM suggests three different behaviors upon deposition. Precursors with $q \geq 7$ and even values of q have the targeted nanoarchitectures after deposition, which are maintained as the products are self-assembled through a near diffusionless process. Significant lateral surface diffusion occurred during the deposition of precursors with $q = 1, 3$, and 5 , resulting in the precursor to have a different nanoarchitecture than targeted. Additional perpendicular long-range diffusion occurs during self-assembly of these precursors, resulting in different final products than targeted. Density functional theory (DFT) calculations of PbSe blocks show that the odd-numbered layers are less stable than the even-numbered layers, which suggests an energetic driving force for the observed rearrangement. This work highlights the importance of understanding the reaction mechanism when attempting to prepare 2D layers of constituents with bulk 3D structures.



INTRODUCTION

The discovery of two-dimensional materials with the so-called emergent properties, those not observed in the constituent bulk compounds, has resulted in a boom in research on monolayers, heterostructures, and ultrathin materials.^{1–4} The expansion of this field is fueled by the predictions of unusual quantum states and properties that might be observable in 2D materials, including unusual quantum spin Hall states,^{5,6} Weyl fermions,⁷ indirect-to-direct band gap transitions,⁸ and topological states.⁹ The surfaces and interfaces in 2D materials are responsible for many of the observed emergent properties. In monolayers, the lack of adjacent layers removes bonding and antibonding interactions between layers, which can result in property changes such as the transition from an indirect to a direct band gap in MoS₂.⁸ Interlayer coupling at the nonepitaxial interface between constituents in heterostructures can produce new properties. For example, charge transfer between constituents can cause modulation doping in heterostructures.^{10,11} The interaction between layers can also prompt structural changes, such as the formation of octahedrally, rather than trigonal prismatic coordinated Mo in MoSe₂ when layered with BiSe.¹² Computational and experimental studies on the thickness-dependent properties of low-dimensional materials have revealed differences between odd- and even-layered thicknesses resulting from the stability of specific crystal surfaces and changes in symmetry.^{13–17} The

rapid development of this field experimentally was initially driven by the ability to obtain monolayers of naturally layered compounds via mechanical cleaving^{18,19} and the ability to detect thicknesses rapidly using optical techniques.²⁰ The large interest in 2D materials as potentially important components of new technologies has resulted in the development of additional approaches to synthesizing films with a precise control of thickness and heterostructures with a controlled nanoarchitecture over wafer-scale surfaces.^{19,21}

While initially focusing on layered materials with obvious cleavage planes, recent theoretical papers have predicted unusual properties associated with the 2D layers of materials with three-dimensional structures.^{22–27} Preparing 2D layers of materials with 3D structures, however, is synthetically more challenging than preparing structurally 2D or naturally layered compounds. As a material becomes more 3D, cleaving thin layers in desired directions becomes increasingly more difficult. During the vapor phase growth, the strength of the interaction

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between the growing layer and the substrate is very important. If the interaction is too strong, it will modify the electronic structure that is being targeted. If it is too weak, there will be a tendency to form islands rather than continuous thin films of uniform thickness.²⁸ Recent calculations have predicted that a free-standing monolayer PbSe could be a 2D topological crystalline insulator, with Dirac-cone-like edge states.²⁹ Ultrathin PbSe films have been grown on SrTiO₃ substrates by codepositing Se and Pb atoms, forming crystalline PbSe islands after postannealing.³⁰ A large compressive strain exists in these epitaxial few-layer PbSe islands, with the lattice parameters changing from 5.85 Å for a three monolayer-thick island to 6.1 Å for a nine monolayer-thick island. Bulk PbSe has a lattice parameter of 6.117 Å.³¹ The large change in the lattice parameters indicates a strong epitaxial interaction between the substrate and PbSe; however, islands rather than constant thickness PbSe layers formed under the growth conditions used.

Here, we report our investigation of the growth of monolayers and a controlled thickness of PbSe layers between VSe₂ layers. This study was prompted by a previous investigation, where smooth PbSe films were grown on VSe₂.³² This report and the thermodynamic stability of misfit-layered compounds containing well-defined bilayers of PbSe alternating with dichalcogenides suggest that a strong interaction exists between these constituents, even though the significant lattice mismatch prevents an epitaxial relationship between the constituents.^{33,34} Precursors were deposited to mimic the nanoarchitecture of [(PbSe)_{1+δ}]_q(VSe₂)₁ heterostructures where *q* is an integer number of PbSe monolayers. The precursors with even layers and with *q* ≥ 7 thicknesses exhibited the expected as deposited nanoarchitecture and evolved into the desired heterostructures. Surface diffusion during the deposition process of the *q* = 1, 3, and 5 precursors, however, resulted in more complex initial nanoarchitectures. The computational and experimental findings reveal that for small values of odd *q*, the formation of odd PbSe rock salt layers has a higher energy compared to segregation into adjacent (*q*+1 and *q*-1) layers. The results suggest that the interaction between VSe₂ and PbSe is not strong enough to stabilize the monolayers, suggesting that its synthesis requires finding a substrate that has a stronger interaction with PbSe. The data presented support an odd–even effect in PbSe monolayers, a 2D structure derived from a bulk 3D structure, due to enhanced stability of even-thickness layers. This points to new opportunities to tune structures by varying the strength and type of interaction between the constituents, potentially opening up avenues for accessing novel properties by varying the layer thickness of 2D layers of compounds with 3D structures.

METHODS

Precursors were deposited on <100> Si wafers (3" × 1") with native oxide using a custom-built physical deposition chamber described by Fister and coworkers.⁴³ Elemental V (99.995%, Alfa Aesar) and Pb (99.8%, Alfa Aesar) were deposited using 6 keV electron beam guns while elemental Se (99.99%, Alfa Aesar) was deposited using a Knudsen effusion cell. Elemental layers were deposited by exposing the substrate to a plume of atoms from the heated sources. The time the substrate is exposed is controlled by pneumatic shutters that close after the desired thickness has been deposited. The desired thickness was measured using a quartz crystal microbalance and the sequence and thickness of elemental layers can be controlled using custom LabView software. The number of atoms of each element deposited is

optimized by measuring the X-ray fluorescence (XRF) of the films *ex situ* using a Rigaku Primus II ZSX spectrometer. The measured XRF intensities are converted into the number of atoms per unit area for each constituent as described by Hamann and coworkers.³⁵ The period of the deposited sequence of layers was measured using X-ray reflectivity (XRR).

Ex situ annealing was performed on a hot plate in an inert N₂ atmosphere (O₂ < 0.8 ppm). The changes as a function of annealing temperature and time were followed using X-ray diffraction. Specular X-ray diffraction (XRD) and X-ray reflectivity (XRR) patterns were collected using a Bruker D8 diffractometer with Cu-Kα radiation (λ = 0.15418 nm). The specular XRD scans contain substrate peaks at 2θ of ≈30 and 60°. The grazing incidence in-plane X-ray diffraction (GIPXRD) pattern was collected using a Rigaku Smartlab diffractometer, also with Cu-Kα radiation (λ = 0.15418 nm). LeBail fitting of the GIPXRD data was performed on FullProf Suite.⁴⁴

An FEI Titan G2 80–200 STEM with a Cs probe corrector and ChemiSTEM technology (X-FEG and Super-X EDS with four windowless silicon drift detectors) operated at 200 kV was used in this study. High-angle annular dark-field (HAADF) images were recorded with an electron probe of size (FWHM) of about 0.13 nm, a convergence angle of 18.1 mrad and a current of ~75 pA, and an annular dark-field detector with a collection range of 60–160 mrad.

Density functional theory (DFT) calculations were performed to compute the energy of PbSe slabs with different layer thicknesses of *q* = 1–8. For these calculations, the slabs were separated by 1.5 nm of vacuum to avoid interactions between the surfaces. To accommodate surface reconstructions, the dimensions of the slab supercells were doubled (relative to the conventional unit cell) in each direction parallel to the surface. The calculations made use of the projector augmented wave (PAW)⁴⁵ method as implemented in the Vienna *ab initio* simulation package (VASP),⁴⁶ in conjunction with the generalized gradient-approximation exchange–correlation potential of Perdew–Burke–Ernzerhof (PBE)⁴⁷ modified for solids: PBEsol.⁴⁸ The choice of PBEsol was made based on previous works, which gave more accurate bulk properties of PbSe relative to PBE.^{49,50} A plane-wave cutoff energy of 500 eV was employed. Wavefunctions were sampled using a Gamma-centered *k*-point grid of 8 × 8 × 1 (where the first two grid spacings are for directions in-plane and the last is normal to the surface) and a Gaussian smearing of 0.1 eV. The calculated lattice parameter for the rock-salt conventional unit cell using these settings is 6.103 Å, which matches well with the reported experimentally measured value of 6.1054(5) Å.⁵¹ All atoms were fully relaxed in the slab supercells to a force convergence of 5 meV/Å, keeping the in-plane lattice vectors fixed to the scaled dimension of the optimized bulk lattice parameter. The charge-density self-consistency was iterated to an energy tolerance of 10^{−4} eV. These settings were found to be sufficient to converge the total energies to within 1 meV/FU and to converge the atomic displacements induced by the surface reconstructions (Figure S13) to within 0.01 Å. Further information comparing the results from PBE and PBEsol can be found in Figure S14, showing that although the total energies change significantly with the choice of these exchange–correlation functionals, the key results concerning the odd–even energy oscillations, the nature of the convex hull features, and displacement patterns are very similar.

RESULTS AND DISCUSSION

A sequence of precursors was designed containing the correct number of atoms of each element in a repeating sequence of elemental layers to mimic the targeted structures. We calculated the number of atoms needed to form a monolayer of rock salt-structured PbSe in the <100> plane and a VSe₂ trilayer from the in-plane lattice parameters of each constituent in [(PbSe)_{1+δ}]_q(VSe₂)₁, which contains a bilayer of PbSe alternating with VSe₂.³⁴ Figure 1 shows the calculated number of atoms of each element required to form [(PbSe)_{1+δ}]_q(VSe₂)₁ compounds plotted as a function of *q*,

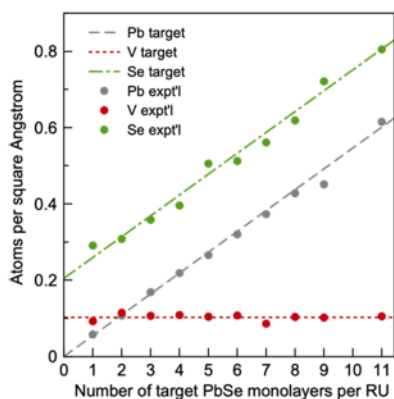


Figure 1. Targeted number of atoms per square Angstrom for each element per repeating unit for each of the designed precursors shown as lines. The circles are the amounts determined using XRF data.

the number of PbSe monolayers. To prepare compounds where q is even, we deposited a repeating unit (RU) of the sequence of elemental layers $[\text{VSe} + q/2(\text{PbSe})]$ r times, where each VSe bilayer is targeted to have the number of atoms required to form a VSe_2 layer and each PbSe layer is targeted to have the number of atoms required to form a PbSe bilayer. To prepare compounds where q is 1, 3, 5, 7, or 9 monolayers (1.5, 2.5, 3.5, and 4.5 bilayers), we deposited a similar sequence of elemental layers, where each PbSe layer contained either the number of atoms required to form a monolayer or a bilayer of PbSe such that the total number of layer atoms deposited equaled the value needed for q monolayers. For example, to prepare a $q = 7$ precursor, we deposited the RU sequence $[\text{VSe} + 3(\text{PbSe})_{\text{bilayer}} + 1(\text{PbSe})_{\text{monolayer}}]$. The compositions and structures of the deposited precursors were determined using XRF, XRR, and XRD.

The total number of atoms of each element deposited in each precursor was measured using XRF, and the average number of atoms per repeating unit was obtained by dividing the total number of atoms of each element by the number of repeating units deposited.³⁵ The measured number of atoms per unit area deposited for each precursor is shown as circles in Figure 1. The number of V and Pb atoms per unit area of all of the odd-numbered precursors is within 5% of the calculated values. The deviations from the calculated lines are a consequence of depositing the targeted numbers of atoms per unit area that are on the order of a monolayer for each element. Excess Se is observed in some precursors, which was anticipated to evaporate during the annealing process, and samples with deficient Se will likely have a small amount of metal oxides or incomplete unit cells. All the precursors contain close to the number of atoms of each element in the repeating sequence of layers to form the targeted compounds.

The XRR patterns of the precursors contain intensity oscillations (Kiessig fringes) due to the finite thickness of the entire film and Bragg maxima due to the repeating sequence of elemental layers in the precursor (Figure 2). The position of the first-order Bragg reflection due to the layering of the precursor systematically shifts to a lower angle as the thickness of the PbSe layer (q) is increased. For the $q = 1$ sample, the Bragg maximum is much broader than for the other samples and shifted to a lower angle than expected, indicating that the repeating period is thicker than the targeted value. However, the precursor modulation length for the $q = 1$ sample calculated from the total thickness divided by the number of

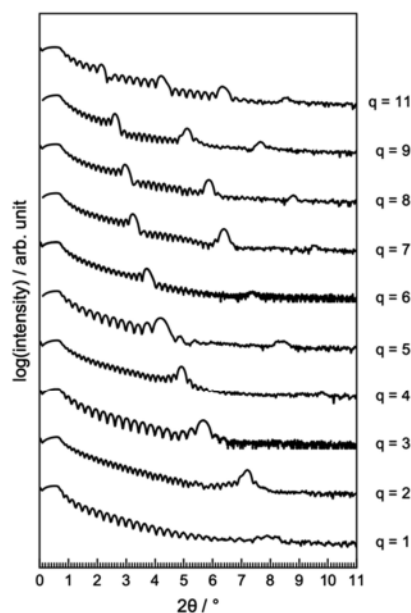


Figure 2. XRR patterns of the 10 as-deposited precursors. The patterns contain Bragg reflections from the nanoarchitecture of the precursor and lower intensity fringes from the interference pattern between the front and back of the sample combined with the incomplete destructive interference from a finite number of repeating layers.

repeating units deposited is as expected from the deposition process (Figure 4). This difference suggests that long-range surface diffusion occurred during the deposition, resulting in the precursor having a different structure than targeted.

The XRD patterns (Figure 3) of the as-deposited samples contain high-angle reflections that indicate that the samples have already begun to self-assemble during the deposition. The positions of these high-angle reflections divide the precursors into two groups. The reflections for the precursors with even-numbered q and odd $q \geq 7$ monolayers thick are at positions consistent with them being indexed as the $00l$ reflections yielding a c -axis unit cell size consistent with the precursor modulation length and the targeted nanoarchitecture. The precursors with $q = 1, 3$, and 5 all have weak reflections in the high-angle scans that cannot be indexed as the $00l$ reflections from the precursor modulation length. For $q = 3$ and 5 , the positions of the weak reflections indicate that the precursor modulation length is double than that expected from the deposition sequence. For the $q = 1$ sample, the weak reflections are not related at all to the precursor modulation length, consistent with segregation during the deposition process.

The data in Figure 4 reflects the differences in the targeted and actual nanoarchitecture deposited. It shows the precursor modulation length based on the deposition, determined by dividing the total thickness by the number of repeating units (black unfilled circles). The red filled circles are the modulation lengths (λ) determined by indexing the high-angle peaks as $00l$ reflections, which indicates the nanoarchitecture of the precursor that has crystallized upon deposition. The XRF, XRR, and XRD data indicate that the precursors with $q = 2, 4$, and 6 or larger all have the correct number of atoms of each element and the targeted nanoarchitecture. The XRD data for the precursors with $q = 3$ and 5 indicate that these precursors have a modulation length that is twice than that expected from the deposited sequence of layers.

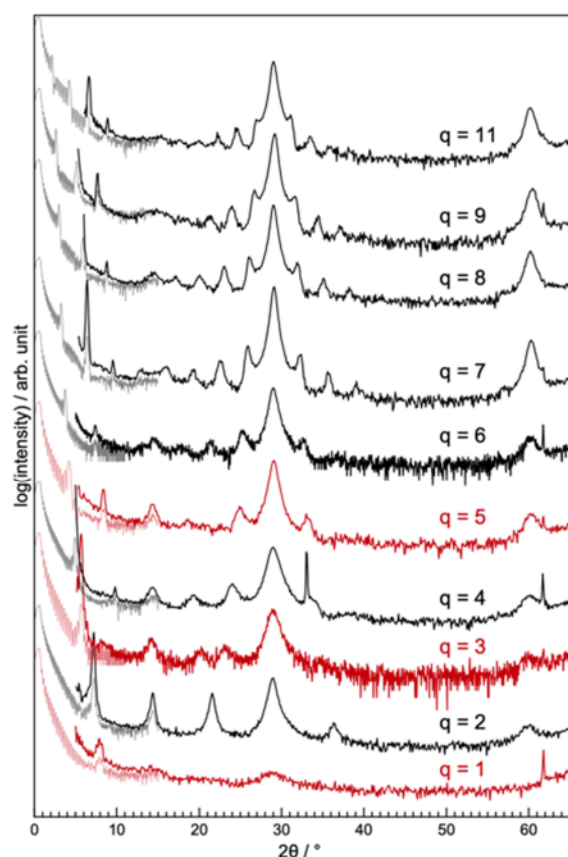


Figure 3. XRD patterns of the as-deposited precursors showing two different groups based on the relationship of the high-angle peaks with the precursor modulation length.

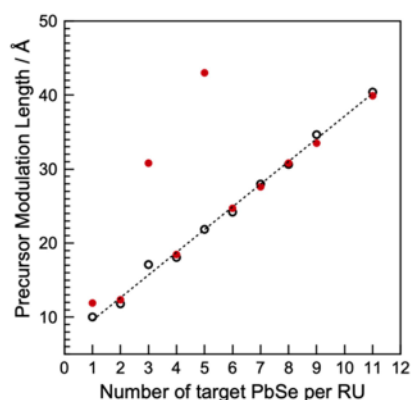


Figure 4. Dependence of the precursor modulation length on q , the targeted number of PbSe monolayers per repeating unit (RU). The black unfilled circles are the modulation lengths determined by dividing the total thickness by the number of deposited layers. The symbols in red are the modulation lengths determined by indexing the as-deposited high-angle reflections as 00 l reflections. For $q = 3$ and 5, these different approaches yield different values, as described in the text.

For these samples, half of the modulation length calculated from the high-angle 00 l reflections falls where expected based on the deposition sequence, our XRF measurements, and the thicknesses of the even-layer thickness samples $q = 2, 4$, and 6. For the $q = 1$ sample, the modulation length calculated from the total thickness divided by the number of repeating units of the elemental layer sequence deposited is close to the

extrapolated value from the even PbSe layer thickness samples. It has the required number of atoms; however, the high-angle XRD (Figure 3) data indicate that the nanoarchitecture is more complicated than the targeted sequence of a PbSe monolayer and a VSe bilayer. The best-fit line between the precursor modulation length and the target number of PbSe monolayers (Figure 4, dotted line) has a slope of 3.07(8) Å, which is the thickness of an elemental PbSe layer that contains the number of Pb and Se atoms to yield a monolayer of PbSe. The intercept (6.5(5) Å) is the thickness of the elemental VSe bilayer, which is slightly thicker than

the thickness of a crystalline VSe₂ trilayer because the precursors are less dense than fully crystallized layers. The deviations from the linear relationship shown in Figures 1 and 4 reflect our ability to reproducibly prepare targeted precursors. Three different behaviors were observed that depend on the targeted number of PbSe monolayers per repeating unit of the precursor.

Precursors with even-numbered q and odd ($q \geq 7$) monolayers evolved to form the targeted heterostructures. The XRR scans collected on the $q = 7$ precursor (Figure 5)

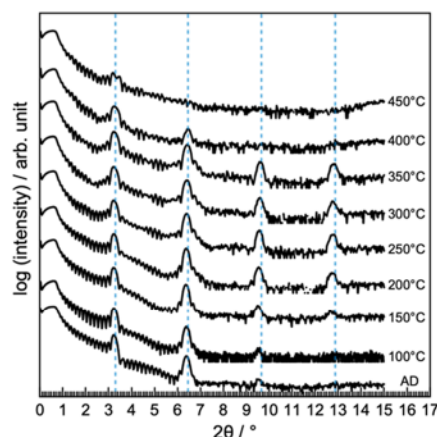


Figure 5. XRR data collected after annealing the $q = 7$ precursor at the designated temperatures. The blue dashed lines are the expected peak positions for the $[(\text{PbSe})_{1+\delta}]_7(\text{VSe}_2)_1$ heterostructure.

collected as a function of temperature illustrate this behavior. The 001 and 002 reflections change in intensity and shift to lower angles as the annealing temperature is increased. The 003 reflection increases in intensity when the precursor is annealed between 150 and 350 °C. The 004 reflection first appears after the 150 °C annealing and grows in intensity up to and including the 350 °C annealing temperature. These changes all indicate that the nanoarchitecture is preserved and the long-range order increases as the precursor self-assembles into the targeted heterostructure. Kiessig fringes due to the reflection of X-rays from the top and bottom of the films and the Laue interference pattern due to the finite number of unit cells in the films^{36,37} are present at each step, suggesting that the films remain smooth throughout the annealing process. The film thickness decreases by a small amount (<5%) as the long-range order develops. The number of diffraction orders decreases when the precursors are annealed above 350 °C, indicating that the initial nanoarchitecture is being lost.

The specular diffraction patterns collected as a function of annealing temperature support the conclusions drawn from the XRR data. Figure 6 contains the data collected on the $q = 7$

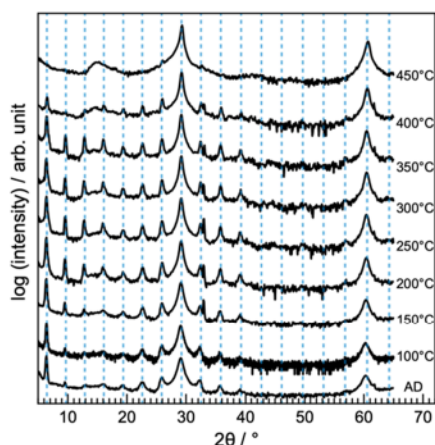


Figure 6. Specular XRD data collected after annealing the $q = 7$ precursor at the designated temperatures. The blue dashed lines are the expected peak positions for $[(\text{PbSe})_{1+\delta}]_7(\text{VSe}_2)_1$.

precursor. Broad high-order $00l$ reflections ($>15^\circ 2\theta$) are observed in the as-deposited precursor, indicating that the sample forms domains with the significant long-range order during the deposition. The higher-angle reflections have the same periodicity ($27.62(8) \text{ \AA}$) as the low-order ($<15^\circ 2\theta$) $00l$ reflections ($27.6(3) \text{ \AA}$), suggesting that the nucleated structure has the same layering of the precursor. As the temperature is increased to 350°C , the low- and high-order $00l$ reflections increase in intensity and converge to have similar peak widths. The c -axis lattice parameter calculated from the position of the reflections after the 350°C annealing is $27.52(6) \text{ \AA}$. At 400°C , the $00l$ reflections start to diminish and we see the growth of a broad VSe_2 reflection at 2θ of $\approx 15^\circ$. At 450°C , the high-angle scan contains only the 001 VSe_2 , and the 002 and 004 PbSe reflections, while the XRR scan shows a very reduced intensity of the 001 reflection from the heterostructure. This suggests that the heterostructure decomposes to thermodynamically most stable products.

Further evidence for the formation of the targeted heterostructures at moderate annealing temperatures comes from GIPXRD pattern of the precursors after annealing to 300°C and the systematic change in c -axis lattice parameters of the products as q is varied. The in-plane diffraction of the $q = 7$ precursor after annealing at 300°C , shown in Figure 7, is representative of the samples with even-numbered q and odd $q \geq 7$. All the observed reflections can be indexed as $hk0$ reflections from either a hexagonal or a square unit cell. The in-plane lattice parameter of the hexagonal unit cell ($3.40(1) \text{ \AA}$) is close to that reported for bulk VSe_2 . The lattice parameter of the square unit cell ($6.12(1) \text{ \AA}$) is close to that reported for

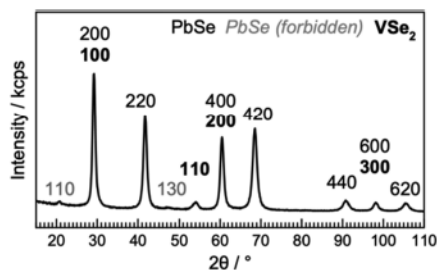


Figure 7. In-plane XRD pattern of a $q = 7$ precursor annealed at 300°C . The indices are shown above the reflections.

bulk PbSe ($6.117 \text{ \AA}$);³¹ however, there are reflections observed that are forbidden in the bulk unit cell, indicating that the structure distorts when q is small. Since only the $00l$ and $hk0$ reflections are observed in the specular and in-plane XRD, respectively, the heterostructure is crystallographically aligned to the substrate with the $\text{PbSe} <100>$ and $\text{VSe}_2 <100>$ planes parallel to substrate. The c -axis lattice parameters of the annealed $q = \text{even}$ and $q \geq 7$ precursors are plotted against q and shown in Figure 8. The linear relationship between the c -

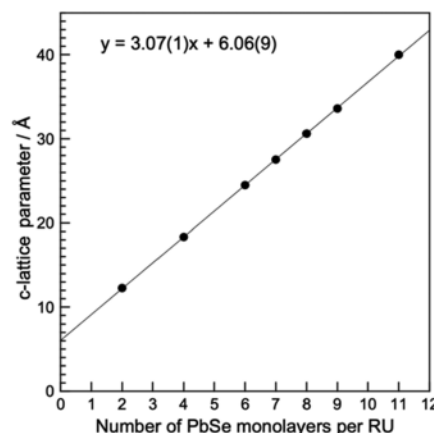


Figure 8. c -Lattice parameters of even and odd samples with $q \geq 7$ monolayers plotted vs q .

axis lattice parameters and q suggests that heterostructures in this category can be predictably synthesized with the correct precursor. The slope ($3.07(1) \text{ \AA}$) is close to the value of half of the lattice parameter of a PbSe unit cell ($6.117 \text{ \AA}$).³¹ The y -intercept ($6.06(9) \text{ \AA}$) is close to the c -axis lattice parameter of bulk VSe_2 ($5.96\text{--}6.11 \text{ \AA}$).³⁸

HAADF-STEM images were collected for annealed precursors to provide additional structural information on the products formed. Figure 9 shows the representative images from the $q = 7$ sample. The whole film cross-section image (Figure 9a) shows that there is a consistent layered structure over the entire sample. The higher-magnification image (Figure 9b) shows that most of the sample consists of a repeating unit cell containing 1 VSe_2 and 7 PbSe monolayers. There are local regions, however, where a repeating sequence of 6 PbSe monolayers– VSe_2 –8 PbSe monolayers– VSe_2 (Figure 9b) replaces the 7 PbSe monolayers– VSe_2 sequence. This replacement occurs randomly throughout the sample. The local information obtained from the HAADF-STEM data is consistent with the average structure inferred from the diffraction data as discussed previously. The PbSe slabs in the film have various in-plane orientations since different zone axes are clearly seen in different slabs, indicating that the film has rotational disorder. The $q = 7$ sample forms mostly $[(\text{PbSe})_{1+\delta}]_7(\text{VSe}_2)_1$ with local regions consisting of $[(\text{PbSe})_{1+\delta}]_6(\text{VSe}_2)_1[(\text{PbSe})_{1+\delta}]_8(\text{VSe}_2)_1$.

A different behavior as a function of annealing was observed for the $q = 3$ and 5 precursors, where the as-deposited precursors have reflections that suggest a doubling of the modulation length. XRR scans for the $q = 3$ precursor collected as a function of annealing temperature are shown in Figure 10. Superimposed on the diffraction scan are blue vertical lines indicating angles where reflections are expected from the targeted $q = 3$ precursor and red vertical lines showing where

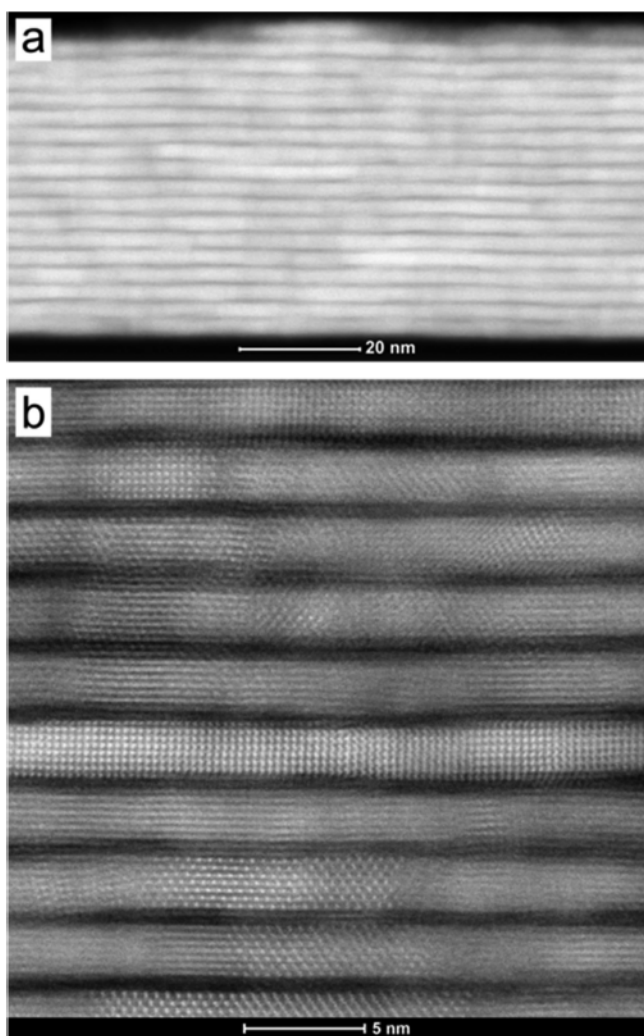


Figure 9. Representative HAADF-STEM images of the annealed $q = 7$ precursor. (a) Image of the entire film thickness. (b) Higher-magnification images demonstrating the presence of mostly $[(\text{PbSe})_{1+\delta}]_7(\text{VSe}_2)_1$ with small areas of $[(\text{PbSe})_{1+\delta}(\text{VSe}_2)_1][(\text{PbSe})_{1+\delta}(\text{VSe}_2)_1]$.

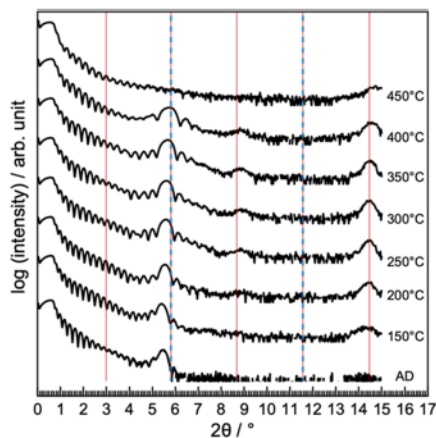


Figure 10. XRR data collected after annealing the $q = 3$ precursor at the designated temperatures. The blue dashed lines are the expected peak positions for a $[(\text{PbSe})_{1+\delta}]_3(\text{VSe}_2)_1$ heterostructure, and the red solid lines are the expected positions for a heterostructure with twice this unit cell size.

additional reflections are expected for a precursor with a doubled modulation length. The 001 reflection of the precursor persists up to 400 °C, but the expected second-order reflection from the precursor does not appear (at the blue vertical dashed line at $\approx 11.4^\circ 2\theta$). Reflections do grow, however, at the approximate locations expected for the third- and fifth-order reflections from a doubled modulation length. The diffraction intensities decrease when annealed at 400 °C and only Kiessig fringes from the interference between the front and back of the film remain after the 450 °C annealing.

The specular diffraction data collected on the $q = 3$ sample, shown in Figure 11, provide additional information about the

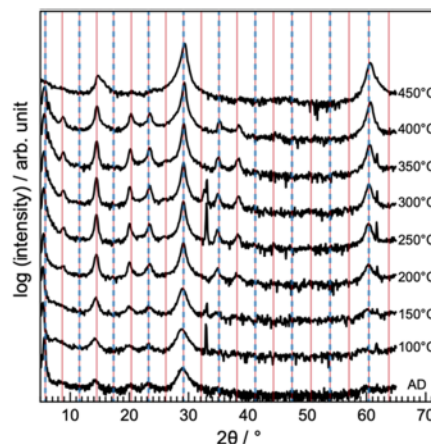


Figure 11. Specular XRD data collected after annealing the $q = 3$ precursor at the designated temperatures. The blue dashed lines are the expected peak positions for a $[(\text{PbSe})_{1+\delta}]_3(\text{VSe}_2)_1$ heterostructure, and the red solid lines are the expected positions for a heterostructure with twice this unit cell size.

structural changes that occur during annealing. The diffraction pattern of the as-deposited sample contains several higher-angle reflections indicating long-range ordering that occurs during the deposition process to form a modulation length twice that which was expected. The high-angle 001 reflections intensify for annealing temperatures between 150 °C and 400 °C, and all of the observed reflections can be indexed as the 001 reflections of a unit cell with twice the repeating period expected from the deposited elemental layers. The positions of several reflections deviate from that calculated from the average c -axis lattice parameter (30.5(1) Å at 350 °C), which is probably a consequence of stacking faults apparent in the HAADF-STEM data discussed in a later paragraph. Only the 001 VSe_2 , and the 002 and 004 PbSe reflections are observed in the specular scan after annealing at 450 °C, indicating that the sample has segregated. The in-plane XRD data collected on the $q = 3$ precursor annealed at 300 °C contain maxima that can be indexed as the $hk0$ reflections from a hexagonal base ($a = 3.42(1)$ Å) and a square base ($a = 6.12(1)$ Å) (Figure SII). These lattice parameters are consistent with the formation of VSe_2 and PbSe respectively. The XRR, specular, and in-plane diffraction data indicate that the $q = 3$ and 5 precursors self-assemble to form superlattices with twice the expected c -axis lattice parameter. The unit cell consists of twice the number of crystallographically aligned VSe_2 and PbSe layers per repeating unit expected from the deposition sequence used to form the precursor.

The HAADF-STEM images were collected to corroborate the structure of the self-assembled $q = 3$ precursor. The sample (Figure 12a) contains a surface region containing light and dark regions without a regular order above a layered film that contains light layers (PbSe) of various thicknesses separated by

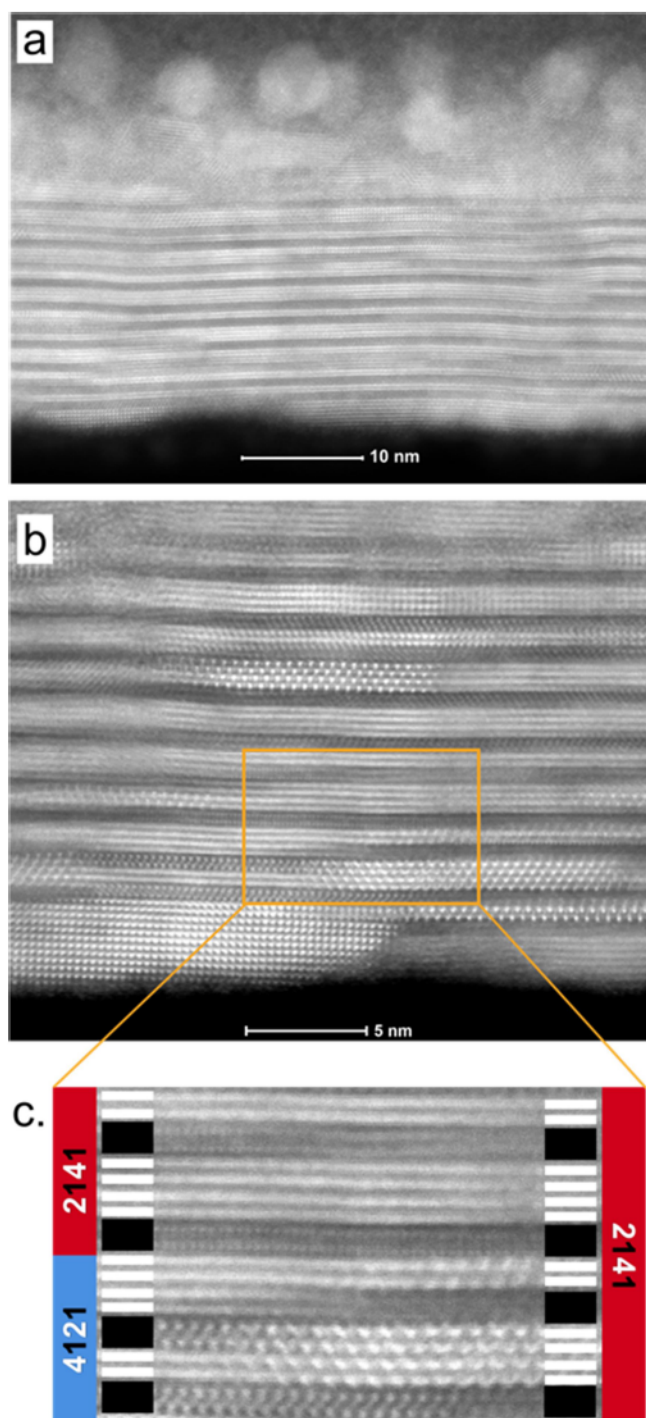


Figure 12. Representative HAADF-STEM images of the annealed $q = 3$ precursor. (a) Image of the entire film thickness, containing regions of $[(\text{PbSe})_{1+\delta}]_2(\text{VSe}_2)_1[(\text{PbSe})_{1+\delta}]_4(\text{VSe}_2)_1$ with many dislocations and stacking errors between them. (b) Atomic-scale resolution image of a selected region, which contains representative stacking errors. (c) Superposition of the image on a model of a grain boundary between different stacking arrangements. Legend: black layers: VSe_2 and white layers: PbSe .

dark layers (VSe_2). Large Pb-rich and V-rich areas are observed at the top of the film indicating that some of the film has already segregated (Figure S12). Within the layered part of the film, there are small domains that contain a regular local stacking pattern. The higher-magnification image (Figure 12b) shows that the light layers are rock-salt PbSe and the dark layers are CdI_2 -structured VSe_2 . Small regions with different stacking sequences appear adjacent to one another. For example, the regions labeled as '2141' and '4121', representing $[(\text{PbSe})_{1+\delta}]_2(\text{VSe}_2)_1[(\text{PbSe})_{1+\delta}]_4(\text{VSe}_2)_1$ and $[(\text{PbSe})_{1+\delta}]_4(\text{VSe}_2)_1[(\text{PbSe})_{1+\delta}]_2(\text{VSe}_2)_1$, respectively, are adjacent to one another. These different stacking regions in the film cannot be distinguished using diffraction alone. The presence of these regions suggests that there are multiple nucleation sites and significant lateral diffusion during the deposition process. The HAADF-STEM sheds light on the structural features that cannot be deduced from the diffraction data, such as the presence of both layering sequences in the film and the domain size of regions of local order.

We prepared a precursor targeting the $[(\text{PbSe})_{1+\delta}]_2(\text{VSe}_2)_1[(\text{PbSe})_{1+\delta}]_4(\text{VSe}_2)_1$ isomer to demonstrate the importance of designing a precursor where only short-range diffusion is required to form the targeted product. Specular diffraction and XRR patterns of the as-deposited and annealed precursors are shown in Figure 13a. The as-deposited

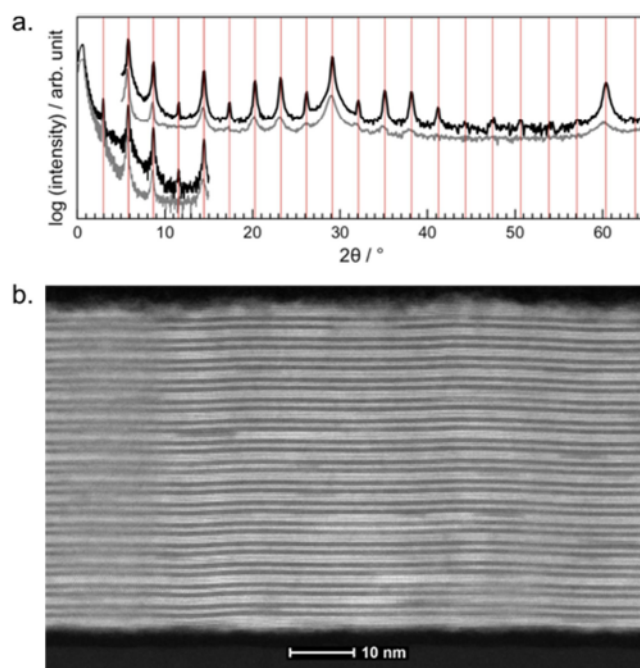


Figure 13. (a) Specular XRD and XRR patterns of the as-deposited (gray) and annealed (black) '2141' precursor. (b) HAADF-STEM image of the annealed precursor film with a nanoarchitecture designed to form $[(\text{PbSe})_{1+\delta}]_2(\text{VSe}_2)_1[(\text{PbSe})_{1+\delta}]_4(\text{VSe}_2)_1$.

precursor has significantly more long-range order than the $q = 3$ precursor. The heterostructure forms at lower temperatures, and the diffraction maxima are significantly more intense and narrower than those shown in Figures 10 and 11, reflecting a more coherent structure. The cross-section HAADF-STEM image of the entire film thickness shown in Figure 13b contains very distinct PbSe and VSe_2 layers and a regular stacking pattern across the entirety of the film. This microscopy data for this sample is similar to those obtained on films with even-

order q and odd $q \geq 7$ monolayers, where only short-range diffusion in the precursor was required during the self-assembly process.

The precursor with $q = 1$ evolves differently than all of the other samples. The XRR data as a function of annealing temperature is shown in Figure 14. The vertical blue dashed

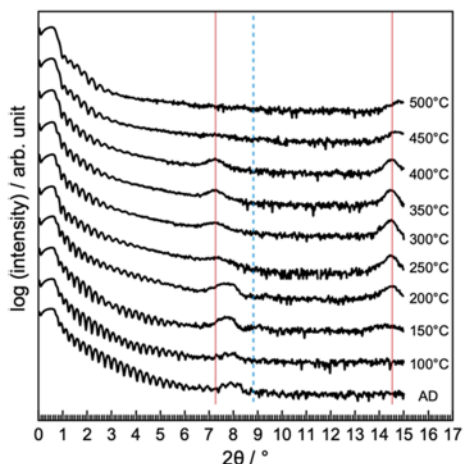


Figure 14. XRR data collected after annealing the $q = 1$ precursor at the designated temperatures. The blue dashed lines are the expected peak positions for the calculated modulation length, and the red solid lines are the expected positions for a $[(\text{PbSe})_{1+\delta}]_2(\text{VSe}_2)_1$ heterostructure.

lines indicate the position of reflections expected from a period calculated from the total thickness divided by the total number of layers deposited. The vertical red lines indicate the position of reflections expected for $[(\text{PbSe})_{1+\delta}]_2(\text{VSe}_2)_1$. The angle of the first reflection observed is significantly smaller than expected in the as-deposited sample and shifts further to lower angles as the precursor is annealed at increasing temperatures. A second reflection appears after annealing at 150 °C and its intensity increases after annealing at higher temperatures. At 300 °C, both of these reflections can be indexed as the 00 l reflections of a heterostructure with a 12.24(3) Å c -axis lattice parameter (red lines), which matches that expected for $[(\text{PbSe})_{1+\delta}]_2(\text{VSe}_2)_1$. The specular diffraction data, shown in Figure 15, contains additional maxima that increase in intensity as annealing temperatures are increased. All of the reflections can be indexed as the 00 l reflections from $[(\text{PbSe})_{1+\delta}]_2(\text{VSe}_2)_1$ after annealing at 250 °C. The even-order reflections appear to have a narrower peak width than the other reflections and higher intensities compared to what is expected from $[(\text{PbSe})_{1+\delta}]_2(\text{VSe}_2)_1$, suggesting that a second phase, VSe_2 , is likely present. This is consistent with the XRF-determined composition of the film. After annealing at 500 °C, the XRR pattern contains only Kiessig fringes and the diffraction pattern contains maxima that can be indexed as the 001 reflection from VSe_2 , and the 002 and 004 reflections from PbSe . The in-plane XRD data also suggest that the film contains crystallographically aligned PbSe and VSe_2 (Figure S11).

The structure of the self-assembled $q = 1$ precursor was further probed by collecting the HAADF-STEM data. The whole film cross-section (Figure 16a) clearly demonstrates a different behavior from the others as the sample contains dark regions laterally separated from the bright regions. This indicates the segregation of large grains of VSe_2 from PbSe .

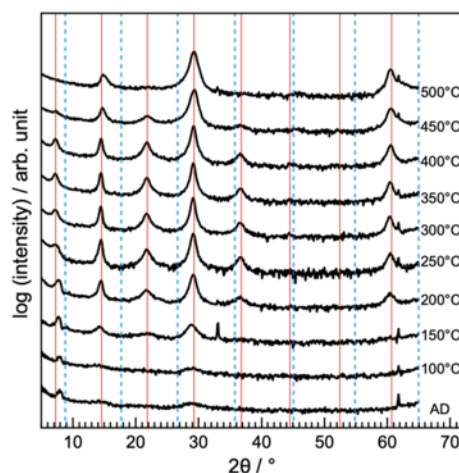


Figure 15. Specular XRD data collected after annealing the $q = 1$ precursor at the designated temperatures. The blue dashed lines are the expected peak positions for the calculated modulation length, and the red solid lines are the expected positions for a $[(\text{PbSe})_{1+\delta}]_2(\text{VSe}_2)_1$ heterostructure.

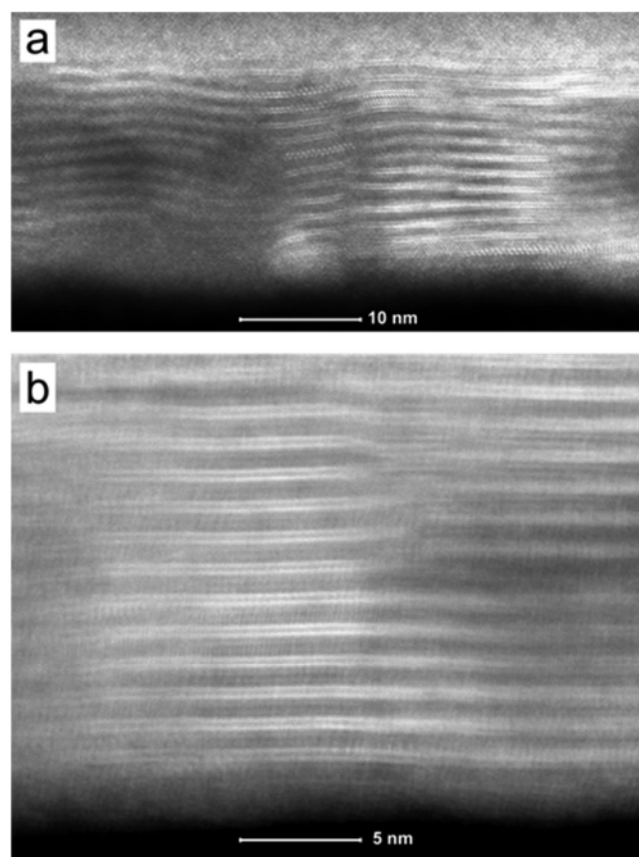


Figure 16. (a) Representative HAADF-STEM image of the annealed $q = 1$ precursor showing brighter regions of $[(\text{PbSe})_{1+\delta}]_2(\text{VSe}_2)_1$ and dark regions containing only VSe_2 . (b) Higher-magnification image of a bright region, showing the alternating layers of PbSe and VSe_2 .

Figure 16b shows that the brighter regions consist of alternate layers of VSe_2 and PbSe bilayers while the darker regions consist of VSe_2 . A higher magnification of the bright region (Figure 16b) suggests that the local structure of the film consists of a mixture of $[(\text{PbSe})_{1+\delta}]_2(\text{VSe}_2)_1$ and VSe_2 . The segregation into these two distinct regions suggests that there

is lateral diffusion taking place during deposition. A consistent theme from the HAADF-STEM data is that the formation of an even number of monolayers of PbSe appears to be favored over odd number of layers, especially for a small odd q value. The XRR and XRD data of the as-deposited sample suggest that the formation of even number of monolayers stems from the initial structure of the precursor.

The underlying assumption of the synthesis approach used here is that the deposition process yields precursors with the nanoarchitecture of a specific target compound. These precursors are expected to form the targeted compounds because atoms do not need to move large distances to form this product relative to more stable alternatives that might require segregation. The nanoarchitecture of the precursor is experimentally controlled by the sequence of elements and the amount of each element deposited. In the system investigated here, the deposition sequence produced precursors close to the desired structure for $q = \text{even}$ and $q \geq 7$, but the nanoarchitecture of the precursors with $q = 1, 3$, and 5 was different than expected from the deposition process. The data presented above suggest that the atoms in the PbSe layer in the $q = 1, 3$, and 5 samples underwent significant lateral surface diffusion during the deposition process to form PbSe layers containing an even number of PbSe monolayers. For the $q = 1$ sample, lateral diffusion of atoms in the VSe layer is also required to explain the uniform thickness and the observed modulation length of the precursor. The precursors preferred to form a defect-rich film with bilayers rather than a more ordered film with a PbSe block containing an odd number of monolayers.

First-principles DFT calculations shed light on an energetic driving force consistent with this behavior. These calculations were used to compute the relaxed total energies of PbSe rock-salt slabs containing different layer thicknesses ($q = 1\text{--}8$), each oriented with the (001) surfaces. Figure 17 shows the plots of

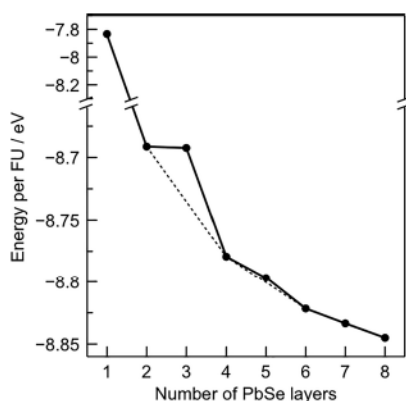


Figure 17. DFT-calculated energies of PbSe blocks in vacuum with varying numbers of monolayers (q). Note the discontinuity in the y axis. The dashed lines indicate the convex hull created by even-numbered blocks.

the calculated energies as a function of q . The energy of the monolayer is much higher than all of the others, consistent with the behavior of the $q = 1$ precursor discussed above. The energies of the odd-numbered layer thicknesses are greater than those derived from the convex hull created by the blocks with even-numbered layers. The results thus indicate that it is more favorable to form a mixture of adjacent even-numbered blocks than odd-numbered blocks. The difference in energy

between the convex hull and the odd-numbered block decreases as the thickness of the odd-numbered block increases. At high values of q , the energy difference between the convex hull and the odd-numbered blocks becomes negligible. There is also a general decrease in energy as the thickness of the block is increased, which is due to the larger number of internal atoms compared to those on the surface.

In DFT calculations, inter- and intra-layer displacements are observed in the relaxed structures due to the termination of the 3D rock-salt structure at the interfaces, as illustrated by the representations of each structure shown in Figure SI3. Within a monolayer, Pb and Se atoms deviate from the ideal rock-salt positions by a shift along the z -axis (normal to the surface), producing a “puckering” pattern in which the sign of the displacements are opposite for Pb and Se atoms. There is also a distinct alternation of short and long distances between the monolayers in the even-thickness PbSe blocks, resulting in the formation of bilayers. The largest puckering occurs in the surface layer, regardless of the thickness of the PbSe block, and the magnitude of the distortion decreases as the PbSe monolayers approach the interior. Overall, the displacement observed reflect the trade-off between the surface reconstruction to lower the surface energy and distortions in the interior layers due to the surface reconstruction. In blocks with an odd number of monolayers, only the exterior slabs form bilayers as the surface reconstructs, resulting in their higher energy relative to the even-thickness PbSe layers. Thus, the slabs with even-layer thicknesses are able to accommodate the bilayer nature of the surface-induced displacements, while this pattern is frustrated in slabs with odd number of layers. We interpret this frustration as the origin of the energetic destabilization of the slabs with odd q values.

While the absolute energies and the distortions in the PbSe layers will be different if the vacuum is replaced by a dichalcogenide layer, these energy calculations suggest an explanation for the observed as-deposited structures and the final structures formed. For the $q = 1$ sample, the energy difference between a single PbSe monolayer between VSe₂ layers versus half the surface being a bilayer and half without PbSe is high enough that the system reconstructs during the deposition as the atoms diffuse on the surface. The instability of monolayer PbSe observed is consistent with the high energy calculated for this structure. Annealing results in continued segregation of the sample into [(PbSe)_{1+ δ]₂(VSe₂)₁ and VSe₂, even though significant diffusion distances are required. For the $q = 3$ and 5 samples, the energy difference between regions with an odd monolayer thickness q versus alternating layers with $q-1$ and $q+1$ is still large enough to reconstruct the PbSe layer during the deposition. Annealing continues the self-assembly of the favored even-layer thickness PbSe regions since the precursor already has a bilayer nanoarchitecture. For $q = 7$, the energy difference is not enough to drive the system to segregate to a layer with a thickness of q monolayers into $q-1$ and $q+1$ layers during the deposition although layers with $q = 6$ and 8 , in addition to $q = 7$, are observed in the HAADF-STEM images.}

In the system investigated here, the stability of PbSe bilayers relative to odd-thickness PbSe blocks drives the diffusion of Pb and Se atoms during both deposition and self-assembly to form coherent bilayers. Similar odd–even alternation based on energy differences between even and odd conformations has been observed in self-assembled alkane monolayers melting points, and the dynamical behavior of liquid alkanes near their

melting points.^{39–42} The results obtained herein highlight the importance of calculations in determining the relative energy of different thickness–thin layers of 3D materials. Different surfaces exposed to the interface will change the relative energies and would aid experimentalists in choosing substrates, heterostructure constituents, and synthetic conditions.

CONCLUSIONS

The data presented here illustrates the importance of the nanoarchitecture of precursors in the self-assembly of the precursors to form heterostructures. The experimental evidence indicates that atoms can undergo long-range surface diffusion during the deposition process to form more favorable configurations than those targeted. Surprisingly, even though long-range diffusion occurs, the precursors evolve into metastable products rather than completely segregating into a mixture of thermodynamically stable binary compounds. Limiting diffusion via low temperatures restricts the topology of the free energy landscape that can be explored, making the structure of the precursor critical in determining what products form. Precursors with a nanoarchitecture close to a specific local free energy minimum self-assemble during deposition and subsequent low-temperature annealing via a near diffusionless process. To form monolayers of compounds with bulk 3D structures, the strength of the bond between the constituents must be strong enough to favor the formation of a monolayer rather than localized islands and the temperature must be low enough to avoid more stable configurations.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.chemmater.0c02922>.

Thickness of each annealed sample determined via analysis of XRR data, grazing incidence in-plane X-ray diffraction patterns of annealed $q = 1$ and 3 precursors, HAADF-STEM and EDX analysis of annealed $q = 5$ precursor, energy-minimized structure of PbSe blocks calculated by DFT, and energies of PbSe blocks as a function of q (PDF).

AUTHOR INFORMATION

Corresponding Author

David C. Johnson – Department of Chemistry and Materials Science Institute, University of Oregon, Eugene, Oregon 97403, United States; orcid.org/0000-0002-1118-0997; Email: davej@uoregon.edu

Authors

Dmitri Leo Mesoza Cordova – Department of Chemistry and Materials Science Institute, University of Oregon, Eugene, Oregon 97403, United States; orcid.org/0000-0002-7527-8950

Shannon Sanaya Fender – Department of Chemistry and Materials Science Institute, University of Oregon, Eugene, Oregon 97403, United States

Mohammad Shahriar Hooshmand – Department of Materials Science and Engineering, University of California, Berkeley, California 94720, United States

Mina R. Buchanan – Department of Chemistry and Materials Science Institute, University of Oregon, Eugene, Oregon 97403, United States

Joshua Davis – Department of Chemistry and Materials Science Institute, University of Oregon, Eugene, Oregon 97403, United States

Taryn Mieko Kam – Department of Chemistry and Materials Science Institute, University of Oregon, Eugene, Oregon 97403, United States

Renae N. Gannon – Department of Chemistry and Materials Science Institute, University of Oregon, Eugene, Oregon 97403, United States

Robert Fischer – Department of Chemistry and Materials Science Institute, University of Oregon, Eugene, Oregon 97403, United States

Ping Lu – Sandia National Laboratories, Albuquerque, New Mexico 87185, United States

Benjamin E. Hanken – Department of Materials Science and Engineering, University of California, Berkeley, California 94720, United States

Mark Asta – Department of Materials Science and Engineering, University of California, Berkeley, California 94720, United States

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acs.chemmater.0c02922>

Author Contributions

The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

XRD, X-ray diffraction; XRR, X-ray reflectivity; XRF, X-ray fluorescence; HAADF-STEM, High-angle annular dark-field scanning transmission electron microscopy

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