Self-Assembly of Designed Precursors: a Route to Crystallographically Aligned New Materials with Controlled Nanoarchitecture

Richard Westover, Ryan A. Atkins, Matthias Falmbigl, Jeffrey J. Ditto, David C. Johnson
*rwestove@uoregon.edu (208) 932-3529

ABSTRACT

Modulated elemental reactants is a method by which new and complex intergrowth compounds can be synthesized by the self-assembly of designed precursors prepared by physical vapor deposition. Careful calibration of the composition and thickness of the precursors ensures the formation of the desired product by precise control of local composition and diffusion lengths. Superstructures of increasing complexity can be realized using binary and ternary systems as starting points. The synthesis of systems based on three different binary compounds, either alloyed together or separated into distinct layers, expands the number of possible superstructures that can be formed using this technique, but provides analytical challenges. The synthesis of $[(\text{SnSe})_{1.15}]_1[(\text{Ta}_x\text{V}_{1-x})\text{Se}_2]_1[(\text{SnSe})_{1.15}]_1[(\text{V}_y\text{Ta}_{1-y})\text{Se}_2]_1$ compound is used to illustrate the preparation of precursors and the challenges in both measuring and limiting the interdiffusion of layers during self-assembly. Systematic changes in the electrical properties of $(\text{SnSe})_{1+\delta}(\text{Ta}_x\text{V}_{1-x})\text{Se}_2$ alloys are observed as x is varied. The electrical resistivity of $[(\text{SnSe})_{1.15}]_1[(\text{Ta}_x\text{V}_{1-x})\text{Se}_2]_1[(\text{SnSe})_{1.15}]_1[(\text{V}_y\text{Ta}_{1-y})\text{Se}_2]_1$ can be modeled as the two constituent layers in parallel.

INTRODUCTION

New synthetic methods have been critical both to advance scientific understanding as well as to advance technology. Traditional approaches have historically focused on using thermodynamic control to make desired products, for example growing doped silicon crystals from a melt of fixed composition. Phase diagrams were determined to understand the thermodynamic relationships between compounds. Kinetic control, typically achieved by controlling temperature as a function of time, was used to influence the microstructure. The search for new materials focused on finding reaction conditions where new compounds would be thermodynamically stable. High temperature synthesis and the growth of new materials from melts were commonly used to overcome slow solid state diffusion rates and to form single crystals for structure determination. New compounds and new phenomena are discovered whenever new approaches are developed, such as vapor transport reactions in the 1960's,[1,2] or new adaptations, such as the use of low temperature fluxes,[3,4] are explored. A grand challenge in the field of materials discovery is the development of approaches to predict new structures and the properties associated with specific compositions, and the development of approaches that will enable their synthesis. Historically, serendipity played a significant role in most new discoveries as unexpected compounds formed in reaction mixtures.

An example of a new crystal growth technique that has significantly advanced both scientific understanding and technology is the development of molecular beam epitaxy (MBE). In the 1960's there was much interest in producing new semiconducting materials with specific compositions and specific doping profiles required for new devices. The development of MBE

by Arthur and Cho,[5-10] was a significant breakthrough because it enabled new materials to be created with known structure and designed composition modulations. The MBE process involves directing a flux of the respective elements at a heated substrate with the goal of controlling the surface equilibrium. The temperature of the substrate controls the surface diffusion rates, such that atoms can find favorable surface sites, and the desorption rates of different species. The relative fluxes of the sources to the surface control the surface composition by balancing the arrival rates with the desorption rates. Done correctly, and when the lattice mismatch between the film and the substrate is slight, the process results in the growth of solids with the structure of the substrate but composition controlled by the fluxes of reactants. Composition gradients can be kinetically trapped via the epitaxial growth process, because the volume diffusion rates at the temperatures used are small compared to the surface diffusion rates. MBE growth has yielded new materials with exceptional properties, as materials with designed structural sequences can be prepared with very low defect levels due to low growth temperatures. An example of an exceptional property resulting from MBE growth is very high mobility values produced when dopants are incorporated in a layer that then donates the resulting carriers to another layer in the grown structure. This process is referred to as modulation doping.[11] The lack of dopant atoms in the transport layer, which normally scatter the charge carriers, results in the exceptionally high mobility values. These new materials have led to the discovery of new phenomena including the fractional Hall effect.[12,13]

The ability to anticipate structures that could be prepared via MBE resulted in theoretical predictions of new phenomena, which resulted in new technologies. Light emitting diodes (LED) are one example where predictions were made about the materials properties and architectures required to observe the emission of light from a diode. Once the phenomenon was observed, predictions were made about how to optimize efficiency and how to produce white light from a LED. MBE practitioners determined how to grow and optimize the predicted structures and the resulting LED technology continues to be enhanced today. An important implication is that synthesis routes that yield materials with predictable structures and compositions enhance synergies between theory and experiment. Starting with reasonable assumptions about structure makes calculations easier and enables extrapolations from existing data, both of which facilitate transforming ideas into technologies.

There is currently significant interest in two dimensional materials, particularly (2-D) - single structural units that are not epitaxially connected to the structure of the substrate, and the stacking of these layers to make 2-D heterostructures, because of the promise of properties that do not exist in the bulk materials or that are enhanced in the heterostructure relative to the bulk or the individual 2-D constituents. The layer-by-layer design provides clear structural starting points for theory, and the surface states present in these 2-D layers have resulted in novel classes of materials such as topological insulators - materials that are bulk insulators but whose surfaces contain conducting states. There is a growing list of potential constituents accompanied by criteria to evaluate stability of potential 2-D layers that have yet to be tried. Heterostructures are an ideal class of materials for the materials genome project to explore materials by design because of their defined starting structure.

Approaches to preparing individual 2-D layers have been developing over time. Initially the preparation was based on the effective but technically challenging cleaving of bulk crystals

followed by searching for single constituent layers. More recently, recipes have been developed to prepare individual layers on specific substrates by reaction of surface layers or growth from vapor phase precursors. Examples of materials prepared to date via these recipes include MoS_2 , [14,15] WS_2 , [16-17] Silicene [18-20] and ZrS_2 , [21] all materials with anisotropic structures. Preparing 2-D heterostructures is much more challenging, as the growth techniques developed for individual 2-D layers are typically not compatible with the sequential growth of one constituent on top of another. Indeed the most common approach to making heterostructures has been the cleaving and stacking of individual layers, which has been described as being analogous to building with Lego blocks. While this technique has yielded many new and exciting structures, it is an exacting task only done by a few groups with very low yield [22-27] and is limited to small sample areas. It is also limited to those compounds that can be cleaved into a single layer thick 2-D layer and that are stable as an atomically thick layer. Geim has suggested three criteria for stability based on existing data. [28] He suggests that 1) the parent 3D structure should have a melting temperature above 1000 °C so that the 2D sheet is stable at room temperature, 2) the 3D structure must be chemically inert so that no decomposed surface layer forms in air or any other environment, and 3) that insulating and semiconducting 2D-crystals are more likely to be stable compared to metallic ones. There is a need for a flexible synthesis approach that is scalable, enables constituents to be layered without epitaxial relationships between layers, and that is applicable to a wide variety of constituents.

This paper provides an overview of the modulated elemental reactants technique and illustrates how increasingly complex materials can be formed from the building blocks of simpler materials. The synthesis of several new compounds, the random alloys $(\text{SnSe})_{1+\delta}(\text{Ta}_x\text{V}_{1-x})\text{Se}_2$ and the ordered alloy $[(\text{SnSe})_{1.15}]_1[(\text{Ta}_x\text{V}_{1-x})\text{Se}_2]_1[(\text{SnSe})_{1.15}]_1[(\text{V}_y\text{Ta}_{1-y})\text{Se}_2]_1$, are used to illustrate the challenges in the synthesis of multiple component systems with miscible constituents. These systems were chosen because the transition metal dichalcogenide alloy $(\text{Ta}_x\text{V}_{1-x})\text{Se}_2$ compounds with x up to 0.6 were previously reported and are thermodynamically stable. [29]. In addition to presenting the synthesis and structure, we report electrical properties, which systematically change with x in $(\text{SnSe})_{1+\delta}(\text{Ta}_x\text{V}_{1-x})\text{Se}_2$ compounds. The resistivity of the ordered alloy can be modeled as the two parent compounds $[(\text{SnSe})_{1.15}]_1[(\text{Ta}_x\text{V}_{1-x})\text{Se}_2]_1$ and $[(\text{SnSe})_{1.15}]_1[(\text{V}_y\text{Ta}_{1-y})\text{Se}_2]_1$ in parallel.

MODULATED ELEMENTAL REACTANTS

The modulated elemental reactant (MER) synthesis approach has been developed over the last two decades at the University of Oregon and is based on controlling local composition and diffusion lengths to control the kinetics of phase formation. The initial concept was that by depositing sequential elemental layers, the layer thicknesses could be reduced such that the layers would mix at low enough temperatures that mixing would be complete before interfacial nucleation could occur. This is illustrated schematically in Figure 1. The initial ratio of layer thicknesses would control the composition of the amorphous intermediate formed. It was shown that the composition of the amorphous intermediate could control the subsequent nucleation process, enabling compounds to be formed kinetically even if they are not thermodynamically stable at the reaction conditions. [30] A high level of selectivity can be achieved. By designing precursors that closely mimic the local composition and structure of targeted compounds, diffusion lengths are greatly reduced relative to more traditional

synthetic approaches, which allows much lower reaction temperatures and shorter times to be used than conventional methods. The combination of mild annealing conditions and the ability to easily modify the precursor structure allows numerous metastable compounds to be formed, which cannot be accessed using other techniques.[31-35]

Figure 1: A schematic of a layered precursor showing the interdiffusion of the layers to form an amorphous intermediate and the subsequent nucleation of the targeted compound.

The structural complexity of products can be increased by adding additional layers with different compositions, leading to the formation of new layered solids containing constituents with different structures. These new compounds can be prepared by combining the precursor layering schemes for single component systems. The structure and composition of each layer is controlled by the composition and thickness of the layer in the precursor. Variations to the layering scheme (nanoarchitecture) of the product can be achieved by simply changing the layering scheme of the precursor. This is illustrated in Figure 2, where the center structures can be combined to yield three different families of layered structures containing two constituents each. The thickness of each block can be individually controlled as well as the order of the layers, resulting in over 20,000 distinct nanoarchitectures for n and m less than 10.[36] The three constituents can also be combined into one heterostructure, either by alloying the constituents that have a common structure[37], to form a random (A,B)C alloy, or by preparing three component heterostructures with distinct layers of each constituent forming an ordered ABAC alloy. These two possibilities provide access to a large number of new compounds, many more than one would like to make, so the challenge is to understand how properties change as the constituent thicknesses, order, and composition are varied to accelerate the search for the optimum properties for a particular application. In the following sections we outline how this approach can be used to prepare increasingly complex compounds with the structure of the initial precursor controlling the nucleation of individual layers and the resulting nanoarchitecture of the final product.

Figure 2: The blue box shows the thinnest structural units of three representative binary constituents, the outside two with a transition metal dichalcogenide structure (TSe_2 and $\text{T}'\text{Se}_2$) and the middle one a rock salt structure (MSe) with two (001) planes. The second row in the red box displays the three simplest binary heterostructures, $(\text{MSe})_1(\text{TSe}_2)_1$, $(\text{TSe}_2)_1(\text{T}'\text{Se}_2)_1$ and $(\text{MSe})_1(\text{T}'\text{Se}_2)_1$. The top row shows the three compounds with the next smallest repeating units, A_1B_2 , A_2B_2 and A_2B_1 , illustrating how the constituents can be assembled with different individual thicknesses and, for thicker repeats, different orders of assembly. The bottom row contains a schematic of compounds where the dichalcogenides have been alloyed to form the compound $(\text{MSe})_1(\text{T}_{1-x}\text{T}'_x\text{Se}_2)_1$ (green box). The thickness of each constituent can be controlled as shown in the top row for the pure dichalcogenides. The image on the bottom left (orange box) shows an ordered alloy, where the three components form the $(\text{MSe})_1(\text{TSe}_2)_1(\text{MSe})_1(\text{T}'\text{Se}_2)_1$ compound. The A, B, and C components can be combined in different thicknesses and sequences to make a very large number of unique nanoarchitectures.

Single Component Systems

The simplest materials to form by MER are compounds containing multiple elements but only one structure or type of material, for example a binary rock salt structure or transition metal dichalcogenide structure. These single constituent systems are the building blocks of the more complex materials to be discussed later. The synthesis of these single constituent systems has provided insights into the formation mechanism as the layered precursor system interdiffuses and ideally nucleates into the desired structures. The interdiffusion of the thin elemental layers in the precursors was shown in the early 1980's to be a low temperature route to amorphous alloys.[38] These mechanistic insights are useful in understanding the evolution and resulting structure and properties of more complex systems containing several constituents. The calibration schemes used for these simple component systems are also applied in the design of the precursors required to form more complex materials.

Calibration of the modulated precursors for single component systems consists of two basic steps. The first step is to adjust the relative deposition times of each element to ensure the desired composition. In a binary system, two elements are deposited typically holding the deposition time of one constituent constant while systematically varying the deposition time of the other. By holding the deposition time of Se constant while that of the Nb is incrementally changed a linear relationship between the atomic ratio of the elements and the ratio of the deposition times results with the slope related to the proportionality factor between the deposition rates measured by the quartz crystal monitors and the actual deposition rates at the sample surface. Scaling deposition times of all sources equally, yields the same composition but different repeat thicknesses. This enables the deposition time corresponding to the desired Nb/Se composition ratio to be interpolated, which can then be scaled to deposit a specific thickness of a desired composition. Typically, a 3-5% excess of selenium is used to compensate for losses during annealing of the precursors to transform them into the targeted products.

Once the composition of the precursor is correct, it is crucial that the thickness of the layering is thin enough that the layers interdiffuse before interfacial nucleation occurs. This is the second step in the calibration. Low temperature annealing causes interdiffusion, and if the layers are thin enough this results in an amorphous intermediate with a constant composition. The average composition has a large impact on what crystallizes as nucleation is controlled by local composition. Figure 3 contains a diffraction pattern of a sample with a Nb to Se composition ratio of one to two after annealing at 400°C. The intensity of the peaks depends on both the percent of the precursor that has crystallized as well as the extent of preferred alignment of the crystallites. The sharpness of the diffraction peaks reflects the size of coherently scattering crystalline domains. As shown in Figure 4, the intensity of the peaks of the assembled ferecystal are sensitive to composition, presumably due to a combination of a reduced amount of product crystallized and the reduced size of the crystallites with increasing deviations of the precursor from the composition corresponding to the stoichiometry of the crystallizing compound. This is presumably caused by the increasing non-stoichiometry at the growing crystallites as the excess element is excluded from the growing crystal. This variation in intensity provides an additional guide when optimizing the correct composition and thickness of the precursor.

Figure 3. Diffraction pattern of NbSe₂ formed at 400°C by annealing a precursor containing Nb/Se elemental bilayers. The y axis is log intensity to highlight low intensity diffraction maxima. Only the 00/ reflections are observed due to the textured nature of the product. Substrate peaks are indicated with an asterisk.

Figure 4. The intensity of the first observed 00/ reflection of NbSe₂, formed at 400°C, as a function of time that the shutter was open depositing Nb at a constant rate. The maximum in the intensity corresponds to the precursor with a 1:2 ratio of Nb to Se.

The goal of the second calibration step is to optimize the thickness of the repeating sequence of elemental layers in a way that each deposited layer evolves into a single structural unit of the targeted constituent, for example, a single Mo/Se bilayer would evolve into one Se-Mo-Se trilayer. The thickness of a single repeating sequence of deposited atomic layers can be determined from an analysis of the X-ray reflectivity (XRR) pattern of the precursor. The XRR patterns contains Bragg reflections from the repeating sequence of layers and Kiessig fringes, which result from the interference pattern from the front and back of the film and intensity from the incomplete destructive interference of the finite number of layers. A plot of monolayer thickness versus deposition time allows the deposition times that correspond to a desired repeat thickness to be determined. If the correct repeat thickness is used, then the number of repeats in the precursor is equal to the number of repeats in the final product. For example Figure 5 contains an NbSe₂ sample in which 58 repeats were deposited giving a product with 58 repeating units by XRR. Having calibrated the thickness in this manner, the number of repeating structural units in the crystalline sample is precisely controlled by changing the number of repeats in the precursor. Samples containing from 2 to 80 repeating structural units have been prepared using this method.[39]

The preparation of metastable crystalline compounds is a challenge and requires control of both nucleation and growth of the targeted compound. The preparation method described above has turned out to be effective for the synthesis of metastable crystalline samples with varying chemical compositions that cannot be obtained applying classical approaches.[40-43] The key for the success of the method is a drastic reduction of the diffusion length to some nm or even down to few Å. As a consequence interdiffusion, nucleation and crystallization occur at low temperatures compared to classic approaches of preparing of inorganic solids.[44-46]

Figure 5. An XRR pattern of a sample containing 58 repeating NbSe₂ trilayers, formed at 400°C, from a precursor containing 58 repeating Nb-Se bilayers in the repeating precursor.

TWO COMPONENT SYSTEMS

The calibration of a precursor designed to form a two-component compound follows the same logical process used for the single component precursor, but the additional constituent adds additional elements that need to be calibrated, requiring more steps. The calibration of the relative compositions and thicknesses of all of the layers in the repeating sequence of elemental layers for two component systems is made easier if the deposition parameters for each of the constituents have already been independently calibrated. In this case, the first step in the calibration is to adjust the relative amount of each of the constituents. The relative amounts depends on the different entities being layered, as there will be a misfit in area between the constituents that depends on the crystal faces of the constituents that are adjacent to one another and the unit cell parameters. This results in a factor $1 + \delta$, where δ is the so called misfit parameter, reflecting the differences, or mismatch, of the lattice parameters of the adjacent planes at the interface between the two constituents giving rise to different numbers of formula units per area. When making derivatives of known compounds containing two different constituents, the desired ratio is simply the reported misfit parameter for the two constituents. When attempting to create new compounds between two constituents that have not been layered before, assumptions about the adjacent crystal phases are made and the bulk lattice parameters are used to calculate misfits. The second step in the calibration is to prepare samples at the desired composition ratios by holding the deposition times of one constituent constant while those of the other are systematically scaled. Plotting the composition ratio versus the deposition time of the varied constituent yields a calibration curve from which the deposition time yielding the desired atomic ratio for the elements can be determined. The third step is to scale thickness of two constituents so that the layers deposited for each constituent yields a single crystallographic unit.

The following example illustrates the process. In the calibration of the SnSe - NbSe₂ system, the difference in area between the (001) planes of SnSe and the (001) planes of NbSe₂ is 1.16 obtained either from the known misfit compound or by using the lattice parameters of the bulk compounds as an estimate. To find the ratio of deposition times to obtain this Sn/Nb ratio, the

Nb and Se deposition times of the NbSe_2 constituent are held constant while the deposition times of the Sn and Se precursor layers for the SnSe component are systematically scaled. A plot of the Sn/Nb ratio vs the amount of time the Sn shutter is open results in a linear relationship for the specific deposition rates and geometry used. This experimental relationship enables the deposition time that gives a Sn/Nb ratio equal to the known misfit parameter for this compound to be determined. After the appropriate composition is achieved, scaling the deposition times of all elements together to achieve the thickness such that layers in the precursor evolve into single structural units of each constituent completes the calibration. If the thicknesses were correct for each of the single component systems, the thickness after scaling the compositions are usually pretty close for the two component system, which simplifies this step.

Using different single component systems as building blocks, a variety of two component systems can quickly be calibrated, precursors prepared, and precursors annealed to form targeted compounds. For example, Figure 6 contains the specular diffraction patterns for four different $[(\text{SnSe})_{1+\delta}]_1(\text{TSe}_2)_1$ compounds with $T = \text{V, Nb, Mo and Ta}$. The specular diffraction patterns for all of these compounds are similar, but the intensities of the 00/ reflections vary mainly due to the different scattering factors for the transition metals in the dichalcogenide component. The c -axis lattice parameters of all of the compounds are similar and can be thought of as the sum of the thickness of two (001) planes of SnSe and a Se-T-Se trilayer. Figure 7 contains the in-plane X-ray diffraction patterns of the same four $[(\text{SnSe})_{1+\delta}]_1(\text{TSe}_2)_1$ compounds with $T = \text{V, Nb, Mo and Ta}$. The reflections in the in-plane diffraction scans of these compounds can be indexed as two families of reflections, each arising from one of the constituents. The in-plane lattice parameters of SnSe do not vary as much as the in-plane a -axis lattice parameter of the transition metal dichalcogenides, leading to the different misfit parameters. In contrast to the crystalline misfit compounds prepared at high temperature which typically have one commensurate in-plane axis, the in-plane lattice parameters of the constituents in the compounds prepared using the MER approach remain incommensurate. Figure 8 contains a representative high angle annular dark field scanning transmission microscopy (HAADF-STEM) image of $[(\text{SnSe})_{1.15}]_1(\text{VSe}_2)_1$. The image shows the regular stacking of the two constituent layers and the random rotational disorder between layers. Due to this extensive random rotational disorder found in all the misfit layer compounds prepared using the MER approach, the term "ferecrystal", from the Latin "fere" meaning almost, has been created to describe them.

Figure 6: Specular diffraction scans of $[(\text{SnSe})_{1.15}]_1(\text{VSe}_2)_1$, $[(\text{SnSe})_{1.16}]_1(\text{NbSe}_2)_1$, $[(\text{SnSe})_{1.09}]_1(\text{MoSe}_2)_1$, and $[(\text{SnSe})_{1.15}]_1(\text{TaSe}_2)_1$. All of the diffraction peaks are 00/ reflections, and the indices for each reflection are indicated above the scan of the $[(\text{SnSe})_{1.15}]_1(\text{VSe}_2)_1$ sample. All samples were annealed at 400°C for 20 min.

Figure 7: In-plane diffraction scans of $[(\text{SnSe})_{1.15}]_1(\text{VSe}_2)_1$, $[(\text{SnSe})_{1.16}]_1(\text{NbSe}_2)_1$, $[(\text{SnSe})_{1.09}]_1(\text{MoSe}_2)_1$, and $[(\text{SnSe})_{1.15}]_1(\text{TaSe}_2)_1$. All of the diffraction peaks can be indexed as $(hk0)$ reflections of the two constituents. The indices for each reflection are indicated above the scan of the $[(\text{SnSe})_{1.15}]_1(\text{VSe}_2)_1$ sample.

Figure 8: Cross sectional HAADF STEM image of $[(\text{SnSe})_{1.15}]_1(\text{VSe}_2)_1$

In addition to these four compounds, many other members of these $[(\text{SnSe})_{1+\delta}]_m(\text{TSe}_2)_n$ families compounds have been prepared as well as quite a few additional families as summarized in Table X. Several ferecrystals containing two different dichalcogenides have been prepared, although the extent of intermixing of the transition metals was not determined, because it is very difficult to experimentally determine the extent of alloying. Two different dichalcogenide- M_2Te_3 systems have been investigated to date, with a large range of different thicknesses of the two constituents. There is an atomically abrupt structural change between the constituents, and the chemical difference between the two structures results in an abrupt composition change as well. The same is true for the dichalcogenide-rock salt compounds, for which the largest number of compounds have been prepared and the most extensive structural studies have been conducted. To our knowledge, this approach has not been tried on other constituents, except for one report of the formation of intergrowths of CoSb_3 and IrSb_3 . [47] While a superlattice was observed, it was not crystallographically aligned with the substrate, making structural characterization challenging. The data suggests that this synthesis approach provides a promising avenue to prepare ferecrystalline materials with a wide variety of different structures.

Table 1: A summary of the different families of compounds that have been prepared utilizing the MER technique.

Compounds	References
Dichalcogenide-Dichalcogenide	
$[(\text{TiSe}_2)_{1+\delta}](\text{NbSe}_2)$	48-51
$\{[(\text{VSe}_2)_n]_{1.06}(\text{TaSe}_2)_m\}_z$	52,53
Dichalcogenide-M_2Te_3	
$[(\text{TiTe}_2)_{1.36}]_x[\text{Bi}_2\text{Te}_3]_y$	54,55
$[(\text{TiTe}_2)_{1+\delta}]_x[\text{Sb}_2\text{Te}_3]_y$	56-58
M_2Te_3 - $\text{M}'_2\text{Te}_3$	
$[\text{Sb}_2\text{Te}_3]/(\text{Bi,Sb})_2\text{Te}_3$	59-61
Rock salt - Dichalcogenide	
$[(\text{SnSe})_{1.15}]_m(\text{VSe}_2)_n$	62-65
$[(\text{SnSe})_{1.16}]_m(\text{NbSe}_2)_n$	66-71
$[(\text{SnSe})_{1.09}]_m(\text{MoSe}_2)_n$	72-75
$[(\text{SnSe})_{1.15}]_m(\text{TaSe}_2)_n$	76,77
$[(\text{SnSe})_{1.20}]_m(\text{TiSe}_2)_n$	78,79
$[(\text{PbSe})_{1.15}]_m(\text{TiSe}_2)_n$	80-82
$[(\text{PbSe})_{1.10}]_m(\text{NbSe}_2)_n$	83,84

$[(\text{PbSe})_{1.00}]_m(\text{MoSe}_2)_n$	85-89
$[(\text{PbSe})_{1.12}]_m(\text{TaSe}_2)_n$	90
$[(\text{PbSe})_{0.99}]_m(\text{WSe}_2)_n$	91-93
$[(\text{BiSe})_{1.15}]_m(\text{TiSe}_2)_n$	94
$[(\text{BiSe})_{1.10}]_m(\text{NbSe}_2)_n$	95
$[(\text{CeSe})_{1.14}]_m(\text{NbSe}_2)_n$	95
$[(\text{PbTe})_{1.17}]_m(\text{TiTe}_2)_n$	96

For any intergrowth of two constituents, there is a large number of compounds that can be formed by varying the layer sequence. For example, there are two distinct structural isomers that contain three layers of each constituent A_3B_3 and $A_2B_2A_1B_1$. Both of these compounds will have the same overall composition and approximately the same c-axis lattice parameter, but different superstructures. When there are three layers of one constituent and two of another, there are also two distinct isomers, A_3B_2 and $A_2B_1A_1B_1$. As the number of layers increases, so does the number of potential structural isomers. When there are four layers of each constituent, there are 6 distinct structural isomers, A_4B_4 , $A_3B_3A_1B_1$, $A_3B_2A_1B_2$, $A_2B_3A_2B_1$, $A_2B_2A_1B_1A_1B_1$, and $A_2B_1A_1B_2A_1B_1$. When there are 10 layers of each constituent, there are over 4700 possible distinct structural isomers. As illustrated in Figure 9, for n and m both equal to ten or less, there are over 20,000 distinct structural isomers that can be formed that might be expected to have different physical properties.

$m \backslash n$	1	2	3	4	5	6	7	8	9	10
1	1	1	1	1	1	1	1	1	1	1
2	1	1	2	2	3	3	4	4	5	5
3	1	2	2	4	5	6	8	10	11	14
4	1	2	4	6	10	14	20	26	35	44
5	1	3	5	10	15	26	38	57	79	110
6	1	3	6	14	26	46	76	122	183	275
7	1	4	8	20	38	76	132	232	375	600
8	1	4	10	26	57	122	232	432	750	1272
9	1	5	11	35	79	183	375	750	1384	2494
10	1	5	14	44	110	275	600	1272	2494	4735

Figure 9: The number of possible structural isomers for a given A_mB_n stoichiometry are given in each of the boxes. The shading of the boxes reflects the rapid increase in the number of isomers as m and n increase.

ADDING ADDITIONAL COMPLEXITY

There are several ways to add complexity beyond that found with two binary constituents. One approach is to alloy one or both of the constituents. Another would be to layer three different constituents, two of which have the same structure to form an ordered intergrowth. A third approach would be to layer three constituents all of which have different structures. In each of these cases, the composition and structure of each constituent and the interaction between constituents will affect physical properties. The following sections discuss strategies to prepare the required precursors for each of these approaches with experimental examples of

new random alloys $(\text{SnSe})_{1+\delta}(\text{Ta}_x\text{V}_{1-x})\text{Se}_2$ and the ordered alloy $[(\text{SnSe})_{1.15}]_1[(\text{Ta}_x\text{V}_{1-x})\text{Se}_2]_1[(\text{SnSe})_{1.15}]_1[(\text{V}_y\text{Ta}_{1-y})\text{Se}_2]_1$. This is followed by a summary of the electrical properties of these new compounds showing systematic changes in properties as a function of alloying.

Preparing Random Alloys

Alloying a particular constituent within a multilayer containing two or more compounds in the repeating structure is based on controlling local composition in the specific layer within the precursor that will evolve into the constituent being alloyed.[37] The composition control is accomplished via calibrations similar to what was discussed earlier. There are at least two different approaches based on the number of sources used. The elements to be alloyed in the targeted constituent can be deposited from one source, which is an alloy itself, or the elements can be deposited from different sources, and composition changed by increasing the amount of one element deposited while decreasing the other by the same amount.

Preparing an alloyed constituent using an alloy source is straightforward if the elements are miscible and have similar deposition characteristics. Depositing from an (A,B) alloy source can allow (A,B)C alloys to be synthesized with only minor adjustments to the calibrations of the parent compounds discussed earlier. $(\text{SnSe})_z(\text{Nb}_x\text{Mo}_{1-x})\text{Se}_2$ alloys, which were recently reported, are one example. One complication of this approach is that the vapor and the melt will have different compositions, and the composition of the vapor as a function of the composition of the melt may not be known. This difference in composition also results in the composition being deposited from the alloy source changing with the amount of time the source has been depositing. This is illustrated in Figure 10 where the composition of $(\text{SnSe})_z(\text{Nb}_x\text{Mo}_{1-x})\text{Se}_2$ samples made by the deposition of Nb/Mo alloy sources results in samples with a lower Nb content than the deposition source. Subsequent samples made with the same deposition source, shown in Figure 11, have increasing Nb content as the source becomes depleted in Mo.

Figure 10: The difference between the initial source composition and the composition of the first sample made from that source, showing the preferential deposition of Mo.

Figure 11: The change in the composition of samples as samples are sequentially made from a specific source. The samples become more Nb rich as the source becomes depleted in Mo.

A second approach is using two different deposition sources to create the alloy, which enables alloys to be made of systems where the elements either do not alloy or have vastly different partial pressures over a melted alloy. Depositing fractions of layers using the calibrations of the original components as starting points works even for systems with very different deposition characteristics such as vanadium and tantalum in the alloy system $(\text{SnSe})_{1+\delta}(\text{V}_x\text{Ta}_{1-x})\text{Se}_2$. Holding the non-alloyed constituent constant, the deposition time of the elements in the constituent that are being alloyed are varied as relative fractions of the calibrated parent compounds. As shown in Figure 12, a linear relationship occurs between relative shutter times and relative compositions of the alloys, allowing the preparation of alloys with precisely controlled compositions.

Figure 12: The change in the atomic percent of Ta in a sample containing an alloyed $(\text{Ta}_{1-x}\text{V}_x)\text{Se}_2$ layer graphed versus the change in the percent of time the shutter of Ta was open divided by the total time that the shutters of Ta and V were opened.

Detecting that one constituent has been alloyed and determining the composition of the alloyed layer is an experimental challenge. Specular XRD of the $(\text{SnSe})_{1+\delta}(\text{Ta}_x\text{V}_{1-x})\text{Se}_2$ system shows systematic changes in relative peak intensities (Figure 13) and in the position of reflections as x goes from 0 to 1. The systematic shift to lower angles of the Bragg peaks with increasing substitution of V by Ta indicates an increase in the lattice parameter in the c direction. As shown in Figure 14, the c -axis lattice parameter increases linearly as the amount of Ta is increased, as expected from Vegard's law due to the larger size of Ta. The c -axis lattice parameter, however, is the sum of the thicknesses of the SnSe and dichalcogenide constituents, so additional data are required to confirm that the alloying is limited to the dichalcogenide layer.

Figure 13: Specular X-ray diffraction scans of a series of $(\text{SnSe})_{1+\delta}(\text{Ta}_x\text{V}_{1-x})\text{Se}_2$ compounds formed at 400°C. The diffraction peaks shift slightly to lower angles as x is increased, indicating an increase in the c -axis lattice parameter. The 00 l indices are shown above the top diffraction scan.

Figure 14: The calculated c -axis lattice parameter for a series of $(\text{SnSe})_{1+\delta}(\text{Ta}_x\text{V}_{1-x})\text{Se}_2$ compounds plotted as a function of x . The linear increase in the c -axis lattice parameter with increasing x is expected from Vegard's law.

In-plane XRD scans of the $(\text{SnSe})_{1+\delta}(\text{Ta}_x\text{V}_{1-x})\text{Se}_2$ compounds, shown in Figure 15, provide information about in-plane structure of both constituents, enabling us to determine how the structure of each constituent changes as a function of x . The relative intensities of the $hk0$ reflections change as the vanadium content increases. For example, the intensity of the (210) reflection of the dichalcogenide decreases relative to the (110) reflection. The relative positions of the peaks also change as a function of x , indicating changing in-plane lattice parameters of both the SnSe and $\text{Ta}_x\text{V}_{1-x}\text{Se}_2$ constituents. Figures 16 and 17 show the change in the a -axis lattice parameters of SnSe and $\text{Ta}_x\text{V}_{1-x}\text{Se}_2$ respectively. The a -axis lattice parameters of both compounds increase linearly as x increases to 0.65. The a -axis lattice parameters for $x=1$, the $\text{SnSe}_{1.15}\text{TaSe}_2$ sample, are smaller than expected from the trends observed as x increases, due to a change in the coordination of the transition metal in the dichalcogenide from octahedral for the V rich samples to trigonal prismatic coordination for Ta in TaSe_2 . This is consistent with prior results reported for alloying of VSe_2 and TaSe_2 . The change in the lattice parameter of SnSe is likely due to changes in charge transfer with the dichalcogenide as the coordination changes. Changes in the lattice parameter of SnSe have been observed both as a function of the thickness of the SnSe layer, and as the dichalcogenide constituent has been varied.[97]

Figure 15: In-plane X-ray diffraction scans of a series of $(\text{SnSe})_{1+\delta}(\text{Ta}_x\text{V}_{1-x})\text{Se}_2$ compounds formed at 400°C . The diffraction peaks shift as x is increased, indicating changes in the a -axis lattice parameter of both constituents. The $(hk0)$ indices are shown above the top diffraction scan with the indices for SnSe indicated in bold.

Figure 16: The calculated a -axis lattice parameter for the $(\text{Ta}_x\text{V}_{1-x})\text{Se}_2$ constituent plotted as a function of x . The linear increase in the a -axis lattice parameter with increasing x is expected from Vegard's law due to the larger size of Ta relative to V. The small a -axis lattice parameter for $x = 1$ results from a change from octahedral coordination for $x=0.8$ to trigonal prismatic coordination when $x = 1$.

Figure 17: The calculated a -axis lattice parameter for the SnSe constituent plotted as a function of x .

To our knowledge, there have not been any solid solution studies of misfit layered compounds reported due to both difficulties in their synthesis and in the analysis of their diffraction patterns. There are only three systems involving alloying of constituents using the MER approach reported, including that of $(\text{SnSe})_{1+\delta}(\text{Ta}_x\text{V}_{1-x})\text{Se}_2$ reported here. The synthesis and properties of $[(\text{TiTe}_2)_{1+\delta}]_x[(\text{Bi}_{2-x}\text{Sb}_x)_2\text{Te}_3]_y$ alloys was reported by Mortensen *et al*, [98] the rock salt constituent was alloyed in $([\text{Pb}_x\text{Sn}_{1-x}]\text{Se})_z\text{TiSe}_2$, [99] and the transition metal constituent was alloyed in $(\text{SnSe})_z(\text{Nb}_x\text{Mo}_{1-x})\text{Se}_2$. [37]

ORDERED ABCB ALLOYS

Ordered $\text{A}_m\text{B}_n\text{C}_p$ or more complex sequences of three compounds, such as $\text{A}_m\text{B}_n\text{C}_p\text{B}_q$, where A, B and C are compounds containing three compositionally different constituents, three structurally different constituents or a mix of these can be prepared expanding the calibration procedure described above. If the calibrated deposition parameters for two component

systems containing the constituents are known, the process is straight forward. The desired atomic ratios of the relative layers are based on known or estimated misfit parameters derived from the structures of the constituents. The first step in the calibration is to prepare a sequence of samples with varying amount of the third component while holding the known parameters for the two component system fixed. Interpolating the resulting curve enables the deposition parameters that yield the correct overall stoichiometry to be determined as shown in Figure 18 for the $[(\text{SnSe})_{1+\delta}]_m(\text{NbSe}_2)_n[(\text{MoSe}_2)_n]_{1.06}$ system. A second step of scaling of all layers simultaneously may be required to ensure appropriate thickness of the precursor. This is not usually necessary, however, as the calibration of the simpler systems is usually accurate enough to produce the desired precursors. If the disordered alloys have already been made by sequential deposition, as in the case of $(\text{SnSe})_{1+\delta}(\text{Ta}_x\text{V}_{1-x})\text{Se}_2$ described above, then the deposition times giving the appropriate metal ratios are already known and can be used for the disordered alloys.

Figure 18: A graph of the Mo to Nb ratio as a function of the time the Mo shutter was open while the Nb shutter time was held constant. The dotted green line describes the misfit between the NbSe_2 and the MoSe_2 constituents and the intercept with the experimental line provides the time the Mo shutter needs to be held open to achieve this composition.

The formation of an ordered alloy can be seen from the additional 00/ reflections in the specular diffraction pattern due to the increased size of the unit cell. Figure 19 compares the specular diffraction patterns of the $(\text{SnSe})_{1+\delta}(\text{Ta}_{0.5}\text{V}_{0.5})\text{Se}_2$ random alloy and the ordered compound $(\text{SnSe})_{1+\delta}(\text{VSe}_2)_{1+\gamma}(\text{SnSe})_{1+\delta}\text{TaSe}_2$. A total of 80 layers were used for the compounds, 40 repeat units for the A(B,C) random alloys and 20 repeat units for the ABAC alloys, making both films approximately 50nm thick. A doubling of the unit cell compared to the $(\text{SnSe})_{1+\delta}(\text{Ta}_{0.5}\text{V}_{0.5})\text{Se}_2$ is indicative of the formation of an ordered $\text{A}_m\text{B}_n\text{C}_p\text{B}_q$ alloy with the general formula of $(\text{SnSe})_{1+\delta}[(\text{Ta}_x\text{V}_{1-x})\text{Se}_2]_{1+\gamma}(\text{SnSe})_{1+\delta}[(\text{V}_y\text{Ta}_{1-y})\text{Se}_2]_1$ where the degree of intermixing of the dichalcogenide layers must be determined before the formula for the new compound is known.

Figure 19: A comparison of the diffraction patterns of $(\text{SnSe})_{1+\delta}(\text{Ta}_{0.5}\text{V}_{0.5})\text{Se}_2$ and $(\text{SnSe})_{1+\delta}(\text{VSe}_2)_{1+\gamma}(\text{SnSe})_{1+\delta}\text{TaSe}_2$ formed at 400°C . The doubling of the number of reflections results from a doubling of the c -axis lattice parameter.

The extent of intermixing between the dichalcogenide layers is difficult to determine experimentally. One estimate of the extent of intermixing can be obtained from the in-plane lattice parameters of the constituents. Figure 20 contains the in-plane X-ray diffraction pattern of the nominally $(\text{SnSe})_{1+\delta}(\text{VSe}_2)_{1+\gamma}(\text{SnSe})_{1+\delta}\text{TaSe}_2$ compound. The splitting of the dichalcogenide peaks, which would be expected for pure VSe_2 and TaSe_2 constituents, is not observed. This suggests that the mixing is significant, larger than 20% from the linewidths of the reflections and the change in the lattice parameters of the $(\text{SnSe})_{1+\delta}(\text{Ta}_x\text{V}_{1-x})\text{Se}_2$ alloys discussed earlier.

Figure 20: In-plane diffraction of the nominally $(\text{SnSe})_{1+\delta}(\text{VSe}_2)_{1+\gamma}(\text{SnSe})_{1+\delta}\text{TaSe}_2$ compound (green) to determine the extent of intermixing. The indices of the $(hk0)$ reflections are given above the top diffraction scan, with those in bold the indices for SnSe reflections and those in italic for the dichalcogenide constituents. The pattern of the of $(\text{SnSe})_{1+\delta}(\text{Ta}_{0.5}\text{V}_{0.5})\text{Se}_2$ (blue) is provided for comparison.

To obtain additional information on the structure, HAADF-STEM images were collected and shown in Figure 21. The structure consists of alternating layers of a dichalcogenide and rock salt

structure in distinct parallel layers. Multiple orientations of each constituent can be seen due to the turbostratic disorder between layers. The coordination of the dichalcogenide atoms in both layers is octahedral, which agrees with what would be expected if the TaSe_2 layer contains at least 20% vanadium. If there was no alloying between the layers, the TaSe_2 layer would be expected to have trigonal prismatic coordination. An intensity difference would be expected between the VSe_2 and TaSe_2 layers due to the difference between the atomic numbers of the transition metals, but only a small intensity difference is observed. This, combined with the observed octahedral coordination and the X-ray diffraction results indicates significant intermixing of the dichalcogenide layers. The data suggests that a more accurate representation of the nominally $(\text{SnSe})_{1+\delta}(\text{VSe}_2)_{1+\gamma}(\text{SnSe})_{1+\delta}\text{TaSe}_2$ compound is $[(\text{SnSe})_{1.15}]_1[(\text{Ta}_x\text{V}_{1-x})\text{Se}_2]_1[(\text{SnSe})_{1.15}]_1[(\text{V}_y\text{Ta}_{1-y})\text{Se}_2]_1$ to account for intermixing and alloying of the dichalcogenide layers.

Figure 21: High Resolution HAADF STEM image of the nominal $(\text{SnSe})_{1+\delta}(\text{VSe}_2)_{1+\gamma}(\text{SnSe})_{1+\delta}\text{TaSe}_2$ compound shows the local structure. The different zone axes in different layers result from rotational disorder which is typical for layered compounds prepared using the MER technique.

A more direct measure of the distribution of the V and Ta atoms between the dichalcogenide layers was obtained via EDX maps of the $[(\text{SnSe})_{1.15}[(\text{Ta}_x\text{V}_{1-x})\text{Se}_2]_1(\text{SnSe})_{1.15}[(\text{V}_y\text{Ta}_{1-y})\text{Se}_2]_1]$ compound, which are shown in Figure 22. The EDX images show alternating regions of brighter and lesser intensity for the V and Ta regions indicating Ta-rich and V-rich dichalcogenide regions, which is consistent with the specular diffraction data.

Figure 22: EDX maps of a region the $[(\text{SnSe})_{1.15}]_1[(\text{Ta}_x\text{V}_{1-x})\text{Se}_2]_1[(\text{SnSe})_{1.15}]_1[(\text{V}_y\text{Ta}_{1-y})\text{Se}_2]_1$ compound. The data is consistent with the HAADF STEM images, with alternating layers of SnSe and the transition metal dichalcogenide. The vanadium and tantalum intensities oscillate out of phase with one another, suggesting alternating layers of a tantalum rich and a vanadium rich dichalcogenide.

EDX line scans (Figure 23) of $[(\text{SnSe})_{1.15}]_1[(\text{Ta}_x\text{V}_{1-x})\text{Se}_2]_1[(\text{SnSe})_{1.15}]_1[(\text{V}_y\text{Ta}_{1-y})\text{Se}_2]_1$ allow the extent of interdiffusion to be estimated. If x is equal to y , then the ratio of the areas of the V peaks in the V-rich layer and the Ta peak areas. With this assumption, x can be calculated from the V peak area in the V rich layer divided by the sum of the areas of the V peaks in both layers. The same calculation can be done using the Ta signal, giving an estimate of the error and the validity of the assumption. Calculating the areas of the peaks using Gaussian fits, a value for x of 0.68(5) was obtained. The relatively large uncertainty comes from the difficulty of choosing a value for the background signal for both of the EDX energies. The quantification is consistent with estimates from the other approaches discussed above.

Figure 23: EDX line scans of $[(\text{SnSe})_{1.15}]_1[(\text{Ta}_x\text{V}_{1-x})\text{Se}_2]_1[(\text{SnSe})_{1.15}]_1[(\text{V}_y\text{Ta}_{1-y})\text{Se}_2]_1$ compound. The out of phase oscillation of the Ta and V layers indicates alternating V and Ta rich dichalcogenide layers.

The data collected on the $[(\text{SnSe})_{1.15}]_1[(\text{Ta}_x\text{V}_{1-x})\text{Se}_2]_1[(\text{SnSe})_{1.15}]_1[(\text{V}_y\text{Ta}_{1-y})\text{Se}_2]_1$ compound illustrates the challenges in limiting the interdiffusion of layers during the self-assembly of the MER precursor into the targeted compound. This case was chosen as a "worst case" scenario, with two metals that form a complete solid solution as dichalcogenides and only a single bilayer of SnSe separating the two of them. One would anticipate a reduction in the amount of mixing of the layers as a result of separating the constituents by thicker rock salt layers and by reducing either the time or temperature of the annealing required to self-assemble the product from the precursor. Changing the identity of the rock salt buffer layer might also reduce the amount of interdiffusion. Choosing components that are less miscible or using three different structural elements would be additional approaches to limit the amount of mixing. More knowledge of the mechanism of the transformation of the precursor to the final product would be useful to identify approaches to better control the final compositions of the constituent layers.

Electrical Properties:

Adding complexity to the structure of the layered compounds provides an additional avenue to control properties. Figure 24a contains electrical resistivity data for the six $(\text{SnSe})_{1+\delta}(\text{Ta}_x\text{V}_{1-x})\text{Se}_2$ alloys prepared in this investigation. The absolute values of the room temperature resistivity is that expected for a metal, agreeing with prior reports of the analogous dichalcogenide alloys reported by DiSalvo, *et al.*[29], but the magnitude of the resistivity is higher due to the interfaces and SnSe bilayer which would not be expected to contribute significantly to the conductivity.[100] Figure 24b plots room temperature resistivity vs. x which has a linear relationship up to $x = 0.85$. The resistivity of the $x = 1$ compound is smaller than expected from the extrapolation of this trend, due to the change in coordination of the dichalcogenide from octahedral to trigonal prismatic in the pure TaSe_2 end member. The temperature dependent resistivity measurements show a suppression of the charge density wave phenomenon previously reported for $(\text{SnSe})_{1.15}\text{VSe}_2$ at doping levels above $x = 0.12$. This is in agreement with previously reported findings for the $(\text{Ta}_x\text{V}_{1-x})\text{Se}_2$ transition metal dichalcogenide alloys.[29] The general increase in the resistivity at lower temperatures apparent in the alloys reported here was also observed in the TMD alloys. Temperature dependent Hall coefficient measurements, shown in Figure 21c, suggest complex behavior. The charge density wave in $(\text{SnSe})_{1.15}\text{VSe}_2$ is clearly evident with an abrupt increase in the Hall coefficient for this compound. The suppression of the charge density wave with substitution of Ta for V results in essentially temperature independent Hall coefficients for all of the other compounds except the alloy with 0.49. This compound shows a change in the sign of the Hall coefficient changing at 134 K and a continuously decreasing Hall coefficient. Additional studies will be required to understand the complex behavior of this alloy.

Figure 24: Electrical transport properties of the $(\text{SnSe})_{1+\delta}(\text{Ta}_x\text{V}_{1-x})\text{Se}_2$ compounds as a function of x . a) Temperature dependent resistivity. b) Room temperature resistivity as a function of x . c) Temperature dependent Hall coefficient.

Figure 25 contains the temperature dependence of the electrical resistivity of the ordered alloy with the targeted composition $(\text{SnSe})_{1.15}\text{VSe}_2$ along with that measured for $(\text{SnSe})_{1.15}\text{VSe}_2$, $(\text{SnSe})_{1.15}\text{TaSe}_2$ and $(\text{SnSe})_{1.15}[(\text{Ta}_{0.5}\text{V}_{0.5})\text{Se}_2]$. The ordered alloy has a slightly higher resistivity than that of the disordered alloy and a similar temperature dependence, consistent with the extensive Interdiffusion of the dichalcogenide constituents discussed earlier. The sharp change in resistivity at low temperature, attributed to a charge density wave in $\text{SeSe}_{1.15}\text{VSe}_2$ is not present in the ordered alloy. Using the compositional results of the EDX scans, both the magnitude and temperature dependence can be modeled by $(\text{SnSe})_{1.15}[(\text{Ta}_{0.7}\text{V}_{0.3})\text{Se}_2]$ and $(\text{SnSe})_{1.15}[(\text{Ta}_{0.3}\text{V}_{0.7})\text{Se}_2]$ layers in parallel.

Figure 25: Temperature dependent resistivity of the $(\text{SnSe})_{1.15}[(\text{Ta}_{0.3}\text{V}_{0.7})\text{Se}_2]_1[(\text{SnSe})_{1.15}[(\text{V}_{0.3}\text{Ta}_{0.7})\text{Se}_2]_1$ compound and the related compounds $(\text{SnSe})_{1.15}\text{VSe}_2$, $(\text{SnSe})_{1.15}\text{TaSe}_2$ and $(\text{SnSe})_{1.15}[(\text{Ta}_{0.5}\text{V}_{0.5})\text{Se}_2]$.

SUMMARY AND CONCLUSIONS

This manuscript summarizes the current status of the MER synthetic approach. Accessing a homogeneous amorphous state via low temperature annealing of a nanolayered precursor enables metastable compounds to preferentially nucleate, controlled by the composition of the amorphous intermediate. Self-assembly of more complex designed precursors through MER provides a method to systematically design materials with designed nanoarchitecture. Once a targeted intergrowth compound is prepared, additional related compounds with different constituent layer thicknesses and/or different layering sequences can be synthesized simply by changing the layering scheme in the precursor. This permits structure-function relationships to be systematically tested, as over 20,000 compounds, including structural isomers, can be prepared with each pair of constituents when the thicknesses of the constituents is ten repeat units or less. Adding additional constituents to make more complex systems is straightforward since the synthesis of simpler systems serves as a starting point for the necessary calibrations. The ability to use three or more different components greatly expands the potential complexity

of the compounds prepared. For an intergrowth of three or more constituents, the number of additional compounds that can be formed by varying the layer sequence is extremely large.

There is much to understand about the structure of the defined thickness constituent layers and how the layers interact electronically with one another. These interactions will control thermal, electronic and magnetic properties. The ability to anticipate the structure of so many potential compounds provides an opportunity for theory to predict both new properties and the nanoarchitectures where optimal performance will be observed. The ability to scale this approach to prepare films over large areas on a variety of substrates will facilitate the development of devices to exploit unique or exceptional properties that are discovered.

ACKNOWLEDGEMENT

We acknowledge support from the National Science Foundation under grant DMR-1266217. We also acknowledge support through the Collaborative Access Team (CAT): Pooled Resources for Electron Microscopy Informatics, Education and Research (PREMIER) Network Program at Pacific Northwest National Laboratory (PNNL) and the Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by DOE's Office of Biological and Environmental Research at PNNL. PNNL is a multiprogram national laboratory operated by Battelle for DOE under Contract DE-AC05-76RL01830.

References

- ¹ H. Schäfer. *Angew. Chem. Int. Edit.* 10 (1971) 43-50.
- ² H. Schäfer. *Chemical Transport Reactions. Academic Press, New York*, (1964).
- ³ T. J. McCarthy, M. G. Kanatzidis, *Inorg. Chem.* 34(5) (1995) 1257-1267.
- ⁴ M. G. Kanatzidis. *Curr. Opin. Solid State and Mater. Sci.* 2.2, (1997) 139.149.
- ⁵ J. R. Arthur, J. J. LePore, *J. Vac. Sci. Technol.* 6 (1969) 545.
- ⁶ J. R. Arthur, *J. Appl. Phys.* 39 (1968) 4032.
- ⁷ A.Y. Cho, F.K. Reinhart, *J. Appl. Phys.* 45 (1974) 1812.
- ⁸ A.Y. Cho, *Appl. Phys. Lett.* 19 (1971) 467.
- ⁹ A.Y. Cho, *J. Appl. Phys.* 42 (1971) 2074.
- ¹⁰ A. Y. Cho, J. R. Arthur, *Prog. Solid State Chem.* 10 (1975) 157-91. Review Article
- ¹¹ R. Dingle, H. L. Störmer, A. C. Gossard, W. Wiegmann, *App. Phys. Lett.* 33(7) (1978), 665-667.
- ¹² H. L. Störmer, D. C. Tsui, A. C. Gossard, J. C. M. Hwang, *Physica B*, 117-118(2) (1983) 688-690.
- ¹³ D.C. Tsui, H.L. Störmer, A.C. Gossard, *Phys. Rev Lett.* 48, (1982) 1559.
- ¹⁴ Y. Yu, C. Li, Y. Liu, L. Su, Y. Zhang, L. Cao, *Scientific reports*, 3, (2013) 1866, DOI: 10.1038/srep01866 .
- ¹⁵ K. M. McCreary, A. T. Hanbicki, J. T. Robinson, E. Cobas, J. C. Culbertson, A. L. Friedman, G. G. Jernigan, B. T. Jonker, *Adv. Func. Mater.* 24(41) (2014) 6449-6454.
- ¹⁶ S. J. Yun, S. H. Chae, H. Kim, J. C. Park, J.H. Park, G. H. Han, J. S. Lee, S. M. Kim, H. M. Oh, J.Seok, *ACS Nano*, 9(5) (2015) 5510-5519.
- ¹⁷ Y. Zhang, Y. Zhang, Q. Ji, J. Ju, H. Yuan, J. Shi, T. Gao, D. Ma, M. Liu, Y. Chen, *ACS Nano*, 7(10), (2013) 8963-8971.
- ¹⁸ A. Fleurence, R. Friedlein, T. Ozaki, H. Kawai, Y. Wang, Y. Yamada-Takamura, *Phys. Rev. Lett.* 108 (2012) 245501
- ¹⁹ L. Meng, Y. Wang, L. Zhang, S. Du, R. Wu, L. Li, Y. Zhang, G. Li, H. Zhou, W. A. Hofer H. Gao, *Nano Lett.* 13 (2013) (2) 685-690.
- ²⁰ D. Chiappe E. Scalise, E. Cinquanta, C. Grazianetti, B. V. D. Broek, M. Fanciulli, M. Houssa, A. Molle, *Adv. Mater.* 24 (2014) 2096-2101.
- ²¹ M. Zhang, Y. Zhu, X. Wang, Q. Feng, S. Qiao, W. Wen, Y. Chen, M. Cui, J. Zhang, C. Cai, *J. Am. Chem. Soc.* 137(22), (2015) 7051-7054.
- ²² L. A. Ponomarenko, A. K. Geim, A. A. Zhukov, R. Jalil, S. V. Morozov, K. S. Novoselov, I. V. Grigorieva, E. H. Hill, V. V. Cheianov, V. I. Fal'ko, K. Watanabe, T. Taniguchi, R. V. Gorbachev, *Nature Phys.* 7 (2011) 958-961.
- ²³ C. Dean, A. F. Young, L. Wang, I. Meric. G.-H. Lee, K. Watanabe, T. Taniguchi, K. Shepard, P. Kim, J. Hone. *J. Solid State Comm.* 152 (2012) 1275-1282.

- ²⁴ J. Yoon, W. Park, G.-Y. Bae, Y. Kim, H. S. Jang, Y. Hyun, S. K. Lim, Y. H. Kahng, W. -K. Hong, B. H. Lee, H. C. Ko, *Small*, 9 (2013) 3295–3300.
- ²⁵ T. Roy, M. Tosun, J. S. Kang, A. B. Sachid, S. B. Desai, M. Hettick, M. C. C. Hu, A. Javey, *ACS Nano*, 8 (2014) 6259–6264
- ²⁶ M. S. Choi, G. -H. Lee, Y. -J. Yu, D. -Y. Lee, S. H. Lee, P. Kim, J. Hone, W. J. Yoo, *Nat. Commun.* 4, (2013) 1624.
- ²⁷ X. Hong, J. Kim, S. -F. Shi, Y. Zhang, C. Jin, Y. Sun, S. Tongay, J. Wu, Y. Zhang, F. Wang, *Nat. Nanotechnol.* 9, (2014) 682–686.
- ²⁸ A. K. Geim, I. V. Grigorieva, *Nature*, 499, (2013) 419-425.
- ²⁹ F. J. Di Salvo, J. A. Wilson, B. G. Bagley, J. V. Waszczak, *Phys. Rev. B*, 12, 6, (1975), 2220-2236.
- ³⁰ T. Novet, D. C. Johnson, *J. Am. Chem. Soc.* 113 (1991) 3398-3403.
- ³¹ N. Pienack, W. Bensch, *Angew. Chem. Int. Ed.* 50(9) (2011) 2014-2034.
- ³² M. D. Hornbostel, E. J. Hyer, J. P. Thiel, D. C. Johnson, *J. Am. Chem. Soc.* 119 (1997) 2665-2668.
- ³³ M. D. Hornbostel, E. J. Hyer, J. H. Edvalson, D. C. Johnson, *Inorg. Chem.* 36 (1997) 4270-4274.
- ³⁴ S. L. Stuckmeyer, H. Sellinschegg, M. D. Hornbostel, D. C. Johnson, *Chem. Mater.* 10 (4) (1998) 1096-1101.
- ³⁵ J. R. Williams, D. C. Johnson, *Inorg. Chem.* 41 (2002) 4127-4130.
- ³⁶ M. Esters, M. Alemayehu, Z. Jones, N. T. Nguyen, M. D. Anderson, C. Grosse, S. Fischer, D. C. Johnson, *Angew. Chem.* 54, (2015) 1130–1134. DOI: 10.1002/anie.201409714.
- ³⁷ R. D. Westover, R. A. Atkins, J. Ditto, D. C. Johnson, *Chem. Mater.* 26 (2014) 3443–3449.
- ³⁸ E. J. Cotts, W. J. Meng, W. L. Johnson, *Phys Rev Lett*, 57, (1986) 2295.
- ³⁹ N. T. Nguyen, P. A. Berseth, Q. Lin, C. Chiritescu, D. G. Cahill, A. Mavrokefalos, L. Shi, P. Zschack, M. D. Anderson, I. M. Anderson, D. C. Johnson, *Chem. Mater.* 22, (2010) 2750–2756.
- ⁴⁰ M. D. Hornbostel, E. J. Hyer, J. P. Thiel, D. C. Johnson, *J. Amer. Chem. Soc.* 119, (1997) 2665-2668.
- ⁴¹ J. R. Williams, M. Johnson, D. C. Johnson, *J. Am. Chem. Soc.* 123, (2001) 1645.
- ⁴² J. R. Williams, D. C. Johnson, *Inorg. Chem.* 41, (2002) 4127.
- ⁴³ A. L. E. Smally, M. L. Jespersen, D. C. Johnson, *Inorg. Chem.* 43, (2004) 2486.
- ⁴⁴ M. Behrens, R. Kiebach, W. Bensch, *Inorg. Chem.* 45, (2006) 2704.
- ⁴⁵ M. Behrens, J. Tomforde, E. May, R. Kiebach, W. Bensch, D. Häußler, W. Jäger, *J. Solid State Chem.* 179, (2006) 3330.
- ⁴⁶ M. Regus, G. Kuhn, S. Mankovsky, H. Ebert, W. Bensch, *J. Solid State Chem.* 196, (2012) 100.
- ⁴⁷ J. R. Williams, A. L. E. Smalley, H. Sellinschegg, C. Daniels-Hafer, J. Harris, M. B. Johnson and D. C. Johnson, *J. Am. Chem. Soc.* 125(34) (2003) 10335-10341.
- ⁴⁸ M. Noh and D. C. Johnson, *Ang. Chem.* 35 (1996) 2666-2669.
- ⁴⁹ H.-J. Shin, K. Jeong, M. Noh, D. C. Johnson, S. D. Kevan, T. Warwick, *J. App. Phys.* 81 (1997) 7787-7792
- ⁵⁰ H. -J. Shin, K. Jeong, D. C. Johnson, S. D. Kevan, M. Noh, T. Warwick, *J. Kore. Phys. Soc.* 30 (1997) 575-579.
- ⁵¹ M. Noh, G. Elliott, D. C. Johnson, *Chem. Mater.* 12 (2000) 2894 -290.
- ⁵² N. T. Nguyen, B. Howe, J. R. Hash, N. Liebrecht, P. Zschack, D. C. Johnson, *Chem. Mater.* 19(8) (2007) 1923-1930.
- ⁵³ N. T. Nguyen, B. Howe, J. R. Hash, N. Liebrecht, D. C. Johnson, *Adv. Mater.* 18 (2006) 118-122.
- ⁵⁴ F. R. Harris, S. Standridge, D. C. Johnson, *J. Amer. Chem. Soc.* 127(21) (2005) 7843-7848.
- ⁵⁵ F. R. Harris, S. Standridge, C. Feik, D. C. Johnson, *Ange. Chem. Inter. Ed.* 42(43) (2003) 5296-5299.
- ⁵⁶ B. A. Schmid, R. Rostek, C. Mortensen D.C. Johnson, Proc. 24th International Conference on Thermoelectrics, Clemson, USA, June 2005, 255-257.
- ⁵⁷ C. Mortensen, M. Beekman, D. C. Johnson, *Sci. Adv. Mater.* 3 (2011) 639-645.
- ⁵⁸ C. Chiritescu, D. G. Cahill, C. Mortensen, D. Johnson P. Zschack, *J. of App. Phys.* 106 (7) (2009) 073503/1-073503/5.
- ⁵⁹ J.D. König, M. Winkler, S. Buller, W. Bensch, U. Schürmann, L. Kienle, and H. Böttner, *J. Electron. Mater.* 40, (2011) 1266-1270.
- ⁶⁰ J.D. König, H. Böttner, J. Tomforde, W. Bensch, Proc. 26th International Conference on Thermoelectronics, Jeju, South Korea, (2007) p. 395.
- ⁶¹ M. Winkler, X. Liu, J. D. König, L. Kerste, H. Böttner, W. Bensch, L. Kienle, *J. Electron Mater.* 41, 6, (2012) 1322-1331.
- ⁶² R. Atkins, S. Disch, Z. Jones, I. Häusler, C. Grosse, S. F. Fischer, W. Neumann, P. Zschack, D. C. Johnson, *J. Solid State Chem.* 202 (2013) 128-133. DOI: 10.1016/j.jssc.2013.03.008.

- ⁶³ R. Atkins, M. Dolgos, A. Fiedler, C. Grosse, S. F. Fischer, S. P. Rudin, D. C. Johnson, *Chem. Mater.* 26 (2014) 2862–2872. DOI: 10.1021/cm5004774.
- ⁶⁴ M. Falmbigl, A. Fiedler, R. E. Atkins, S. F. Fischer, D. C. Johnson, *Nano Lett.* 15, (2) (2015) 943–948 DOI; 10.1021/nl503708j.
- ⁶⁵ R. Atkins, S. Disch, Z. Jones, I. Haeusler, C. Grosse, S. F. Fischer, W. Neumann, P. Zschack, D. C. Johnson, *J. Solid State Chem.* 202 (2013) 128–133.
- ⁶⁶ M. B. Alemayehu, M. Falmbigl, C. Grosse, K. Ta, S. Fischer, D. C. Johnson, *J. Alloys Compd.* 2015, 619, (2015) 861–868.
- ⁶⁷ M. Alemayehu, M. Falmbigl, K. Ta, S. Bauers, D. C. Johnson, *Chem. Mater.* 27 (2015) 867–875.
- ⁶⁸ M. B. Alemayehu, K. Ta, M. Falmbigl, D. C. Johnson, *Nanoscale*, 7 (2015) 7378–85.
- ⁶⁹ M. B. Alemayehu, K. Ta, M. Falmbigl, D. C. Johnson, *J. Am. Chem. Soc.* 137 (2015) 4831–4839.
- ⁷⁰ M. B. Alemayehu, M. Falmbigl, K. Ta, D. C. Johnson, *Chem. Mater.* 27 (6) (2015) 2158–2164.
- ⁷¹ M. B. Alemayehu, M. Falmbigl, K. Ta, D. C. Johnson, *ACS Nano*. 9 (2015) 4427–4434.
- ⁷² M. Beekman, S. Disch, S. Rouvimov, D. Kasinathan, K. Koepernik, H. Rosner, P. Zschack, W. S. Neumann, D. C. Johnson, *Angew. Chem. Int. Ed.* 52 (2013) 13211–13214.
- ⁷³ N. S. Gunning, J. Feser, M. Beekman, D. G. Cahill, D. C. Johnson, *J. Am. Chem. Soc.* Just Accepted.
- ⁷⁴ M. Ludemann, O. D. Gordan, D. R. T. Zahn, M. Beekman, R. Atkins, D. C. Johnson, *Langmuir* 30(27) (2014) 8209–8214.
- ⁷⁵ N. S. Gunning, J. Feser, M. Falmbigl, M. Beekman, D. G. Cahill, D. C. Johnson, *Semicond. Sci. Technol.* 29 (2014) 124007.
- ⁷⁶ C. Grosse, R. Atkins, H. Kirmse, A. Mogilatenko, W. Neumann, D. C. Johnson, *J. Alloys Compd.* 579 (2013) 507–515.
- ⁷⁷ R. Atkins, J. Wilson, P. Zschack, C. Grosse, W. Neumann, D. C. Johnson, *Chem. Mater.* 24(23) (2012) 4594–4599.
- ⁷⁸ D. R. Merrill, D. B. Moore, S. Bauers, M. Falmbigl, D. C. Johnson, *Materials*, 8 (2015) 2000–2029
- ⁷⁹ D. R. Merrill, D. B. Moore, J. Ditto, D. R. Sutherland, M. Falmbigl, M. Winkler, H. –F. Pernau, D. C. Johnson, *Eur. J. Inorg. Chem.* 2015(1) (2015) 83–91.
- ⁸⁰ D. B. Moore, M. J. Stolt, R. Atkins, L. Sitts, Z. Jones, S. Disch, M. Beekman, D. C. Johnson, *Emerging Materials Research*, 1 (2012) 292–298.
- ⁸¹ S. R. Bauers, D. B. Moore, J. Ditto, D. C. Johnson, Accepted, *J. Alloys and Compounds*.
- ⁸² D. B. Moore, M. Beekman, S. Disch, P. Zschack, I. Hausler, W. Neumann, D. C. Johnson, *Chem. Mater.* 25(12) (2013) 2404–2409.
- ⁸³ M. B. Alemayehu, G. Mitchson, J. Ditto, B. E. Hanken, M. Asta, D. C. Johnson, *Chem. Mater.* 26 (2014) 1859–1866.
- ⁸⁴ M. Esters, M. B. Alemayehu, Z. Jones, N. T. Nguyen, M. D. Anderson, C. Grosse, S. F. Fischer, D. C. Johnson, *Angew. Chem. Int. Ed.* 54(4) (2015) 1130–1134.
- ⁸⁵ M. M. Smeller, C. L. Heideman, Q. Lin, M. D. Anderson, P. Zschack, I. M. Anderson, D. C. Johnson, *Z. Anorg. Allg. Chem.* 638 (2012) 2632–2639.
- ⁸⁶ C. L. Heideman, S. Tepfer, Q. Lin, R. Rostek, P. Zschack, M. D. Anderson, I. M. Anderson, D. C. Johnson, *J. Am. Chem. Soc.* 135(30) (2013) 11055–11062.
- ⁸⁷ C. Heideman, D. C. Johnson, *Semicond. Sci. Technol.* 29 (2014) 064007.
- ⁸⁸ M. D. Anderson, C. L. Heideman, M. Smeller, R. Kykyneshi, A. A. Herzing, I. M. Anderson, D. A. Keszler, P. Zschack, D. C. Johnson, *Ang. Chem. Int. Ed.* 52 (2013) 1–5.
- ⁸⁹ Heideman, C. L.; Rostek, R.; Anderson, M. D.; Herzing, A. A.; Anderson, I. M.; Johnson, D. C., *J. Electron. Mater.* (2010), 39(9), 1476–1481.
- ⁹⁰ C. Heideman, N. Nyugen, J. Hanni, Q. Lin, S. Duncombe, D. C. Johnson and P. Zschack, *J. Solid State Chem.* 181 (2008) 1701–1706
- ⁹¹ A. Mavrokefalos, Q. Lin, M. Beekman, J. H. Seol, Y. J. Lee, H. Kong, M. T. Pettes, D. C. Johnson, L. Shi, *App. Phys. Lett.* 96, (18) (2010) 181908/1–181908/3
- ⁹² Q. Lin, S. Tepfer, C. Heideman, C. Mortensen, N. Nguyen, P. Zschack, M. Beekman, D. C. Johnson, *J. Mater. Res.* 26 (2011) 1866–1871
- ⁹³ Q. Lin, M. Smeller, C. L. Heideman, P. Zschack, M. Koyano, M. D. Anderson, R. Kykyneshi, D. A. Keszler, I. M. Anderson, D. C. Johnson, *Chem. Mater.* 22(3) (2010) 1002–1009
- ⁹⁴ D. R. Merrill, D. B. Moore, M. N. Coffey, A. W. Jansons, M. Falmbigl, D. C. Johnson, *Semicond. Sci. Technol.* 29(6), (2014) 064004/1–064004/6, 6 pp.

- ⁹⁵ C. Heideman, N. Nyugen, J. Hanni, Q. Lin, S. Duncombe, D. C. Johnson, P. Zschack, *J. Solid State Chem.* 181(7) (2008) 1701-1706.
- ⁹⁶ D. B. Moore, M. Beekman, S. Disch, D. C. Johnson, *Angew. Chem. Int. Ed.* 53(22) (2014) 5672-5675.
- ⁹⁷ M. Falmbigl, M. B. Alemayehu, D. R. Merrill, M. Beekman, D. C. Johnson, *Crys. Res. Technol.* 50(6) (2015) 464-472. DOI: 10.1002/crat.201500019
- ⁹⁸ C. Mortensen, M. Beekman, D. C. Johnson, *Sci. Adv. Mater.* 3, (2011) 639-645.
- ⁹⁹ D. R. Merrill, D. R. Sutherland, J. Ditto, S. Bauers, M. Falmbigl, D. L. Medlin, D. C. Johnson, *Chem. Mater.* 27(11) (2015) 4066-4072 10.1021/acs.chemmater.5b01071.
- ¹⁰⁰ G. A. Wiegers, G.A. *Prog. Solid State Chem.* 24, (1996), 24, 1-139.

Modulated Amorphous Precursor

Single Component Systems

or

Two Constituent Families A_nB_m

or

Alloy $(A_xB_{1-x})C$

Three Constituent
ACBC