Articles

Synthesis of Designed W−WSe_2 Heterostructures from Superlattice Reactants

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A nanocomposite consisting of alternating, orientated, crystalline layers of tungsten and tungsten diselenide was prepared using a designed elemental superlattice as the initial reactant. In binary tungsten−selenium multilayers, tungsten diselenide was observed to interfacially nucleate upon deposition and grow preferentially along the interface. This information was used to design a multilayer reactant containing a thick tungsten layer in addition to thin tungsten and selenium layers in the repeating unit. The evolution of the structure of the superlattice reactant as a function of annealing temperature was followed using both low- and high-angle diffraction. The diffraction data confirmed the formation of a superlattice or nanostructured composite consisting of alternating layers of tungsten and tungsten diselenide containing crystallites limited in *c*-axis domain size by the layer repeat.

Introduction

The design, synthesis, and properties of supramolecular systems and nanoscale-engineered advanced materials have been of current interest due to their unusual structure and properties.[1,2] Small particles of semiconducting materials have electronic and optical properties determined by the size of the particles as well as the extent of confinement of the valence electrons.[3,4] Preparing metals in nanocrystalline form can lead to enhanced mechanical and physical properties such as strength, ductility, wear characteristics, and corrosion behavior.[2] The enhanced properties of nanocomposites over those expected from simple composite mixtures along with the short length scale of the particle size raises the interesting question of when does a nanocomposite become a new compound. To explore this question and to understand the interrelationships between properties and the size of crystallites, it is necessary to prepare composites with a narrow distribution of crystallite sizes and explore how the properties change as a function of crystallite size.

The synthetic challenge of preparing supramolecular and nanoengineered materials with controlled superstructures, particularly with long-range order or regular periodicity rather than as a material with a broad range of particle sizes and interparticle distances, has resulted in a variety of novel synthetic approaches.[5] Heterostructures with exceedingly low impurity and defect densities, important parameters to control for device applications, are prepared using molecular beam epitaxy. Epitaxial growth limits the disorder normally found at the interfaces, but it greatly restricts the range of superlattice components. While the development of strained layer epitaxy[6] and van der Waals epitaxy[7,8] has relieved these restrictions somewhat, the components of the structure must be lattice matched. In addition to vapor deposition based synthetic approaches, chemists have developed a number of synthetic approaches to nanoscale materials. Templating is an example of one of these approaches, which exploits the preexisting, periodic, single-sized, and single-shaped void spaces found in nanoporous materials to prevent agglomeration of clusters formed in the pores.[1]

Our approach to this synthetic challenge has been to use superlattice reactants which consist of a regular repeat of the desired elemental layers deposited in a UHV deposition chamber. To prepare a nanocomposite in the form of a superlattice structure with a regular spacing of the desired components, one prepares a modulated elemental reactant containing the correct composition to crystallize the desired components, as shown in Figure 1. Upon low-temperature annealing, the elemental components react to form the desired components of the superlattice while maintaining the nanoscale structure of the larger superlattice.[9] The nanoscale structure is kinetically trapped by the slow diffusion rates existing during the relatively brief, low-temperature annealing. Long-range structural coherence was observed to develop during the annealing of reactants designed to yield interwoven layered dichal-

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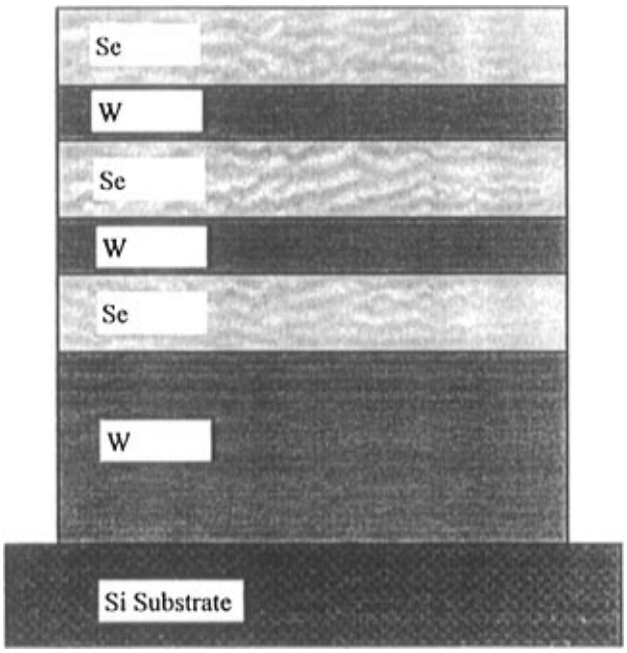

Figure 1. Schematic of the structure of the repeating unit of a reactant designed to evolve into a nanocomposite containing alternating layers of tungsten diselenide and tungsten metal.

cogenide components.[9] An advantage of this approach is the ability to change either the thicknesses or the repeat sequence of elemental layers within the initial superlattice structure to control the component thicknesses in the product superlattice or nanocomposite.

This article reports our first attempts at applying this approach to materials without any structural similarities or epitaxial relationships between the components of the superlattice. The lack of epitaxial relationships and structural similarities between the components of the proposed superlattice makes it doubtful that long-range structural coherence will develop across many layers of the material. Tungsten and tungsten diselenide were chosen as the initial system to investigate for several reasons. These materials have widely different properties (tungsten is a hard metal, while tungsten diselenide is a semiconductor isostructural with molybdenum disulfide which is used as a lubricant) and a nanocomposite of these materials might have interesting tribological properties. The tungsten−selenium phase diagram also suggests that it should be possible to prepare an abrupt tungsten diselenide−tungsten interface,[10] making this a promising first system in which to test our synthetic approach. We first discuss the evolution of structure of simple W−Se superlattice reactants as a function of annealing temperature, concluding that WSe_2 nucleates and grows at the internal interfaces. This information is used to prepare an initial reactant with a thick tungsten and several thin tungsten and selenium layers in the repeating unit designed to evolve into a nanocomposite of tungsten and tungsten diselenide. We discuss the evolution of this superlattice reactant as a function of annealing temperature and time.

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Experimental Section

Sample Preparation. A custom-built ultrahigh-vacuum chamber with independently controlled deposition sources was used to prepare the multilayer films used in this study. Tungsten was deposited at a rate of 0.4 Å/s using a Thermionics e-beam Gun source independently controlled by a Leybold-Inficon XTC quartz crystal monitor. A Knudsen source controlled by an Omega 9000 temperature controller maintained selenium at a temperature of 250 °C. This resulted in a deposition rate of approximately 0.8 Å/s for selenium as monitored by a separate quartz crystal monitor. The intended thickness of the repeating unit containing an tungsten and selenium layer varied between 17 and 22 Å in all of the samples prepared. To obtain sufficient sample mass for the DSC and TGA experiments, typically 50 layers were deposited resulting in a total film thickness of approximately 1000 Å.

Thermogravimetric Analysis (TGA). Thermogravimetric analysis was used to determine the actual stoichiometry of the calibration samples containing various layer thicknesses of tungsten and selenium. These samples were heated to 470 °C in flowing air and then held at this temperature for 30 min. The weight change recorded is the difference between mass loss due to the evaporation of excess selenium and the weight gain resulting from the oxidation of the tungsten forming WO_3, as confirmed by X-ray diffraction. A calibration curve was constructed which allowed determination of target layer thicknesses required to obtain a given stoichiometry. Subsequent samples were prepared using this calibration curve, and stoichiometry was checked for each sample by thermal gravimetric analysis.

Thermal Analysis. Reactions between the elemental layers in the samples as a function of increasing temperature was monitored by DSC utilizing a TA Instruments TA9000 calorimeter fitted with a 910DSC cell. The temperature difference detected in this experiment was greatly enhanced by examining the sample free of the substrate. This was accomplished by depositing the multilayer composite on a PMMA-coated wafer. The wafer was then immersed in acetone, which dissolved the PMMA and floated the multilayer film free of the substrate. The resulting pieces were collected by filtration through a teflon filter and placed into an aluminum DSC crucible. The sample was then dried under reduced pressure to remove any residual acetone.

Two different calorimetry experiments were completed on each sample. A portion of each sample was heated at a constant temperature ramp from 50 to 550 °C at 10 °C/min, immediately followed by a subsequent run using the same sample and temperature ramp. Typically, a third such run was also collected. The difference between the first and second run records the irreversible changes in the superlattice as a function of temperature. The difference between the second and third runs is used to obtain a measure of the repeatability of the experiment.

In the second experiment, a portion of each sample was ramped at 10 °C/min to the temperature of interest. After they had cooled to room temperature, the samples were examined using high-angle X-ray diffraction. The samples were then returned to the DSC module and heated to the next higher temperature of interest. This technique permits structural changes to be correlated with either exotherms or endotherms found in the calorimetry data.

X-ray Diffraction. High-angle diffraction data were used to determine whether the as-deposited, floated, and annealed samples contained crystalline elements or compounds. Low-angle diffraction data were collected to determine if the samples contained a periodic layered structure and to determine the total film thickness and smoothness by observing the interference between X-rays scattered from the front and the back of the film. These data were collected on a Scintag XDS 2000 $\theta-\theta$ diffractometer using copper radiation with a sample stage modified to allow rapid and precise alignment. X-ray flux was adjusted to optimize the low-angle diffraction data for each sample.

Table 1. Intended Layer Thicknesses and Experimentally Determined Repeating Units for Samples Prepared as Part of This Study

sample	intended tungsten thickness (Å)	intended selenium thickness (Å)	no. of repeating layers	measd repeat layer thickness (Å)	measd stoichiometry x in WSe_x
WSe-6	10.5	9.2	60	18.6(1)	1.07(3)
WSe-7	10.5	11.5	50	21.5(1)	1.11(3)
WSe-8	8.1	11.5	50	19.5(1)	1.86(3)
WSe-9	6.5	11.5	50	17.9(1)	2.09(3)
WSe-10	6.5	13.7	50	19.0(1)	2.06(3)
WSe-11	8.1	13.7	13	22.0(1)	2.10(3)

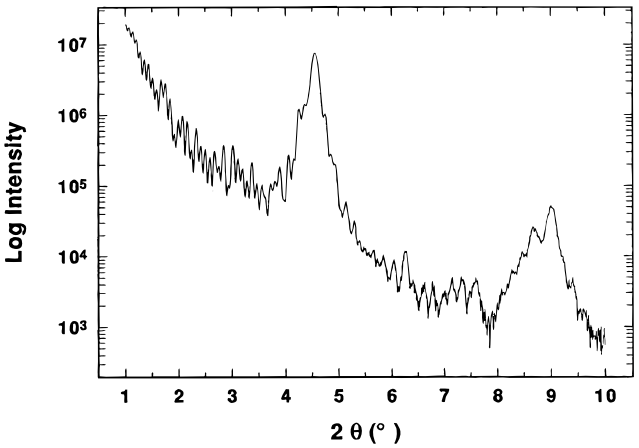

Figure 2. Low-angle X-ray diffraction pattern of a superlattice reactant containing 8.1 Å of tungsten and 11.5 Å of selenium in the repeating unit.

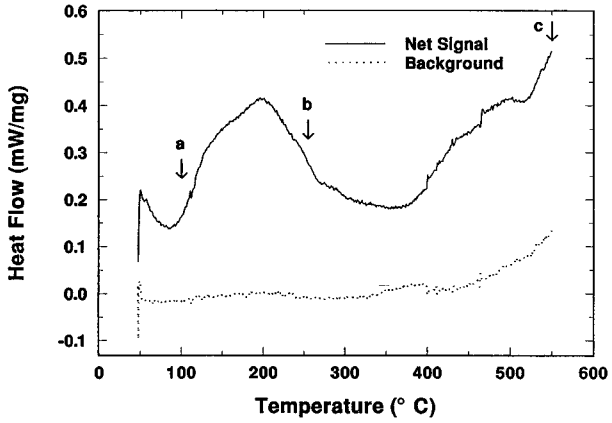

Figure 3. Differential scanning calorimetry data of a tungsten−selenium superlattice reactant. The arrows indicate the temperature where X-ray diffraction data (shown in Figure 4) were collected.

Results and Discussion

Six tungsten−selenium samples of varying composition and layer thicknesses were prepared as part of this investigation. The intended elemental layer thicknesses, the experimentally determined layer spacings, and the experimentally determined compositions using TGA analysis for these samples are summarized in Table 1. As expected, a linear relationship was found between the ratio of the intended layer thicknesses and composition which was used as a calibration to prepare samples with desired composition and layer thicknesses. Slight shifts in the exact positions of the crystal monitors relative to the sources and samples produced systematic discrepancies between the ratio of the intended W and Se thicknesses and the experimentally determined compositions between samples made in different sets.

A typical low-angle diffraction pattern of an initial superlattice reactant, shown in Figure 2, contained Bragg diffraction maxima out to approximately 10°, indicating that the interfaces contain Fourier components with wavelengths less than 8−9 Å. The width of the mixing of the elements at the interface upon deposition is therefore on the order of 10−20 Å. The diffraction data combined with the short repeat spacings of approximately 20 Å for all the samples studied imply that their composition essentially modulates between regions that are relatively tungsten rich and regions that are tungsten poor. Subsidiary maxima were also observed between the Bragg maxima (see Figure 2). These subsidiary maxima result from the interference of X-rays scattered from the front and back surface of the superlattice reactant as well as incomplete destructive interference from the internal interfaces. Typically, these subsidiary maxima were observed out to 7−9°, suggesting that the elemental layers are smooth and uniform in thickness, as variations in layer thickness and/or roughness increasingly broaden the subsidiary maxima with increasing angle.[11]

The high-angle diffraction pattern of all of the as-deposited samples contain a broad diffraction peak at 13° corresponding to the (002) reflection of WSe_2, indicating that tungsten diselenide has nucleated on deposition. No diffraction maxima were observed for tungsten metal in the diffraction patterns of the simple binary samples containing tungsten layers less than 15 Å thick. This suggests that the as-deposited samples contain a tungsten-rich, tungsten−selenium alloy separated from a tungsten-poor, tungsten−selenium alloy by poorly crystalline WSe_2. In reactants with tungsten layers thicker than 25 Å, a broad diffraction maxima approximately 10° in width centered at about 40°, corresponding to the (110) peak of tungsten metal, was observed.

To follow the interdiffusion and crystallization of the samples, DSC and diffraction data were collected as a function of annealing temperature. The DSC data of the simple binary W−Se elemental reactants, shown in Figure 3, contain a broad exotherm from about 120−250 °C followed by a second broad exotherm starting at 370 °C. Diffraction data collected before and after these exotherms, shown in Figure 4, suggest that the first exotherm corresponds to continued interfacial nucleation and growth of WSe_2. The observation of only 00*l* diffraction lines suggest that only those nuclei with their 00*l* planes aligned with the interface grow on low-temperature annealing. After annealing to 550 °C, the line widths of the WSe_2 00*l* diffraction peaks have significantly narrowed, suggesting that this exotherm is associated with crystal growth. These data confirm

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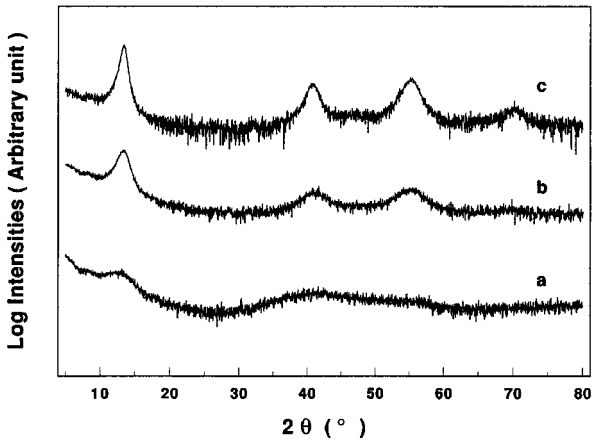

Figure 4. High-angle X-ray diffraction data of a tungsten−selenium superlattice collected at the temperatures indicated in Figure 3.

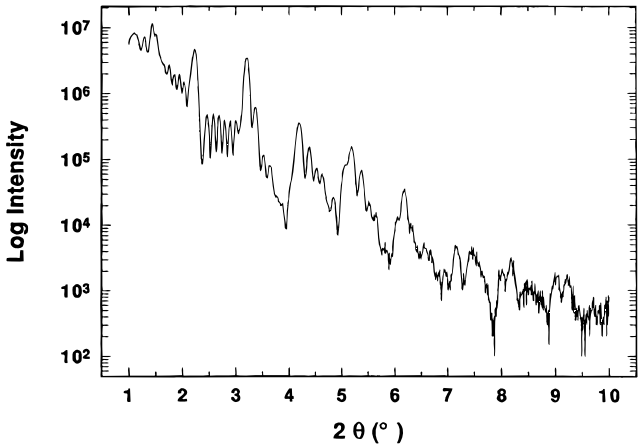

Figure 5. Low-angle diffraction data collected on a superlattice reactant containing three W−Se layers, each with 6.5 and 13.7 Å of W and Se, respectively, and a 26 Å thick W layer in the repeating unit.

that the initial interfacial product at a reacting W-Se interface is WSe_2 and that the WSe_2 layers are aligned with the interfaces of the initial modulated reactant.

Upon reviewing data collected on the six simple tungsten−selenium multilayer reactants summarized above, we speculated that an initial superlattice reactant with a repeating unit such as that illustrated in Figure 1 would, upon annealing, nucleate WSe_2 at the W−Se interfaces. Continued annealing would result in crystal growth of both the tungsten layers and the diselenide layers. The low diffusion rates combined with the constrained structure of the reactant might kinetically trap a nanocomposite product, consisting of tungsten layers separated by tungsten diselenide layers. Changing the initial layering of the superlattice reactant would permit independent control of the thickness of the tungsten and dichalcogenide layers in the product nanocomposite.

To test this proposed reaction pathway, we prepared an initial reactant containing three W−Se layers, each with 6.5 and 13.7 Å of W and Se, respectively, and a 26 Å thick W layer in the repeating unit. The low-angle diffraction scan of the as-deposited sample, shown in Figure 5, has 10 Bragg diffraction maxima. Using the positions of these diffraction maxima, the repeating unit of the as-deposited sample was determined to be 86 Å, which is close to that expected from the calibration data.

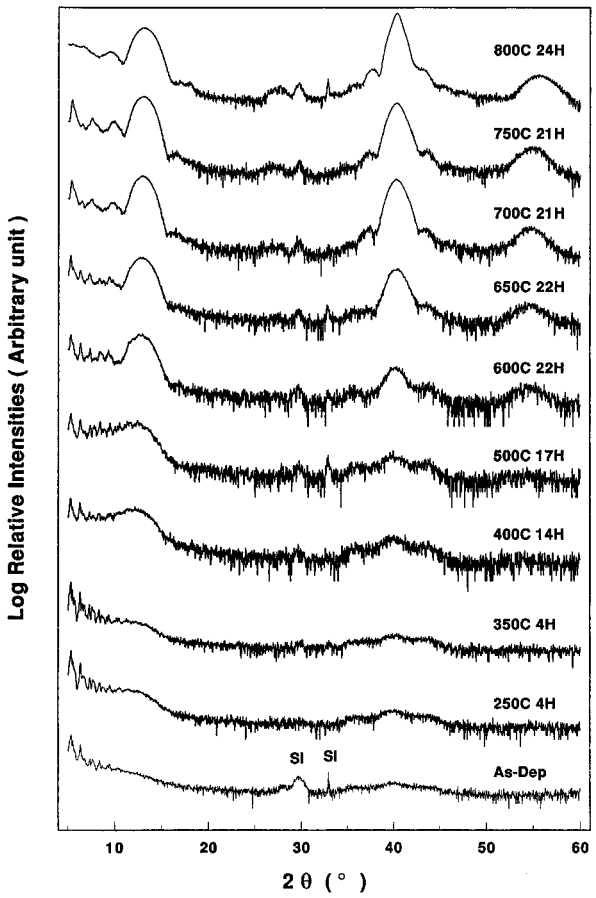

Figure 6. High-angle diffraction data collected on a superlattice reactant containing three W−Se layers, each with 6.5 and 13.7 Å of W and Se, respectively, and a 26 Å thick W layer in the repeating unit as a function of annealing temperature and time. The diffraction intensity at 30 and 33° are from the silicon substrate.

The high-angle diffraction scan of the as-deposited sample, shown in Figure 6, has only a broad diffraction maxima at 40° resulting from nanocrystalline tungsten in the as-deposited film.

The evolution of the structure of this reactant with annealing time and temperature was followed using both low- and high-angle X-ray diffraction after each anneal. The evolution of the high-angle diffraction data with annealing is shown in Figure 6. In the high-angle diffraction data, the broad diffraction maxima centered at 13° which appears after annealing the sample at 250 °C suggests that WSe_2 has nucleated. Upon continued annealing up to 500 °C, both the tungsten and WSe_2 peaks show an increase in intensity and little change in peak width, indicating that continued nucleation but little Ostwald ripening of the grains perpendicular to the substrate. After the 600 °C anneal, there is a significant increase in the intensity and a decrease in the line widths of both the tungsten and WSe_2 high-angle diffraction maxima, suggesting crystal growth perpendicular to the substrate. The higher order 00*l* diffraction maxima of WSe_2 also become observable as broad maxima at approximately 55°. After annealing at 750 °C, the line widths correspond to a tungsten particle size of 45 Å and WSe_2 particle size of 40 Å in the layering direction, consistent with the superlattice period of 86 Å determined from low-angle diffraction data. The aligned nature of the crystallites was confirmed by collecting rocking curve data. The rocking

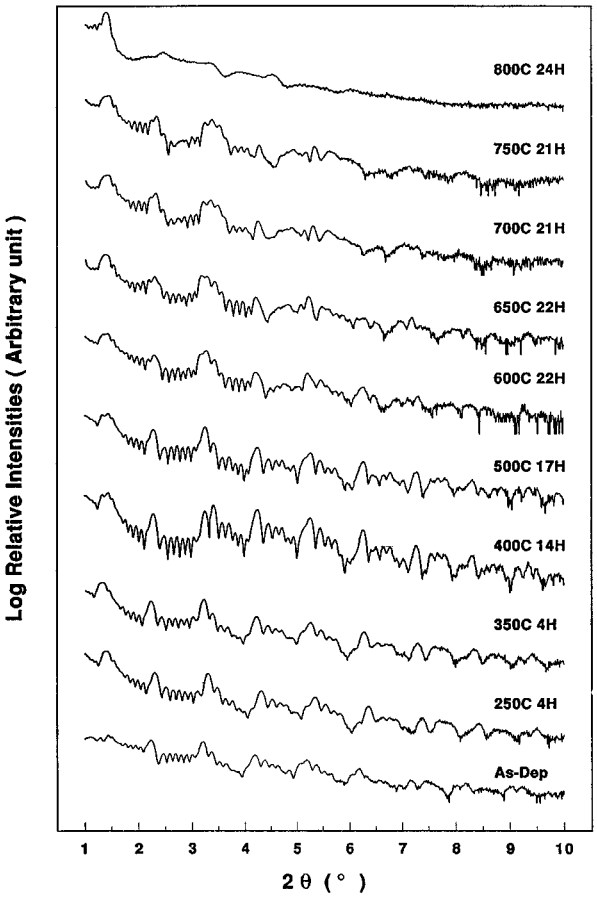

Figure 7. Low-angle diffraction data collected on a superlattice reactant containing three W−Se layers, each with 6.5 and 13.7 Å of W and Se, respectively, and a 26 Å thick W layer in the repeating unit as a function of annealing temperature and time.

curve data collected on the (002) diffraction peak of the tungsten diselenide had a full width at half-maximum intensity of 4° while the width of the rocking curve peak of the tungsten (110) diffraction maxima was 4.5°. The low-intensity broad maxima on either side of the tungsten (110) Bragg maxima near 40° are a consequence of the small grain size and a narrow size distribution of the grains. A similar broad, low intensity maxima can be seen on the high-angle side of the (002) Bragg diffraction maxima of WSe_2 near 13°.

The evolution of the low-angle diffraction data is summarized in Figure 7. The diffraction intensities of both the superlattice Bragg diffraction maxima and the low-angle subsidiary maxima between the Bragg diffraction peaks increase as the sample is annealed below 400 °C. This increase in the intensity of the subsidiary maxima reflects a decrease in the roughness of the interfaces as WSe_2 grows along the interfacial planes. The increase in intensity and the appearance of higher order Bragg maxima reflect the sharpening of the concentration gradient at the interface as the structure of the interface changes from a concentration gradient through an amorphous alloy to an abrupt tungsten−tungsten diselenide interface.[12,13] On annealing at higher temperatures, the low-angle diffraction pattern begins to degrade as grain growth of tungsten and the diselenide increase the roughness of the interfaces. Significantly, the composite structure is kinetically stable even on extended annealing at 750 °C. After extended annealing at 800 °C, the low-angle diffraction pattern is significantly degraded, and continued grain growth on annealing at higher temperatures completely destroys the regular period of the nanocomposite.

Summary

In binary tungsten−selenium multilayers, tungsten diselenide was observed to interfacially nucleate upon deposition and grow preferentially along the interface. This information was used to design a multilayer reactant containing a thick tungsten layer in addition to thin tungsten and selenium layers in the repeating unit. The superlattice structure in the initial reactant, followed using both low- and high-angle diffraction, was enhanced with annealing time and temperature. The diffraction data suggest that the structure of the nanostructured composite consists of alternating layers of tungsten and tungsten diselenide containing orientated crystallites limited in size by the layer repeat. The alternating nanoscale layers of tungsten and tungsten diselenide are only kinetically stable as annealing above 800 °C destroys this periodicity. This nanostructure is kinetically trapped by the structure of the initially modulated elemental reactant and the slow diffusion rates existing during annealing. The thickness of the tungsten and dichalcogenide layers in the product nanocomposite can be controlled by changing the thickness of the elemental layers in the initial superlattice reactant.

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