Self-assembly of designed precursors: A route to crystallographically aligned new materials with controlled nanoarchitecture

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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 $[(SnSe)_{1.15}]_1([Ta_xV_{1-x}]Se_2)_1[(SnSe)_{1.15}]_1([V_yTa_{1-y}]Se_2)_1$ 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 $(SnSe)_{1+\delta}(Ta_xV_{1-x})Se_2$ alloys are observed as x is varied. The electrical resistivity of $[(SnSe)_{1.15}]_1([Ta_xV_{1-x}]Se_2)_1[(SnSe)_{1.15}]_1([V_yTa_{1-y}]Se_2)_1$ can be modeled as the two constituent layers in parallel.

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1. 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

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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 $(SnSe)_{1+\delta}(Ta_xV_{1-x})Se_2$ and the ordered alloy $[(SnSe)_{1.15}]_1([Ta_xV_{1-x}]Se_2)_1[(SnSe)_{1.15}]_1([V_yTa_{1-y}]Se_2)_1$, are is 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 $(Ta_xV_{1-x})Se_2$ 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 $(SnSe)_{1+\delta}(Ta_xV_{1-x})Se_2$ compounds. The resistivity of the ordered alloy can be modeled as the two parent compounds $[(SnSe)_{1.15}]_1([Ta_xV_{1-x}]Se_2)_1$ and $[(SnSe)_{1.15}]_1([V_yTa_{1-y}]Se_2)_1$ in parallel.

2. 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 Fig. 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 then 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].

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
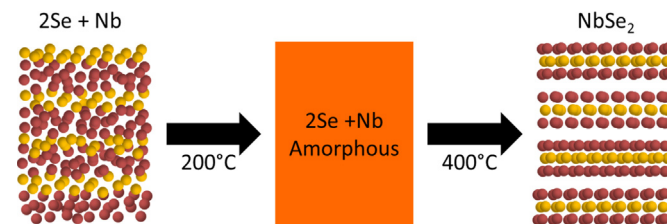

Fig. 1. A schematic of a layered precursor showing the interdiffusion of the layers to form an amorphous intermediate and the subsequent nucleation of the targeted compound.