Synthesis of Crystalline Superlattices by Controlled Crystallization of Modulated Reactants

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A series of crystalline superlattice compounds containing an integral number of intergrown transition metal-dichalcogenide layers was prepared through controlled crystallization of Ti/Se/Nb/Se superlattice reactants rather than through epitaxial growth. The component elemental-layer thicknesses and annealing sequence were chosen to favor interfacial nucleation of the component binary compounds. The layered reactants contracted in the *c*-axis direction during an initial low-temperature anneal as NbSe₂ and TiSe₂ crystallites nucleated and grew along the interfaces, kinetically trapping the desired superlattice structure. The *c*-axis domain size increased gradually as a function of annealing time and temperature, yielding high-quality *c*-axis-oriented TiSe₂/NbSe₂ crystalline superlattices after annealing at 500°C. The large number of observed 00ℓ diffraction orders permitted the average crystal structure of the superlattice in the direction of the *c* axis to be determined through a Rietveld analysis.

The ability to prepare well-defined heterostructures on a nanometer scale has not only led to new technology [for example, higher electronic device speeds (1) and "band gap" engineering of materials (2)] but also has revealed fundamentally new phenomena such as the quantum Hall effect (3) and the fractional quantum Hall effect (4). Several synthesis techniques based on layer-by-layer epitaxial growth have been developed that involve sequential exposure of the growing crystal surface to fluxes of the components. The substrate is typically heated in order to optimize the surface mobility of the components, and the flux rates are carefully controlled to compensate for the relative sticking coefficients of the component species. Reactants can be supplied by evaporation, sputtering, and chemical vapor deposition. With molecular beam epitaxy (MBE), the composition of the growing film can be controlled and varied on length scales as short as 5 to 10 Å. Liquidand solid-phase epitaxial growth techniques have also been developed for the preparation of modulated structures, but the length scales on which the composition can be modulated are typically greater by a factor of 10 than those achieved with MBE (5).

Within heterostructure superlattices, interfaces constitute a large fraction of the total material. In semiconductor devices, where defect and impurity concentrations dominate electrical properties, controlling interfacial quality is crucial. The low background pressure and epitaxial nature of interfaces in MBE lead to heterostructures with very low impurity and defect densities. Although epitaxial growth limits the disor-

Department of Chemistry and Materials Science Institute, University of Oregon, Eugene, OR 97403, USA. der normally found at the interfaces, it greatly restricts the range of superlattice components. Although the development of strained layer epitaxy (6) and van der Waals epitaxy (7) has reduced the stringent latticematching requirement for epitaxial growth, lattice-matching of the components of a heterostructure is still an important synthesis parameter. In addition, growth conditions for the component materials of a heterostructure must be compatible, an issue that becomes progressively more problematic as the number of elements in the heterostructure compound increases.

Here we describe an alternative approach to the production of new heterostructures, based not on epitaxial growth but on the kinetic trapping of the desired crystalline superlattice from the solid-state reaction of an elementally modulated reactant. In spirit, this approach parallels methods used by organic chemists, who might carefully synthesize two reactant molecules that would be coupled through kinetic control in the key reaction step in the synthesis of a large natural product. Instead of two molecules, we prepared interwoven layers of the elements within a superlattice reactant. Choices regarding layer sequence and thickness were based on mechanistic studies of the initial stages of the solid-state reactions between the binary components. Lowtemperature annealing nucleated the binary compounds at interfaces. These crystallites grew along the interfaces, kinetically trapping the desired superlattice structure. This synthetic approach provides advantages in the preparation of heterostructures containing ternary compounds and structures containing nonlatticed matched components, both of which would be difficult to prepare through epitaxial growth.

The new compounds we describe are

intergrowths of two-dimensional transition metal dichalcogenides [MY₂ (M: Nb, Ti, Zr, Hf, V, Ta, Mo, W or Sn; Y: S, Se or Te)]. Heterostructures of MY₂ species were attractive targets for three reasons. First, the effects of composition and layer thicknesses on interfacial reactivity in M-Se systems provided the mechanistic background information necessary to design the initial reactants (8). We also suspected that the layered structure of these compounds could facilitate the preparation of compositionally abrupt interfaces. Finally, heterostructures of MY₂ species, which range from semiconducting to metallic depending on the metal used (9), allow study of the interplay between the length scale of the individual layers and a host of physical phenomena. For example, the availability of suitable superlattice structures permits assessment of the effects of superlattice structure on intercalation phenomena (10) such as stagingthe selective intercalation of molecular species into the van der Waals gaps of every nth layer.

The idea for this synthetic approach to heterostructures evolved from experimental results obtained during examination of the early stages of the reaction between layers of elemental Nb and Se. Crystalline NbSe₂ formed after extended low-temperature annealing and was oriented with its *c* axis along the normal to the substrate. At this point, the sample was still compositionally modulated (Fig. 1), with x-ray diffraction (XRD) and differential scanning calorimetry (DSC) data suggesting that the NbSe₂ product both nucleated and grew along each reacting planar interface. We observed the interfacial

002)

10 20

Relative intensities



30 40 50 60 70 80

d

с

b

а

1181

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formation of NbSe₂ over a wide range of compositions and thicknesses. Reference to the Nb-Se phase diagram showed that other solid-state compounds were thermodynamically more stable than was a mix of the elements and NbSe₂ at these compositions, which suggested that the initial formation of NbSe₂ at the interface was a kinetic phenomenon. Extended annealing resulted in the ratio of compounds predicted by the phase diagram, confirming that NbSe₂ was only a kinetic reaction intermediate.

The reaction mechanism suggested by these results-interfacial nucleation and oriented crystal growth of the kinetic product NbSe₂—had intriguing possibilities when extended to the more complicated initial superlattice reactant shown in Fig. 2. If this reaction mechanism was applied to the ternary superlattice, we predicted that the respective MY₂ products would each nucleate and grow along the reacting M-Se interfaces during low-temperature annealing. Because the nucleation of a solid solution or ternary product would be hindered by the slow diffusion of the Nb and Ti through the intervening Se layers, further annealing should result in the dichalcogenide heterostructure shown as the kinetically trapped product.

We tested the proposed reaction sequence by preparing a series of superlattice reactants that had the overall structure shown in Fig. 2, varying the thickness and number of Nb and Ti layers. The composition of each Nb-Se and Ti-Se period was chosen to be that of the desired MY_2 compounds, and an amount of each element was deposited to yield an integral multiple of the known crystallographic unit cell so that there would be no elemental reactants left in the superlattice after extended annealing. The evolution of the high- and lowangle XRD patterns of a sample with 3.5 NbSe₂ layers and 3.5 TiSe₂ layers is shown in Fig. 3 as a function of annealing temperature. The low-angle XRD data indicated that the compositionally modulated nature of the sample persisted throughout annealing. The broad XRD maxima evident at high angles upon low-temperature annealing result from the nucleation of the MY_2 layers. The DSC data collected on this sample showed the continuous evolution of heat up to 500°C, indicative of the growth of MY₂ crystallites. The XRD patterns showed the continuous growth of the highangle 00l Bragg diffraction peaks as the MY₂ nuclei grew.

Diffraction data were then collected on a sample that was deposited directly on a Si wafer containing the appropriate masses of the elements to form six NbSe₂ layers and six TiSe₂ layers. Rocking-curve XRD scans of the (0 0 12) superlattice diffraction peak taken as a function of annealing temperature narrowed as annealing time and temperature increased, with the peak widths decreasing from $>3^\circ$ to 0.08°. The superlattice gradually evolved into the desired kinetically trapped crystalline structure, with the 00l XRD planes aligned parallel with the initial interfaces present in the reactant. After this sample was annealed at 500°C for 197 hours, the XRD pattern contained many well-resolved maxima (Fig. 4) that were indexed as 00l diffraction maxima, as was consistent with a *c*-axis lattice parameter with six $NbSe_2$ layers and six $TiSe_2$ layers in the repeating unit of the superlattice. The XRD pattern met the qualitative expectation for the intended structure, consisting of the convolution of the supercell XRD on top of the pattern expected for the dichalcogenides. Given the amorphous nature of the initial superlattice reactant, the high quality of this XRD pattern was surprising.

To determine the structure perpendicular to the layering direction, we searched for



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Fig. 2. The suggested reaction pathway of a superlattice reactant containing alternating Nb and Ti layers, each separated by intervening layers of Se. During low-temperature annealing, the as-deposited layers (far left) begin to interdiffuse (left of center). Continued annealing results in interfacial nucleation (center) and lateral growth of the respective binary components (right of center), kinetically trapping the desired superstructure as the final product (far right).

Fig. 3. Diffraction data collected on a superlattice reactant in which elemental layers were deposited in appropriate thickness to yield 3.5 NbSe₂ layers and 3.5 TiSe₂ layers in the final product. The sample was deposited on a polymer-coated substrate and removed from this substrate by dissolution of the polymer (8). The resulting particles were then annealed at the indicated temperatures in an oxygen-free environment. XRD pattern a is that of the as-deposited sample, b is the pattern after annealing for 2 hours at 200°C, c is the pattern after annealing for 2 hours at 350°C, and d is the pattern after annealing for 2 hours at 500°C. The lattice parameter of the superlattice is 43.50 \pm 0.44 Å after annealing at 500°C.

Fig. 4. XRD data collected on a superlattice reactant in which elemental layers were deposited in appropriate thickness to yield six NbSe₂ layers and six TiSe₂ layers in the final product. This sample was annealed for a total of 197 hours at 500°C. All of the XRD maxima can be indexed as 00ℓ lines of the superlattice as indicated. The curve under the data points is a calculated XRD pattern obtained from a leastsquares Rietveld structural refinement resulting in the structure shown in Fig. 5.





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and found the 10l XRD intensity in reflection mode on a single-crystal diffractometer for a sample annealed for 10 hours at 500°C. The diffraction signal consisted of a ring of intensity indicating well-formed MY₂ layers that were not uniformly oriented in the ab plane, because multiple domains were present. This result was consistent with interfacial nucleation of the layers, as suggested in the mechanism shown in Fig. 2, whereas epitaxial growth would have resulted in a preferred orientation of the *ab* plane relative to the substrate. As order in the plane perpendicular to the *c* axis develops, the ring of intensity should evolve into a hexagonal pattern of intensity. Observation of all of the expected 62 00l XRD orders between 1° and 80° highlighted the well-formed structure that developed along the c axis as we kinetically trapped the



Fig. 5. The refined structure (after annealing for a total of 197 hours at 500°C) for the superlattice unit cell containing six NbSe₂ layers and six TiSe₂ layers. The structure has inversion symmetry. Indicated next to the respective layers are the percent occupancy of each of the metals (Nb/Ti ±2%) and the interlayer and intralayer spacing between Se layers (±0.01 Å). The intralayer spacing for the Nb and Ti layers brackets those observed in the binary compounds. There is a distinct change in interlayer van der Waals spacing through the interface region between the NbSe₂ and TiSe₂ blocks resulting from the *a*-axis mismatch between the dichalcogenide components.

superlattice structure.

Standard analysis of XRD in superlattice materials treats the superlattice as a perturbation effect on top of the original structures of the components (11). In this approach, the superlattice XRD peaks are indexed as $\pm n$ relative to the main XRD maxima in the component materials. Frequently, the observation of these maxima is used mainly as proof that a superlattice structure exists. The quality of the 00l XRD data shown in Fig. 4 permitted us to gain further insight into the structure of our superlattices by treating the structure as if it were composed of a single large unit cell containing multiple layers similar to those of the parent structures. We refined the positions and occupancies of the atoms using Rietveld analysis (12). The curve under the data points in Fig. 4 is a calculated XRD pattern for the structure along the z axis (shown in Fig. 5) that resulted from leastsquares analysis of these data.

The refined structure of the crystalline superlattice (Fig. 5) contained the expected structural components based on the structure of the initial multilayer reactant. As designed, the structure contained six layers of TiSe₂ and six layers of NbSe₂, with interlayer distances comparable to those found in polytypes of the pure MY₂'s. Refining the occupancies of the metals in the layers, we found little Ti in the Nb layers as compared with the amounts of Nb in the Ti layers. This may be best explained by the fact that Ti is always octahedrally coordinated in the dichalcogenides, but Nb in NbSe₂ can be either octahedrally or trigonal prismatically coordinated. At the boundary between the NbSe2 and TiSe2 layers, we found one layer with a substantially mixed metal population. Additionally, the van der Waals gaps in both the NbSe₂ and TiSe₂ regions were comparable to those found in the pure dichalcogenides, although the gap between the Ti and Nb dichalcogenide blocks was slightly larger because of the *a*-axis mismatch between the dichalcogenide components.

We conducted several annealing experiments to probe the rate and extent of interdiffusion of the metal atoms within the superlattices. At 500°C, we observed crystal growth but little intermixing of the different metal layers. When we increased the temperature to 600°C, we observed slow intermixing of TiSe₂ and NbSe₂ layers. Raising the temperature to 650°C resulted in nearly complete intermixing of the metal layers within 12 hours, destroying the superlattice periodicity as the dichalcogenide solid solution formed. This result confirmed that these layered structures were not equilibrium phases but were kinetically stable only at lower temperatures. Because the $T\Delta S$ term (temperatures times entropy) of the free energy increases with increasing T, intermixing of the metals is favored at higher T. Thus, these structures cannot be prepared by traditional synthetic methods such as direct reaction of the elements at high T, as they are thermodynamically unstable.

The growth sequence we observed was far from equilibrium as we kinetically trapped the desired superlattice products. Understanding the reaction mechanism is crucial to extending this approach to new superlattice materials. Based on analysis of XRD data collected as the superlattice was formed, our working hypothesis concerning the reaction mechanism includes an initial interdiffusion of the elements along the interfaces, followed by interfacial nucleation of the binary components, as shown in Fig. 2. These crystals grow in an oriented manner because of the asymmetric nature of the initial reactant. Grains misoriented relative to the initial layering must be smaller than those that grow along the layers. Ostwald ripening of the grains therefore leads to an increasingly more oriented material as annealing time increases. Annealing at higher temperatures leads to the mixing of the metals and the destruction of the superlattice. Although further studies investigating the reaction mechanism in other systems are required to ascertain its general applicability, this model is conceptually easy to extend to many reacting systems.

What determines whether a superlattice product is a composite or a new compound? On a micron modulation scale, the material is a composite whose physical properties result from the component compounds. As the length scale of the compositional modulation decreases to a few Å, a transition from composite behavior to that of a new compound should occur, in which observed physical properties do not derive from the component compounds. Exploration of the evolution of properties throughout this transition region presents an opportunity to gain insight into the design of materials with desired properties. Such research is multidisciplinary in nature and presents challenges in the synthesis of new materials with designed structures, in determination of their atomic structure (particularly through the transition region between materials), and in measurement of their physical properties. Controlled crystallization of superlattice reactants provides an additional route to synthesis of these materials and increases the variety of compounds that can be intergrown.

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Giant Facets at Ice Grain Boundary Grooves

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The energy barrier for nucleation on the basal plane of ice has a striking manifestation when the basal orientation is present in a grain boundary groove. As the ice-water interface containing the groove advances, large planar facets grow out of the grain boundary. The facets exhibit dramatic hysteresis, and they can be up to 30 times larger than predicted by equilibrium models. Measurements of the growth direction of the facets yield insight into the nature of the nucleation process. The facets also provide a way to study the relaxation of twist along grain boundaries.

When a polycrystalline solid comes into contact with another phase, small indentations of the solid surface form where grains of different orientations meet. These indentations, termed grain boundary grooves, are observed in a number of contexts, such as at the surface of a polished solid ingot that has been annealed or at the boundary of a solid with its own melt. Grain boundary grooves have a long history in the study of metallurgy (1). They are well understood theoretically and experimentally and can provide useful information about material properties, such as interface energies and diffusion constants (2).

Grain boundary grooves at a solid-melt interface are analogous to the meniscus of a liquid that wets the wall of a vessel. The liquid rises to a certain height L because it can reduce the surface energy by an amount proportional to σL , where σ is the difference in surface energy between the dry and wet wall. However, the rise in height is limited by the cost in gravitational energy, proportional to $L^3\rho g$, where g is the gravitational constant and ρ is the liquid density. Apart from geometrical factors, the rise *L* is $(\sigma/\rho g)^{1/2}$. For a grain boundary groove, instead of the cost due to gravity, there is a free energy cost due to the presence of supercooled liquid inside the groove. This cost is given by the product of the volume of supercooled liquid and the difference in free energy between solid and liquid at the average temperature in the groove. Replacing ρg , then, we have $(q_{\rm m}/T_{\rm Q})(dT/dx)$, where $q_{\rm m}$ is the latent heat of melting per unit volume of the solid, T_0 is the melting temperature, and dT/dx is the temperature gradient in the groove. The groove size is given by

$$L \propto \sqrt{\frac{\sigma'}{q_{\rm m}} \frac{dT}{dx}}$$
 (1)

where σ' is the grain boundary interface energy. Anisotropy in the interface energies and the difference in thermal conductivities between the solid and liquid must be considered to calculate the exact groove shape. Indeed, a measurement of the shape can be used to determine the anisotropy in the crystal surface free energy (3). Nevertheless, the overall size scale for the groove should be set by the "capillary length" *L* as given above.

We were therefore surprised to observe plane-faceted grooves in ice whose linear dimensions exceeded the expected value by more than a factor of 30. Adjacent to these faceted grooves were typical rounded grooves whose dimensions were correctly given by the capillary length. Moreover, the facet size was not a single-valued function of the temperature gradient: Considerable hysteresis in facet size was observed as the ice-water interface advanced or retreated. This behavior is explained by a nucleation barrier to growth normal to the plane facets, in contrast to the growth of rounded orientations.

The cell used for the ice growth measurements has been described previously (4). Ice is grown in the shape of a thin disk (Fig. 1A). The temperature can be controlled both at the center of the disk as well as around the perimeter of the cell. By (1980); M. S. Whittingham, *Prog. Solid State Chem.* **12**, 41 (1978).

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adjusting both temperatures, the radius of the ice and the radial temperature gradient can be set independently. The ice was nucleated by briefly touching a cotton tip cooled in liquid nitrogen to the center of the cell. The ice then grew out to some steady-state radius determined by the temperature conditions. Once steady state was reached, the temperature could be ramped so that the ice disk radius slowly increased or decreased. The ice was examined along the axial direction with a microscope, either directly or between crossed polarizers. Images were digitized and stored on computer disk or were recorded on photographic film. A typical ice disk contained from 6 to 10 different domains, divided by grain boundaries. The grain boundaries generally extended radially out to the ice-water interface, where grooves were observed.

There was a large difference in size between faceted grooves and rounded grooves on adjacent grain boundaries (Fig. 1B). To understand the origin of these large facets, we observed their development. As the ice disk radius decreased (Fig. 2A, top row), the facets shrank, but the intersection between the facets did not move until the facets reached a minimum size. After that, the whole groove receded without change of shape or size. As the ice was regrown (Fig. 2A, bottom row), the facets grew, but again the line of intersection was initially fixed. When the facets reached a maximum size, the ice disk edge and facets moved in unison. The facet size was not a single-valued function of the conditions but depended on the manner in which the facet was formed (Fig. 2B). This behavior was reproduced numerous times for the facet shown and for several other facets as well.

The explanation is as follows: The surface of a crystal may have orientations that are either "flat" or "rough" (5, 6). A flat orientation is smooth on a molecular scale and consists of a single crystal plane. Growth on a flat plane requires the undercooling to be larger than a threshold value to nucleate a two-dimensional (2D) island. The value of the threshold undercooling ΔT corresponds to an energy barrier for the formation of a nucleus of a critical radius; nuclei smaller than this will shrink, whereas larger ones will grow (7). Conversely, there is no barrier to growth on a rough orienta-

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