Control of Reaction Pathway and the Nanostructure of Final Products through the Design of Modulated Elemental Reactants

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This review focuses on the use of designed reactants, consisting of ultrathin elemental layers sequentially deposited in ultrahigh vacuum, to control reaction pathways and the structure of compounds formed. Two reaction pathways are discussed. The first uses controlled nucleation of an amorphous intermediate to kinetically access compounds under conditions where they may be thermodynamically unstable. The second approach takes advantage of the controlled diffusion lengths in elementally modulated reactants and slow diffusion rates at low temperatures to prepare superlattice and heterostructure compounds with controlled composition and structure.

Introduction

The synthesis of solid-state compounds is often at the mercy of the slow rate of mass transfer between the solid particles of reactants and products.[1] These diffusion rates are typically increased by the use of high reaction temperatures. This leads to thermodynamically stable products which precludes the study of compounds and structures which are stable only at low temperatures. This limitation can be overcome by either increasing diffusion rates or decreasing diffusion distance. Increasing diffusion rates is typically accomplished through the use of liquid- or gas-phase reactants or intermediates, for example, vapor-phase transport,[2] reactive flux growth, and growth from molten salts. Diffusion distances are decreased from microns down to angstroms by using precursors, sol–gel techniques, and modulated ultrathin-film reactants. These approaches provide important access to novel compounds which are not accessible through traditional high-temperature routes.

As a consequence of the traditional use of high reaction temperatures and long reaction times to prepare thermodynamically stable products, the emphasis in solid-state chemistry has been on determining the structure of the products formed and correlating structure with observed physical properties. There has been little attention paid by synthetic solid-state chemists to the mechanism of product formation. This is true even in most of the low-temperature synthetic routes due to the complexity of the reacting systems. An understanding of reaction mechanism, however, provides important synthetic advantages because mechanisms permit the rational modification of reactants and reaction conditions to prepare new products. The importance of controlling kinetics and understanding reaction mechanisms increases as low-temperature approaches to new materials are developed. An elegant example of the development and use of a reaction mechanism in solid-state chemistry has been in the area of soft chemical

approaches to modify existing solid-state structures and prepare metastable compounds. In this approach, sometimes referred to as "chimie douce," low-temperature ion-exchange reactions are used to rationally modify the structure of a known precursor phase which is then transformed at low temperature to produce a desired metastable product.[3]

In the past 20 years the importance of nucleation kinetics in the early stages of solid-state reactions between reacting elements and compounds has also been increasingly recognized. The behavior of thin-film diffusion couples, consisting of several hundred angstrom thick elemental layers, provide a striking illustration of the importance of kinetics in the early stages of solid-state reactions. It is well established experimentally that the evolution of thin-film, planar, binary diffusion couples proceeds through a sequence of binary compounds. In some systems, for example, transition-metal silicides, it is common to have only a single compound grow between the reactants until either the metal or the silicon reactant is exhausted (Figure 1).[4] Several empirical rules have been formulated to predict the phase which will form using information in equilibrium phase diagrams. For example, the first phase rule of Walser and Bené states "The first compound nucleated in planar reaction couples is the most stable congruently melting compound adjacent to the lowest temperature eutectic on the bulk equilibrium phase diagram." This rule is based on the assumption that an amorphous material forms between the reactants with a composition near that of the lowest temperature eutectic, the most stable liquid in the equilibrium phase diagram. It is then assumed that the easiest compound to nucleate will be the most stable compound closest in composition to the glassy, interfacial phase.[5]

More quantitative predictions of the sequence of phase formation are not available since real systems are very complex, involving both interdiffusion and nucleation, both of which depend upon composition, defect concentrations, crystallographic orientations of the re-
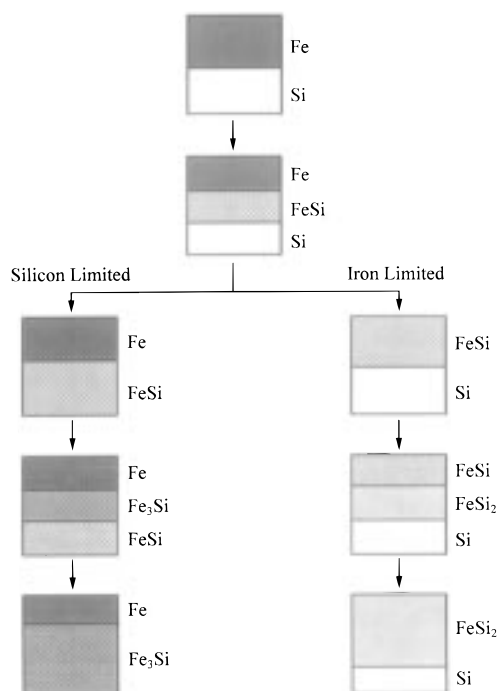
Figure 1. Schematic of the evolution of a thin-film iron–silicon diffusion couple as a function of temperature and time.

acting particles and changing composition profiles at the reaction interface. However, several qualitative arguments have been proposed to explain the observed lack of some equilibrium phases in thin-film diffusion couples. It has been argued that nucleation barriers prevent phase formation,[6] that the formation of the missing phases is thermodynamically unlikely because of the low diffusion temperatures used in the experiments,[7] and that interfacial reaction barriers result in a growth instability which leads to the absence of phases.[8]

In the early 1980s, Johnson's group discovered that amorphous metal alloys could be prepared by solid-state amorphization reactions.[9-12] In this process, thin films consisting of alternate layers of crystalline elemental constituents are transformed into an amorphous alloy during a solid-state reaction. This transformation is hypothesized to be driven by a large negative heat of mixing of the constituent elements so that the amorphous alloy product has a lower free energy than the two-phase multilayer reactant. The formation of the equilibrium crystalline compounds was originally thought to be frustrated by the kinetic constraints imposed by the low reaction temperatures.[10] Early work revealed that the growth of the amorphous alloy was consistent with diffusion controlled growth[9] and it was found that one component was typically the dominant diffuser through the amorphous phase.[13] Structural relaxation of the amorphous alloy was found to further decrease the growth rate of the amorphous alloy.[14] As in the thin-film diffusion couples discussed above, when the amorphous alloy reaches a critical thickness, a equilibrium crystalline phase was found to nucleate. This upper limit to the thickness of amorphous alloy severely limits the ability to form bulk amorphous materials from bilayers of the reacting elements. Bulk amorphous alloys can be formed using this mechanism by keeping each elemental layer thinner than this upper limit and building up a thicker film by repeating the elemental layers sequentially, creating a multilayer structure. This

pioneering work in the area of solid-state amorphization reactions provided the inspiration for us to investigate the general use of amorphous alloys as metastable reaction intermediates. We reasoned that by avoiding the formation of binary compounds at reacting interfaces we could potentially crystallize ternary compounds directly from amorphous alloys. Nucleation of the amorphous intermediates would then be the key kinetic step in the formation of a crystalline solid-state compound.

Several methods are known to produce amorphous alloys including solid-state amorphization reactions, codeposition of films, and quenching from melts. Each of these techniques has drawbacks for the general preparation of amorphous alloys. Amorphous phase formation by rapid quenching of a high-temperature liquid is complicated by the importance of experimental variables such as local quench rate.[15] In codeposition, the structure of the amorphous alloy depends upon the relative and absolute deposition rates as well as the substrate temperature during deposition. In particular it becomes increasingly difficult to avoid fluctuations of the relative deposition rates as the number of deposition sources increases. In addition, accessing the structure of the as-deposited co-deposited films is difficult. The formation of amorphous alloys via solid-state amorphization reactions does not work in all systems and critical layer thicknesses can be as small as only a few angstroms. A more general problem of all of these approaches is the limited range of compositions that can be prepared.[16]

We chose to form our amorphous alloys using solid-state amorphization reactions for several reasons. Most importantly, the technology to deposit a desired thickness of a single element at a time is well developed[17] and the layered nature of the as-deposited sample permits the initial structure as well as the structural evolution to be followed using low-angle X-ray diffraction.[18-20] This permits the initial structure of samples prepared at various times to be compared and correlated with observed reactivity. An additional advantage of using solid-state amorphization reactions is the ability to follow the enthalpy changes in both the interdiffusion and subsequent nucleation of the amorphous solids using differential scanning calorimetry.[9,21] The use of low-angle X-ray diffraction to follow changes in interfacial structure has recently been reviewed.[20,22,23] In this review we focus on use of modulated reactants to access and control the nucleation of the amorphous reaction intermediates as well as the use of modulated reactants to prepare nanostructured products.

The obvious parameter which can be used to control the subsequent kinetics of crystalline phase formation from an initially modulated elemental reactant is the thickness of the elemental layers in the repeating unit. The following discussion is organized into two regimes dependent upon the thicknesses of the elemental layers within the repeating unit. We first briefly discuss variation in the magnitude of the "critical thickness" in different binary systems and the evolution of films modulated below the critical thickness. In this section we review experimental variables which have been shown to control the nucleation of a desired crystal structure from an amorphous intermediate. The second regime discussed involves more complex sequences of elemental layers in the repeating unit which contain
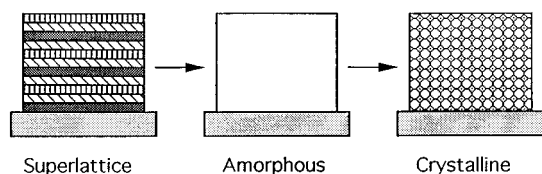
Figure 2. Schematic of the evolution of a modulated elemental reactant containing elemental layers below the critical thickness for interfacial nucleation as a function of temperature and time.

length scales both smaller and larger than the critical thickness. These sections are followed by a discussion of challenges and opportunities resulting from the research reviewed.

Reactants with Modulation Thicknesses below the "Critical Thickness": Controlled Nucleation of Amorphous Reaction Intermediates

The key experimental parameter when using modulated elemental reactants to prepare amorphous reaction intermediates is the critical thickness, below which the system will interdiffuse without interfacial nucleation. The magnitude of the "critical thickness" has been found to vary considerably among binary systems. In early transition metal–late transition metal systems such as Ni–Zr, it has been found that critical thicknesses of the repeating unit are from several hundred to a thousand angstroms while in transition metal–amorphous silicon systems critical thicknesses are from 50 to 250 Å.[4,21] In transition metal–selenium systems such as molybdenum–selenium[24] or niobium–selenium[25] the critical thicknesses of the repeating bilayer are from 10 to 100 Å in thickness. In some systems, for example iron–aluminum, it is not possible to avoid interfacial nucleation of a particularly stable and easily nucleated compound such as FeAl regardless of how thin the elemental layers are in the initial reactant.[26] Fortunately, the majority of the systems which we have investigated have been observed to form amorphous intermediates when modulated on a short enough length scale.

The critical thickness is also a function of the overall composition of the amorphous intermediate. The niobium–selenium system illustrates this point. Around compositions containing 55% niobium,[25] the critical thickness is approximately 100 Å while for compositions more selenium rich than 45% niobium, the compound $NbSe_2$ was observed to nucleate while the reactant was still compositionally modulated even when the bilayer repeat thickness was reduced to 15 Å.[27] Presumably, this composition dependence results from differences in the diffusion rates as a function of composition although the "critical thickness" in a binary system can depend upon many other factors including the density of the deposited elements and the different driving forces for the crystallization of different binary compounds.

The reaction mechanism of an elementally modulated reactant with layer thicknesses below the critical thicknesses is shown schematically in Figure 2. The key feature of this reaction route is to have nucleation, rather than diffusion, be the rate-limiting step in the formation of a crystalline solid. Nucleation is an attractive rate-limiting step in the formation of crystalline solids from amorphous intermediates for the same
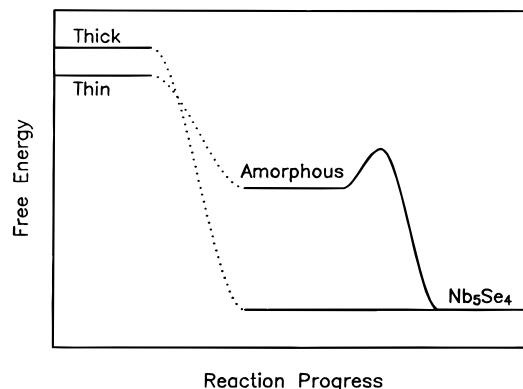

Figure 3. Change in free energy of two niobium–selenium multilayer composites, one with layer thicknesses above the critical thickness and one with layer thicknesses below the critical layer thickness, as they react to form Nb_5Se_4.

reasons it has been important in synthetic molecular chemistry. Historically, molecular chemists have utilized crystallization processes as an effective means of purifying substances, especially for the separation of enantiomers. This process uses nucleation barriers to prevent the crystallization of minority components and takes advantage of the rapid growth of crystals once nucleated from a supersaturated solution. The kinetic nature of nucleation also provides a significant additional advantage, since what crystallizes is the easiest compound to nucleate, not necessarily the most thermodynamically stable compound.

The rate-limiting nature of nucleation from an amorphous intermediate is readily apparent from the changes in nucleation temperature as a function of layer thickness of modulated reactants. For example, for films modulated above the critical distance in the molybdenum–selenium system, $MoSe_2$ was observed to nucleate heterogeneously near 200 °C. For films modulated below the critical distance for forming a bulk amorphous alloy, $MoSe_2$ was observed to homogeneously nucleate above 500 °C.[28] Similar data were obtained for niobium–selenium samples with composition near 55% niobium, with films containing bilayer repeats greater than 100 Å in thickness nucleating Nb_5Se_4 below 250 °C. X-ray diffraction data suggest that the Nb_5Se_4 nucleates and grows out from the niobium–selenium interfaces. Films modulated on a length scale less than 60 Å were found to nucleate Nb_5Se_4 between 550 and 600 °C. X-ray diffraction data collected after annealing below 500 °C indicate that the samples are X-ray amorphous while diffraction data collected after nucleation indicates that the crystallite sizes are several orders of magnitude larger than the modulation length in the initial elementally modulated reactant.[25]

The kinetic stability of amorphous reaction intermediates can be studied by collecting differential scanning calorimetry data as a function of scan rate to estimate the activation energy of the nucleation and growth process. Such nonisothermal DSC data are typically analyzed using a relationship originally derived by Kissinger[29] in which the activation energy is obtained from the change in the exotherm peak temperature as the scan rate is varied. For nucleation of Nb_5Se_4 from an amorphous intermediate, an activation energy of 2.7 eV was obtained.[25] Figure 3 illustrates how the free energies of niobium–selenium multilayer composites vary as they evolve, contrasting the evolution of elemen-

tally modulated reactants with thicknesses above and below the critical thickness in this system. Entropy effects have not been included, but such effects are usually small in solid-state reactions. The thin multilayers start at a lower free energy than the thick because a greater fraction of the thin multilayer is within the 20 Å thick interface regions. The thick multilayer samples interdiffuse and heterogeneously nucleate Nb_5Se_4 at the interfaces at low temperatures resulting in a drop in free energy from the reactants immediately to the products. The thin multilayer samples, however, evolve to an amorphous intermediate which is kinetically stable with respect to nucleation. The nucleation barrier is considerable, being approximately 25 kJ/mol of Nb_5Se_4 nuclei, if we assume a critical nuclei size of approximately 7 Å in radius containing 10 Nb_5Se_4 formula units. This large activation barrier is the reason the amorphous reaction intermediate is stable even after extended annealing at 500 °C. At higher temperatures the sample nucleates homogeneously.[25]

The two main advantages of using nucleation as a rate-limiting step in a reaction are conveniently illustrated in Figure 3 discussed above. The first is the ability to keep the sample in a high-energy state by preventing the heterogeneous formation of stable binary compounds. The second advantage is that the energetics of the nucleation process control the compound eventually formed, giving kinetic control. In principle, the ability to form a high-energy metastable intermediate allows the synthesis of compounds which are inaccessible by traditional approaches. A synthetically important example would be the preparation of ternary compounds which are unstable relative to disproportionation into binary components. The ability to prepare such compounds depends upon controlling nucleation energetics such that the compound with the desired composition and structure nucleates preferentially.

Since controlling nucleation is of technological importance, there is considerable literature on this subject. The nucleation of precipitates, for example, has been the topic of considerable interest given the commercial significance of precipitation hardening of alloys. One such technologically important process is the controlled precipitation of $CuAl_2$ from supersaturated aluminum–copper solid solutions forming "duralumin", a hard dispersion of $CuAl_2$ in an aluminum matrix. In such cases, the nucleation energy of precipitates can be described by an expression which is similar to those for homogeneous nucleation from a pure melt. Additional terms are added to account for compositional differences between the alloy and the nuclei as well as distortion energy from changes in lattice parameters. These expressions permit the rate of nucleation to be calculated as a function of undercooling or supersaturation. It is difficult to test these nucleation theories directly since nucleation rates are experimentally difficult to determine. However, interfacial surface energies and distortion energies have been found to be very important in determining which precipitates nucleate. In the aluminum–copper system, for example, a sequence of metastable compounds, structurally similar to aluminum, nucleate before the thermodynamically more stable $CuAl_2$.
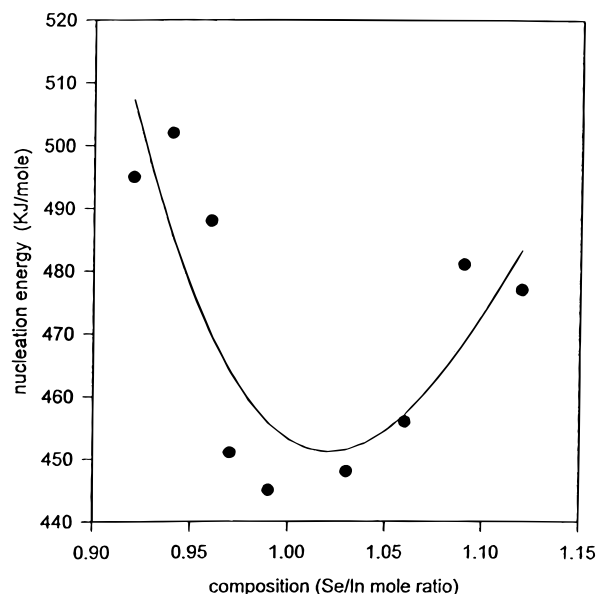

Figure 4. Variation of the activation energy for crystallization of InSe from an amorphous intermediate as a function of the average composition of the amorphous intermediate.

There is also a large literature referring to nucleation rates and the extent of undercooling observed in liquid metals and alloys. However, reports on the effect of amorphous solid composition on solid-state nucleation energies are scarce. To explore the effect of the composition of an amorphous alloy on nucleation energy, Oyelaran et al.[30] prepared a series of amorphous indium–selenium alloys with variable composition. The measured activation energies for the nucleation of InSe as a function of composition from these amorphous intermediates was derived from nonisothermal DSC data.[29] These activation energies, shown in Figure 4, reflect the barriers to nucleation and growth of the more stable crystalline InSe from the metastable amorphous intermediate. A pronounced minimum in the activation energy for the nucleation and growth of InSe is found near one-to-one composition of the amorphous intermediate. This minimum activation energy can be explained by considering the energy decrease during nucleation per unit volume transformed. In the In–Se binary system, the driving force for nucleation is a maximum at the stoichiometric composition, decreasing symmetrically as one moves off stoichiometry leading to the observed composition dependence. It is worthwhile to also consider the atomic rearrangements which must occur in the amorphous alloy during the formation of a critical nucleus. If the overall composition is that of the line-phase InSe, then only local rearrangements in bond angles and lengths need occur to form the critical nucleus. If the amorphous intermediate has a different composition from the compound being nucleated, a composition fluctuation of the volume of the critical nucleus must also occur. Keeping the size of the critical nucleus constant as a function of composition, this composition fluctuation becomes more unlikely the farther in composition the amorphous alloy is from that of the nucleating compound, again leading to the observed composition dependence.[30]

The rapid increase in the activation energy for nucleation of InSe as the composition of the amorphous intermediate is varied from the stoichiometric ratio

implies that the nucleation energy of adjacent compounds in the phase diagram will eventually become comparable to that of InSe. Indeed, samples prepared both more selenium rich or more indium rich than those used to prepare Figure 4 have two exotherms in the DSC data between room temperature and 400 °C. Samples more indium rich than in composition than Se/In = 0.9 formed a mixture of InSe and In_4Se_3 as expected from the phase diagram.[31] Samples more selenium rich than Se/In = 1.12 formed a mixture of InSe and In_2Se_3, skipping the intermediate phase In_6Se_7 expected from the published phase diagram.[31] Since In_2Se_3 nucleates first from an amorphous intermediate of composition "In_6Se_7", In_2Se_3 must have a lower nucleation energy than In_6Se_7. Curiously, the first phase rule of Walser and Bené predicts that In_2Se_3 should be the first phase formed at an In−Se interface (In_2Se_3 melts congruently at 885 °C while In_6Se_7 peritectically decomposes at 630 °C into In_2Se_3 and a molten In−Se alloy and InSe peritectically decomposes at 600 °C into a mixture of molten In−Se alloy and In_6Se_7).[30,31]

These results have several implications for any synthetic technique attempting to use nucleation to provide phase selectivity. As suggested by Spaepen for nucleation of solid alloys from liquid solution, the compound most likely to form from an amorphous alloy is that with the largest driving force for nucleation.[32] If amorphous intermediates are prepared at various compositions across a binary system it is possible to select the crystalline product which will nucleate from the intermediates using the overall composition. For example, in the iron−silicon system, the compound Fe_5Si_3 was selectively nucleated even when it was thermodynamically unstable with respect to disproportionation into Fe_3Si and FeSi.[21] The observed composition dependence of the nucleation energy for InSe provides a possible rationale for this kinetic selectivity, suggesting that the large composition fluctuations required to nucleate the thermodynamically more stable Fe_3Si and FeSi from an amorphous alloy containing 62.5% iron are not probable due to the longer range diffusion necessary to form a critical nucleus of either compound. Since nucleation is the rate-limiting step in forming a crystalline product from the amorphous intermediate, the relative nucleation energies of the various crystalline products determine which compound will form, not the absolute thermodynamic stability of the products.

In principle, the ability to form a high-energy metastable intermediate allows the synthesis of compounds that are inaccessible by traditional approaches. The ability to prepare such compounds will depend upon controlling nucleation energetics such that the compound with the desired composition and structure nucleates preferentially. From ternary amorphous intermediates, preferred crystallization of ternary compounds rather than binary compounds has been observed.[33] Composition dependence of the nucleation temperature provides a rationale for this observation; adjusting the concentration of the ternary component lowers the nucleation barrier for the ternary compound while raising the nucleation energy of the possible binary compounds. Whether this results in ternary phase formation, however, depends upon the relative nucleation energies of the two compounds.
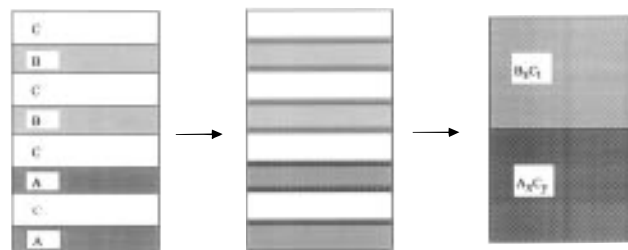

Figure 5. Schematic of a modulated elemental reactant designed to evolve into a crystalline superlattice or heterostructure, containing alternating layers of component A and B interleaved with component C. A possible reaction pathway resulting in a superlattice product, corresponding to interfacial nucleation as described in the text is also illustrated.

Reactants with Modulation Thicknesses above a "Critical Thickness": Nanostructured Composites and Crystalline Superlattices

In examining the polycrystalline films that result from interfacial nucleation of elementally modulated multilayers, we have frequently observed a high degree of preferred crystallographic orientation. This preferred orientation is a consequence of different growth rates in different crystallographic directions. For example, in selenium-rich niobium−selenium multilayer reactants, low-angle diffraction data collected as a function of annealing temperature and time suggest that nucleation of niobium diselenide, a compound with a layered structure, occurs along the plane of the reacting interfaces. In niobium diselenide, growth in the *a−b* crystallographic plane is faster that growth in the *c* direction. Nuclei with their *a−b* plane coinciding with the interface of the multilayer reactant therefore grow more rapidly than nuclei oriented in other directions. Ostwald ripening then leads to polycrystalline niobium diselenide films that are highly oriented, with rocking curve half-widths of less than a tenth of a degree.

The low-temperature interfacial nucleation and crystallographic orientation observed when the modulation thickness is above the "critical thickness" suggested an opportunity to prepare nanostructured products. Consider a modulated elemental reactant with the structure shown in Figure 5, containing alternating layers of component A and B interleaved with component C. On the basis of the results discussed above, we hypothesize that the compounds A_xC_y and B_uC_v will nucleate at the A−C and B−C interfaces, respectively. Following nucleation, rapid growth of these compounds along the plane of the interface is expected, since a plane at the interface is the only region in the initial reactant with the correct composition for these compounds to grow. Subsequent low-temperature annealing will lead to growth of A_xC_y and B_uC_v perpendicular to the interfaces. Since diffusion rates can be constrained by low annealing temperatures and diffusion distances can be optimized using the initial structure of the modulated reactant, the growth process can be controlled to produce a modulated final structure with minimal interdiffusion of the components. Changing the design of the initial modulated elemental reactant offers the potential to control composition in a mesoscopic regime, permitting structure and composition to be controlled in the synthesis of nanostructured products.

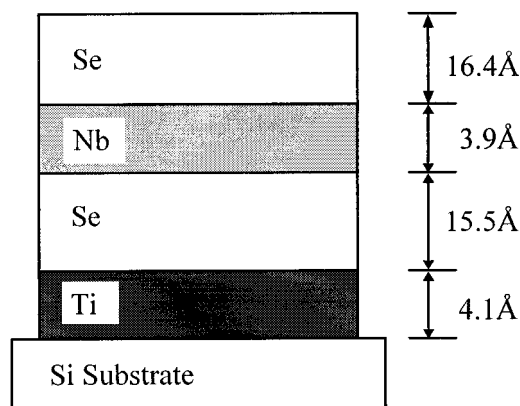We tested this proposed reaction sequence by preparing a series of superlattice reactants with the overall

Figure 6. Structure of the initial reactants used to prepare the [NbSe₂]₃[TiSe₂]₃ superlattice showing the thickness of Se, Nb, and Ti layers in the repeating unit used for this sample.
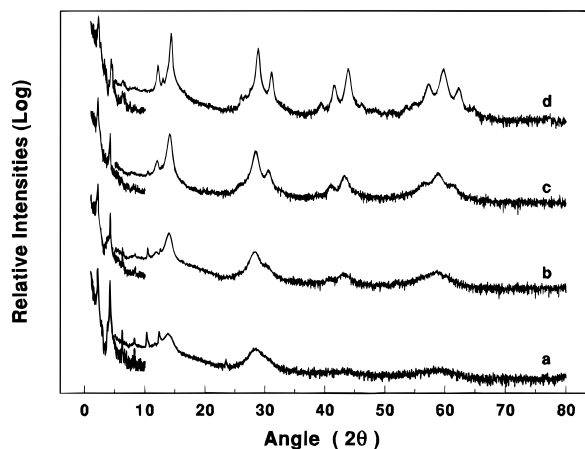

Figure 7. Diffraction data collected on a superlattice reactant in which elemental layers were deposited of appropriate thickness to yield 3.5 NbSe₂ layers and 3.5 TiSe₂ layers in the final product. Diffraction pattern a is that of the as-deposited sample, b is after annealing 2 h at 200 °C, c is after annealing 2 h at 350 °C, and d is after annealing 2 h at 500 °C. The lattice parameter of the superlattice is 43.472 ± 0.005 Å after annealing at 500 °C.

structure shown in Figure 6, containing varying amounts of Se, Nb and Ti layers in the repeating unit. The composition of each Nb–Se and Ti–Se period was controlled to be that of the desired MSe_2 compounds, and an amount of each element was deposited to yield an integral multiple of the known crystallographic unit cells so that there would be no elemental reactants left in the superlattice after extended annealing. The evolution of the high- and low-angle XRD patterns of a sample with 3.5 $NbSe_2$ layers and 3.5 $TiSe_2$ layers, shown in Figure 7, illustrates the evolution of structure as a function of annealing temperature. There are three important conclusions that can be inferred from this data. First, the low-angle XRD data of this free-standing film indicates that the compositionally modulated nature of the sample persists throughout annealing. Second, the broad XRD maxima evident at high angles upon low-temperature annealing result from the nucleation of the MSe_2 layers. Upon low-temperature annealing, the intensity of the broad maxima increase without a decrease in the line width. This suggests that the crystallites are growing along the interfaces with little perpendicular growth. Third, on higher temperature annealing, the line widths of the diffraction peaks

narrow and higher order, high-angle 00*l* Bragg diffraction peaks of the heterostructure become resolved as the MSe_2 nuclei grow.[27] DSC data collected on this sample show the continual evolution of heat with increasing temperature up to 500 °C, indicative of the continuous growth of the MSe_2 crystallites.

More detailed diffraction data are consistent with a reaction mechanism which involves low-temperature interfacial nucleation of the binary components followed by grain growth. The diffraction data suggest that the optimum growth conditions for obtaining crystalline superlattices begins with a low-temperature annealing to nucleate and grow the desired component compounds along the interfaces. Subsequent higher temperature annealing leads to grain growth and eliminates defects and misoriented crystallites. The time required for this annealing depends upon diffusion rates; however, the maximum temperature of this anneal is limited by the energy required to interdiffuse the metals in the respective dichalcogenides. A schematic of this reaction pathway is shown in Figure 8.

Optimizing the annealing temperatures and times, as suggested by the reaction pathway, results in diffraction patterns containing many well-resolved diffraction maxima, all of which can be indexed as 00*l* Bragg peaks from the superlattice. For example, Figure 9 contains the diffraction pattern of [NbSe₂]₆[TiSe₂]₆ after annealing this sample at 500 °C for 197 h. All of the diffraction maxima in the diffraction patterns can be indexed as 00*l* diffraction maxima resulting in a *c*-axis lattice parameter consistent with 6 $NbSe_2$ layers and 6 $TiSe_2$ layers in the repeating unit of the superlattice sample. The diffraction pattern is qualitatively what is expected for the intended structure consisting of the convolution of the super-cell diffraction on top of that expected for the dichalcogenides. To determine the structure perpendicular to the layering direction, we searched for and found the 10*l* diffraction intensity in reflection mode on a single-crystal diffractometer for a sample annealed for 10 h at 500 °C. The diffraction signal consisted of a ring of intensity indicating well-formed dichalcogenide layers that are not uniformly oriented in the *a*–*b* plane due to multiple domains. This is consistent with interfacial nucleation of the layers as suggested in case 1 above, whereas epitaxial growth would result in a preferred orientation of the *a*–*b* 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. The existence of all 62 of the expected 00*l* diffraction orders between 1 and 80°, however, highlights the well-formed structure which develops along the *c*-axis as the superlattice structure is kinetically trapped.

The quality of the 00*l* diffraction data shown in Figure 9 permitted us to study the structure of our superlattices by considering the structure as being composed as a single large unit cell that consists of multiple units similar to those of the parent structures. We refined the positions and occupancies of the atoms using Rietveld analysis.[34] The curve under the data points in Figure 9 is a calculated diffraction pattern for the structure along the *z* axis (shown in Figure 10) which resulted from least-squares analysis of these data. The refined crystalline superlattice contains the expected structural components based upon the structure of the
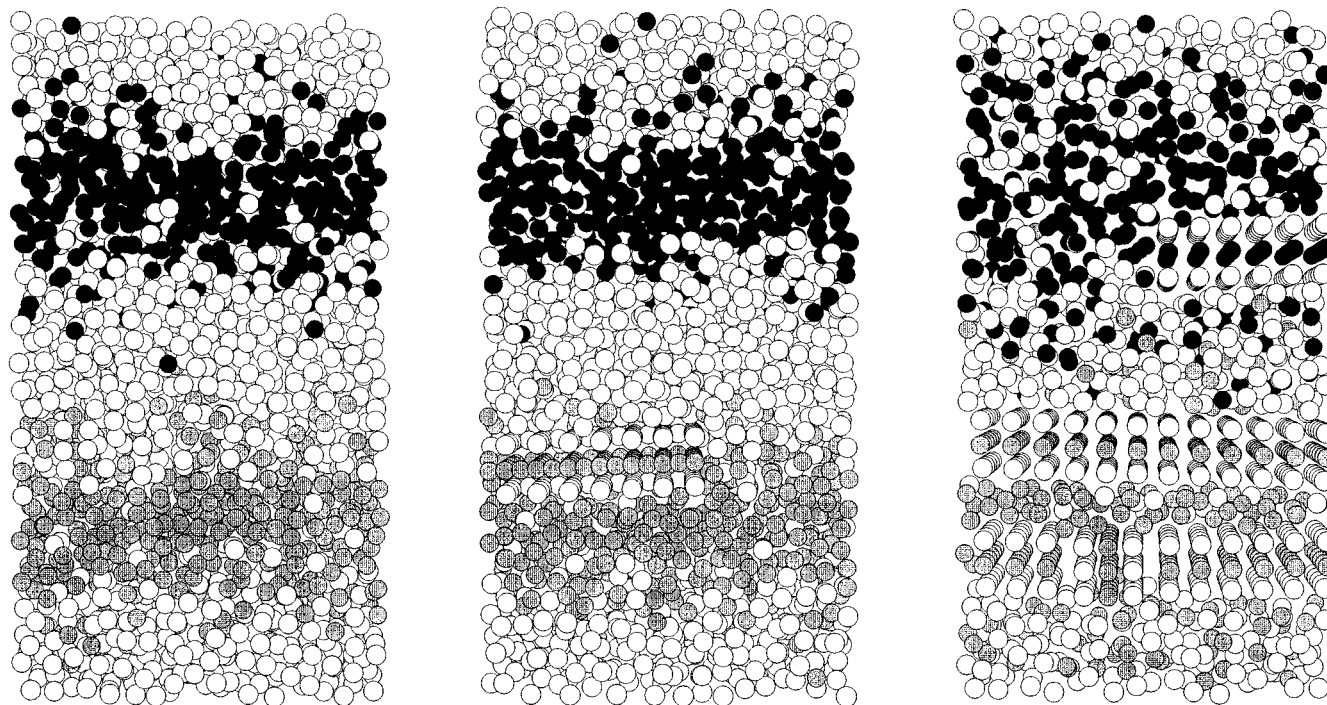
Figure 8. Suggested reaction pathway of a superlattice reactant containing alternating niobium and titanium layers each separated by intervening layers of selenium. On low-temperature annealing, the as-deposited layers (a) begin to interdiffuse. Continued annealing results in interfacial nucleation (b) and lateral growth of the respective binary components (c), kinetically trapping the desired superstructure as the final product.
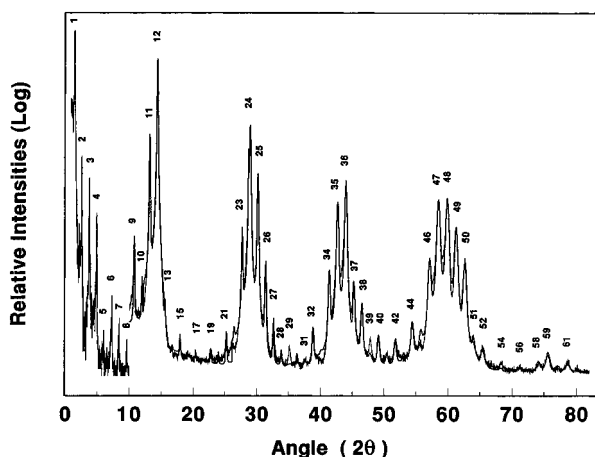

Figure 9. Diffraction data collected on a superlattice reactant in which elemental layers were deposited of appropriate thickness to yield 6 NbSe₂ layers and 6 TiSe₂ layers in the final product. This sample has been annealed a total of 197 h at 500 °C. All of the diffraction maxima can be indexed as 00*l* lines of the superlattice as indicated. The curve under the data points is a calculated diffraction pattern obtained from a least-squares Rietveld structural refinement resulting in the structure shown in Figure 10.

initial multilayer reactant and is shown in Figure 10. As designed, the structure contains 6 layers of titanium diselenide and 6 layers of niobium diselenide with interlayer distances bracketed by those found in polytypes of the pure dichalcogenides. Refining the occupancies of the metals in the layers, we find little titanium in the niobium layers compared with niobium in the titanium layers. At the boundary between the niobium and titanium dichalcogenides we find one layer with significant mixed-metal population. The van der Waals gaps in both the niobium and titanium dichalcogenide regions are comparable to those found in the

pure dichalcogenides. Significantly, the gap between the titanium and niobium dichalcogenides is slightly larger resulting from the *a*-axis mismatch between the dichalcogenide components. This structure demonstrates that this technique can be used to prepare superlattice compounds with little interdiffusion at the interfaces.

The reaction mechanism shown in Figure 8 provides a framework for the rational synthesis of new compounds with structures similar to that of $[NbSe_2]_6$-$[TiSe_2]_6$ shown in Figure 10. In this mechanism, the thicknesses of the individual component layers are determined by the structure of the initial reactant which can be controlled on an angstrom level. Figure 11 contains the diffraction patterns resulting from the annealing of a series of elementally modulated reactants designed to evolve into the indicated crystalline superlattices. The diffraction patterns contain many well-resolved diffraction maxima, all of which can be indexed as 00*l* diffraction maxima. The refined *c*-axis lattice parameters are consistent with the desired number, *N*, of NbSe₂ layers and TiSe₂ layers in the repeating unit of the superlattice sample as shown in Figure 12. These compounds are all structural isomers of one another. The preparation of the compositionally modulated superlattice $[Nb_{1-x}Ti_xSe_2]_1[Ti_{1-x}Nb_xSe_2]_1$ again highlights the ability to limit interdiffusion between the components of the superlattice by optimizing annealing conditions.

Several annealing experiments were conducted 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 titanium- and niobium-containing dichalcogenide layers. Raising the
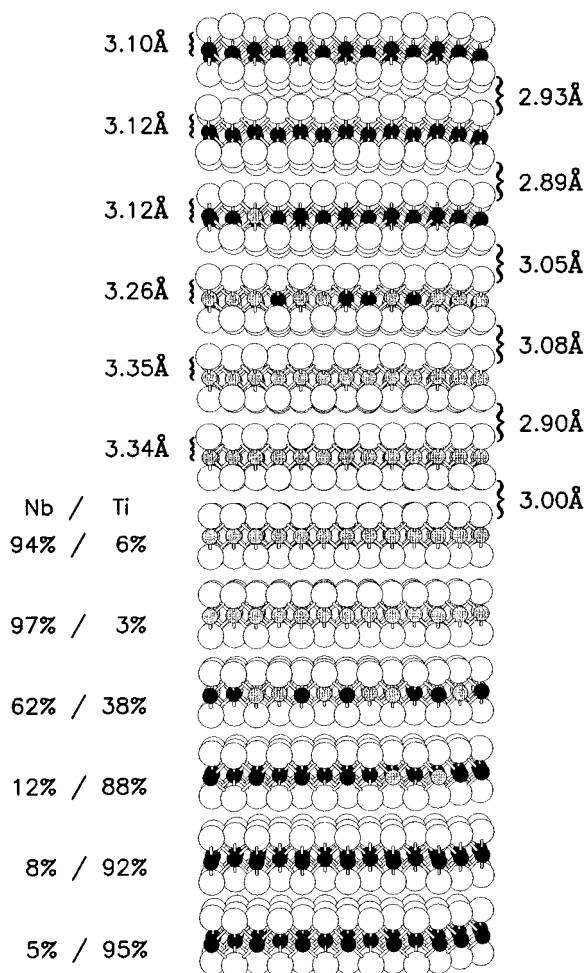
Figure 10. Refined structure after annealing a total of 197 h at 500 °C for the superlattice unit cell containing 6 NbSe$_2$ layers and 6 TiSe$_2$ layers. Indicated next to the respective layers are the percent occupancy of each of the metals and the interlayer and intralayer spacing between selenium layers. The intralayer spacing for the niobium and titanium layers bracket those observed in the binary compounds. There is a distinct change in interlayer van der Waals spacing through the interface region between the niobium diselenide and titanium diselenide blocks resulting from the *a*-axis mismatch between the dichalcogenide components.

temperature to 650 °C resulted in the complete intermixing of the metal layers within 12 h, destroying the superlattice periodicity as the dichalcogenide solid solution forms. This suggests that the layered structures are not equilibrium phases but are only kinetically stable at low temperatures. The intermixing of the metals at higher temperatures indicates that these structures cannot be prepared by traditional synthetic methods such as direct reaction of the elements at high temperatures.

As evidenced by the above diffraction patterns, this synthetic approach to superlattices can be used to prepare artificially structured materials that have previously been synthesized only using epitaxial growth techniques such as molecular beam epitaxy. This new approach has potential advantages and disadvantages relative to epitaxial growth techniques. The major disadvantage of this new approach relative to epitaxial synthesis techniques is crystallographic disorder in the *a*−*b* crystallographic plane which is probably inherent to the mechanism of formation. The potential advantages relative to epitaxial growth techniques include the
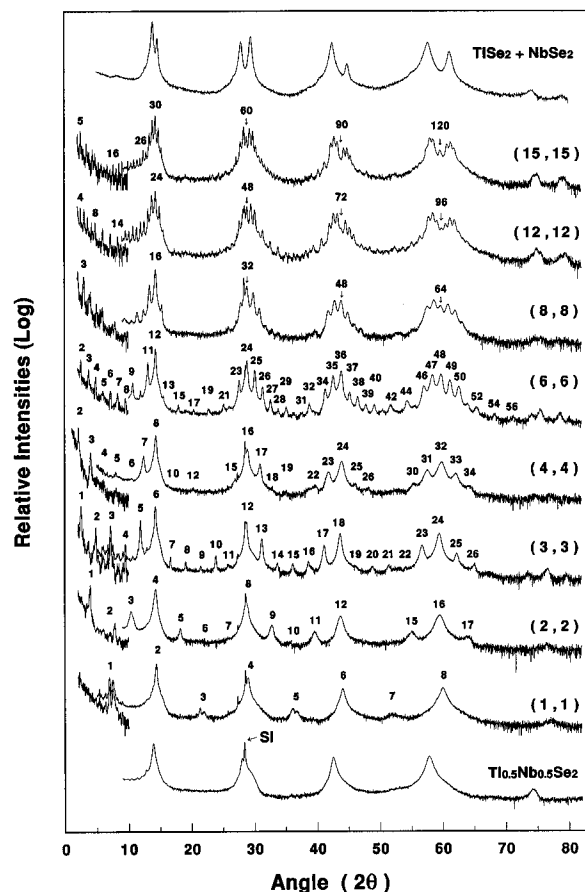

Figure 11. Diffraction data collected on series of structural isomers of composition TiNbSe$_4$ containing equal numbers of crystallographic layers of the respective dichalcogenide compounds in the unit cell. The diffraction patterns of the members of this series containing the homogeneous alloy (bottom diffraction pattern): 1/1, 2/2, 3/3, 4/4, 6/6, 8/8, 9/9, 12/12, 15/15 TiSe$_2$/NbSe$_2$ units as the unit cell of the superlattice, and a mixture of the binary compounds (top diffraction pattern) are shown offset for clarity.
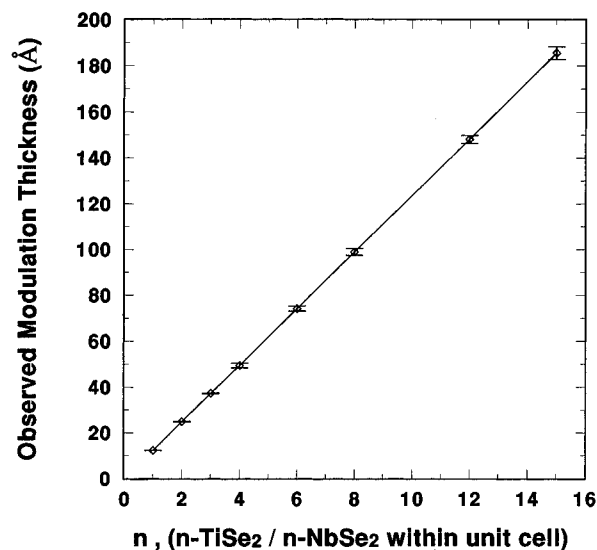

Figure 12. A plot of the refined *c*-axis lattice parameters versus the desired number of repeating units, *N*. The linear relationship between these parameters highlights the ability of this approach to design the structure of the desired final product through control of the initial reactant.

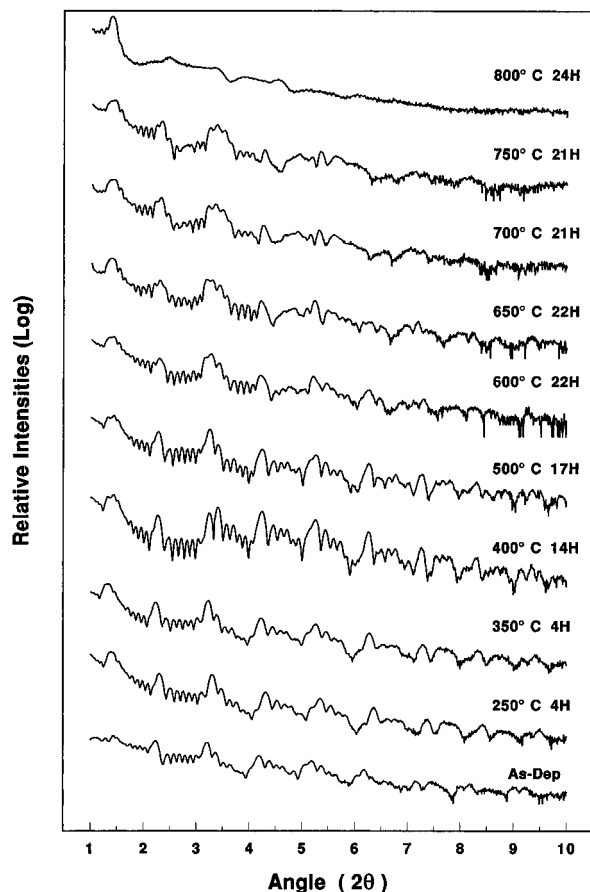relative ease of depositing a uniform layer of a single element rather than a combination of elements simul-

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Figure 13. Evolution of the low-angle diffraction data as a function of annealing temperature for a modulated tungsten—tungsten/selenium multilayer reactant.
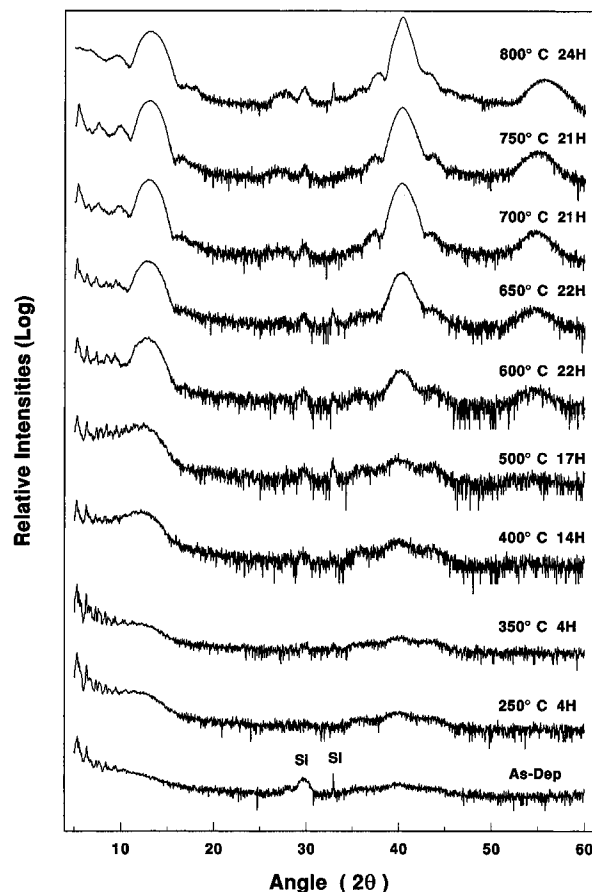

Figure 14. Evolution of the high-angle diffraction data as a function of annealing temperature for a modulated tungsten—tungsten/selenium multilayer reactant.

taneously while maintaining uniform composition across a substrate, the design freedom to deposit different layers using different techniques, and the relative ease of maintaining composition over large lateral distances. The stacked elemental layer method for the preparation of copper indium diselenide uses these inherent advantages and has attracted considerable interest. Since one is not trying to control a complicated surface equilibrium, higher deposition rates can also be used leading to greater overall production. This new synthetic method is also ideally suited for exploratory work on new materials and on testing new ideas on new materials systems since it is relatively easy to change between materials systems and rapidly explore a host of annealing conditions using in situ diffraction techniques.

This new synthesis approach opens up new opportunities to explore novel materials combinations since it depends upon controlled crystallization of pre-deposited layers rather than upon epitaxial growth. This synthesis approach, for example, should be able to prepare nanocomposites containing compounds with grossly different crystal structures. The ability to prepare such nanostructures is illustrated in Figures 13 and 14, which contains the evolution of the low- and high-angle diffraction pattern of an elementally modu-lated reactant designed to evolve into a W−WSe$_2$ heterostructure. The broad diffraction maxima centered at 12° 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 which were formed. After the 600 °C anneal, there is a significant increase in the intensity and a decrease in the line widths of both the W and WSe$_2$ high-angle diffraction maxima. After annealing at 800 °C, the line widths correspond to W particle size of 40 Å and WSe$_2$ particle sizes of 45 Å consistent with the superlattice period of 86 Å deter-mined from low-angle diffraction data. These diffraction data are consistent with the mechanism suggested in Figure 8.

This new synthesis approach also opens up op-portunities to prepare superlattices containing compo-nents such as carbides which would require prohibi-tively high growth temperatures in an MBE-based synthesis. Preliminary data suggest that transition-metal carbides will form superlattices using this ap-proach. Data obtained on the reaction of binary early transition metal−carbon superlattices with repeat spac-ings less than 20 Å show that they form X-ray amor-phous alloys after short anneals followed by nucleation and crystal growth on annealing at higher tempera-tures. On the basis of these results, a modulated reactant containing layers of molybdenum and carbon designed to form 30 Å of Mo$_2$C alternating with layers of tungsten and carbon designed to form 30 Å of W$_2$C was prepared. This sample had the expected low-angle diffraction pattern resulting from the modulated reac-tant and no high-angle diffraction peaks indicating that it was X-ray amorphous. Upon performing a DSC experiment on this reactant, a single sharp exotherm
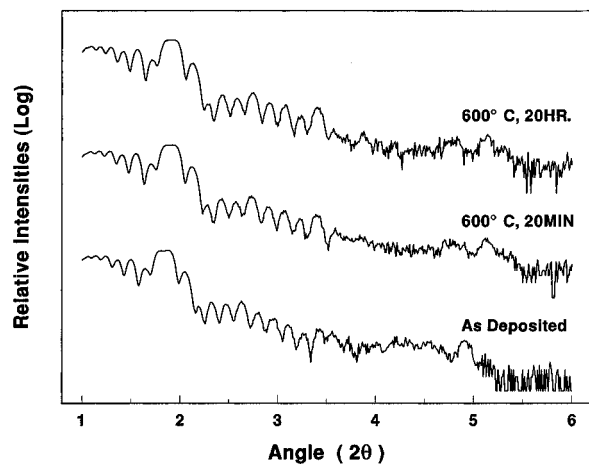
Figure 15. Evolution of the low-angle diffraction pattern of a modulated elemental reactant designed to evolve into a W_2C-Mo_2C heterostructure.

is observed at 550 °C, between those observed for the individual binary components (tungsten carbide, W_2C is observed to nucleate at 600 °C and molybdenum carbide, Mo_2C, at 500°C). Diffraction data shown in Figure 15, indicate that the sample is still modulated after the exotherm, and the high-angle diffraction data indicate that the expected carbide structure has formed. Work is continuing to determine the atomic structure of these modulated carbide superlattices.

Future Research Directions

Significant progress has been made in understanding the reaction pathways made available through the use of elementally modulated reactants. A general synthetic route to amorphous intermediates has been developed through low-temperature interdiffusion of multilayer reactants. Nucleation has been shown to be the rate-limiting step in creating crystalline solids in this synthetic approach. Nucleation energies have been shown to depend upon composition of the amorphous intermediate, allowing the control of product formation by using the overall composition of the amorphous intermediate. A second synthetic route, based on interfacial nucleation and crystal growth of the component structures, leads to the kinetic trapping of products with superlattice structures. By altering the layer sequence and structure of the initial elementally modulated reactant, one can control the superlattice structure of the product by integral multiples of the unit cells of the constituent structures.

Despite this progress, significant challenges remain. For the reaction pathway using amorphous intermediates, the two largest challenges are to develop techniques to control the structure of the product by controlling nucleation and to develop approaches to structurally characterizing the small crystallites produced. Many challenges also remain in the development of multilayer elemental reactants as a source of superlattice products with designed superstructure. The generality of this approach will depend on the energetics of the many diffusion processes throughout the evolution of the reactant to the product. A better understanding of diffusion at reacting interfaces is needed to permit the control of these diffusion processes. In addition to these synthetic parameters, further work needs to

address the degree of structural order between the components of the superlattice and the dependence of this order on processing conditions.

A potential method to control nucleation which may permit the structure, in addition to the composition, of the final product to be controlled is seeding the amorphous intermediate with known compounds which are isostructural to desired products. This potentially can be accomplished by adding a small fraction of seed-forming layers within the initial multilayer reactant. Further studies are required to explore how the activation energy for nucleation is modified by seeding or epitaxial nucleation. The existing metallurgical literature on precipitation reactions will provide important background for designing these experiments. Additional experimental techniques need to be developed that permit nucleation rates to be determined. The ability to measure solid-state nucleation rates experimentally will lead to renewed theoretical interest in solid-state nucleation, since nucleation rates are considerably more sensitive to theoretical models than measurements of nucleation barriers.[35] The resulting increased understanding of the factors governing nucleation will greatly aid the development of synthetic control of nucleation energies and thus the structure of crystalline products. In addition to these synthetic challenges, new structural characterization techniques need to be developed for the characterization of the small crystallites produced.

The structural characterization of new compounds formed through nucleation of amorphous intermediates by X-ray diffraction alone is a significant challenge for a number of reasons. The products usually consist of small crystallites (typically less than 100 nm on a side) with significant strain and defect concentrations due to slow diffusion rates during their formation, resulting in broad diffraction maxima. Preferred alignment and growth of the crystallites along the original layering plane is frequently observed and greatly complicates determination of relative diffraction intensities. If the product is thermodynamically unstable with respect to binary compounds, there is limited opportunity for extended annealing to reduce strain and defect concentrations. Higher temperature annealing will result in decomposition of the compound. Finally, the total amount of sample is small (usually less than 5 mg) which makes quantitative powder diffraction difficult to acquire.

In contrast, materials produced by this method are ideally suited to characterization by electron diffraction because the initial thickness of the multilayer limits the thickness of the crystallites that grow. Since this can be made as thin as necessary, the samples do not need to be thinned before imaging in an electron microscope. Several major advances in electron microscopy have made it possible to obtain quantitative convergent beam diffraction patterns from dislocation-free regions of single crystallites on spots which have a well-defined thickness. Energy filtering can be used to remove most of the inelastically scattered electrons, dramatically reducing the background intensity in measured patterns. The final advance is in the use of digital detectors instead of photographic film to record the patterns. The remaining challenge is to work backward from the data to determine an unknown structure. One particular

effort by Bird and Saunders is noteworthy as they calculated a convergent beam diffraction pattern of gallium phosphide and were able to work backward from the simulated data to the original structure.

The ability to prepare superlattices from multilayer elemental reactants will depend upon designing initial reactants that favor nucleation and crystal growth of the component structures rather than intermixing of the components. Since this approach follows a distinctly different reaction pathway than layer-by-layer epitaxial growth, using modulated elemental reactants presents significant advantages for the preparation of intergrowths of ternary compounds, heterostructures of compounds with incompatible MBE growth conditions or significant lattice mismatch. Through control of diffusion lengths and using low temperatures to limit diffusion rates, we anticipate that this approach may be successful in preparing heterostructures in a wide variety of materials. The minimum length scale of the heterostructure will, of course, depend on the ability to control diffusion. Determining the average structure in the layering direction from the resulting diffraction patterns can also be problematic. The major difficulty is that the difference in intensity between the large diffraction maxima, resulting from constructive interference of the diffraction from the respective layers, and the small diffraction maxima, resulting from the incomplete destructive interference of diffraction from the respective layers due to the compositional modulation in the superstructure, can be greater than 5 orders of magnitude. Errors in fitting the tails of the larger peaks due to errors in the chosen profiles significantly change the fitted intensity of the small peaks. Further X-ray diffraction and transmission electron microscopy experiments need to be performed to elucidate the changes in structure perpendicular to the layering direction as a function of annealing parameters.

Summary

The ability to kinetically access new compounds, controlling composition and the structure of the final products is important in solid-state chemistry and materials science. Both of these fields are built on developing and understanding the interrelationships between structure and physical properties. The level of understanding often depends on the ability to prepare new compounds with desired structure or composition variations from that of a parent compound with a desirable property. The ability to control the nucleation of amorphous alloys and gain access to ternary and higher order compounds that are thermodynamically unstable with respect to binary components provides an important new synthesis tool. The ability to prepare heterostructures and superlattices also provides access to new materials. The ability to design multilayer elemental reactants which will evolve into superlattices with the desired structure and composition will greatly facilitate the investigation of property−superlattice structure interrelationships. This will permit the design of heterostructure and superlattice structures with tailored mechanical or electrical properties. The design of superlattice materials with desirable properties will also result from continued improvements in both synthesis and understanding of structure−function relationships.

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