

Synthesis of and Structure-Function Relationships in Heterostructures Of Quasi-2D Materials

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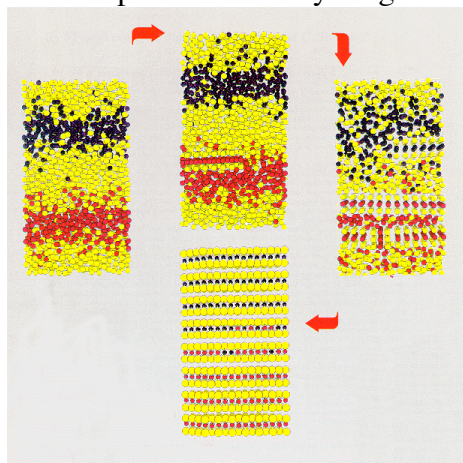
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The artificial layering of different materials often leads to novel phenomena when the layer dimension is comparable to a characteristic length scale of some underlying physical property.¹ In this circumstance, the material can no longer be considered to be composed of independent constituent layers and may possess unique and useful properties. Relevant length scales include the de Broglie wavelength of electrons, the phonon wavelength, the elastic and inelastic mean free path of elementary excitations, the spatial extent of localized wave functions, the dielectric screening length or depletion width in semiconductors, the cyclotron radius of carriers in a magnetic field, and the coherence lengths and domain sizes of ordered magnetic, superconducting, spin- and charge-density-wave-distorted, and ferroelectric phases. These lengths range typically from a few to a few thousand Ångstroms. An interesting length scale has proven to be larger than atomic but smaller than macroscopic dimension, i.e., the so-called mesoscopic length scale. The past 10-15 years have produced a spectacular series of advances in this area, including but not limited to the quantum Hall effect, electrooptic switches based upon quantum confinement of excitonic levels, quantized transport in nanostructures, and perpendicular magnetic anisotropy and giant magnetoresistance in magnetic multilayers. Materials have been fabricated in which phenomena on virtually all of the above length scales have been modified by artificial layering, often leading to interesting results.

Despite this successful activity, the diverse range of possibilities in artificial layering has certainly not been exhaustively studied. For example, while much success has been achieved in growing metals epitaxially on semiconductors, the reverse process has been much more problematic. Thus, the production of epitaxial paramagnetic, ferromagnetic, or superconducting metal/semiconductor superlattices has not been accomplished. Another interesting but relatively poorly achieved possibility is an epitaxial magnetic metal/superconducting metal heterostructure. The primary reason for this lies in the difficulty in growing well-defined epitaxial, crystalline heterostructures using materials having a large entropic and possibly energetic driving force for intermixing. Exploratory research using the standard growth techniques, e.g., molecular beam epitaxy, is both expensive and time consuming. When searching a dense parameter space, including layer spacing, composition, preparation conditions, etc., for interesting material properties, throughput becomes a serious issue. This is true even when a well-defined and theoretically predicted target property is available, as has recently been the case for thermoelectrics.²⁻⁷

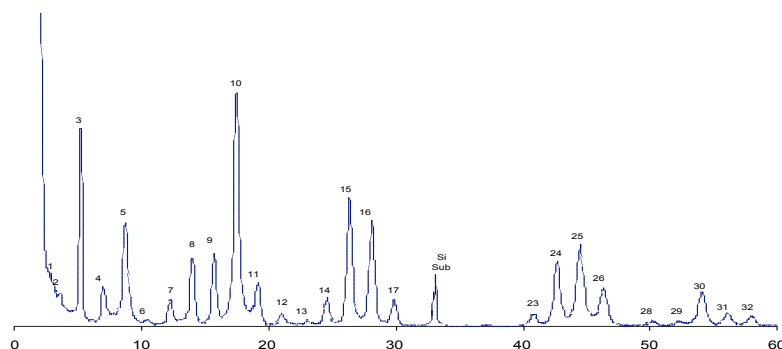
The goal of the research in this proposal is to apply a new synthetic approach based upon kinetic trapping from a designed superlattice reactant to synthesize a wide variety of novel heterostructures and superlattices based upon transition metal dichalcogenide compounds and their 3d transition metal intercalates,⁸⁻¹⁷ to characterize the structure of the resulting superlattices using x-ray diffraction and transition electron microscopy, and then to characterize the physical properties of these new materials with a variety of analytical techniques. The component materials offer a dazzling array of physical properties, including wide and narrow gap semiconductors, semimetals, and normal, magnetic, and superconducting metals. Essentially all exhibit phenomena characterized by mesoscopic length scales, and some of these may be

classified as exotic: anisotropic transport and superconductivity, charge density wave formation, local moments and highly anisotropic magnetic structures, etc. The non-directional van der Waals cohesion between the elementary chalcogenide trilayers ensures that crystalline epitaxial films can be grown even in the presence of large degrees (>20%) of lattice mismatch.¹⁸ These chalcogenide compounds thus provide a wealth of opportunities to observe novel phenomena based upon artificial layering of materials having very different properties.



Our synthesis approach is based on controlling composition and diffusion distances through vapor deposition of a nanolaminated reactant designed to evolve into the desired crystalline product with a designed modulation of two constituents as illustrated on the left. Four systems are currently being investigated: $[(\text{Bi}_2\text{Te}_3)_x(\text{TiTe}_2)_y]_z$, a system with immiscible constituents; $[(\text{TaSe}_5)_x(\text{VSe}_2)_y]_z$, a system with miscible constituents; $[(\text{CrSe}_2)_x(\text{NbSe}_2)_y]_z$, a system with a component stabilized by charge transfer; and $[(\text{NbSe}_2)_x(\text{CeSe})_y]_z$, an extension of known misfit-layered compounds. Initial synthetic efforts indicate that all of these systems can be prepared using this synthetic approach.

The furthest along of these systems synthetically is $(\text{Bi}_2\text{Te}_3)_x(\text{TiTe}_2)_y$, where we have been able to prepare a series of compounds with unit cell control of both x and y . To illustrate the quality of the resulting compounds, the diffraction pattern below is that obtained for the new compound $(\text{Bi}_2\text{Te}_3)_3(\text{TiTe}_2)_3$ (the numbers above the



diffraction maxima refer to the indexing of the observed 001 Bragg reflections). The diffraction patterns of this family of compounds agree with those calculated by using the binary compounds as models. Annealing above 350°C decomposes these compounds into a mixture of their binary constituents.

The $[(\text{TaSe}_5)_x(\text{VSe}_2)_y]_z$ compounds prepared have shown surprising stability with respect to intermixing of the constituents, being stable to interdiffusion below 600°C. Currently we are optimizing the thickness of the elemental layers in the reactants to obtain integral numbers of unit cells of the constituents in each repeating unit. The $[(\text{CrSe}_2)_x(\text{NbSe}_2)_y]_z$ and $[(\text{NbSe}_2)_x(\text{CeSe})_y]_z$ samples made to date show growth of the expected superstructures as a function of annealing. We are currently also optimizing the deposition parameters of these compounds to obtain unit cell control of the superlattice units.

We have begun physical measurements of the properties of these new materials. Initial transport measurements parallel to the layering direction of $[(\text{Bi}_2\text{Te}_3)_x(\text{TiTe}_2)_y]_z$ samples indicate that these materials are either heavily doped semiconductors or semimetals. Transport measurements perpendicular to the layering direction are currently underway. We have been able to prepare a bulk pellets of these $(\text{Bi}_2\text{Te}_3)_x(\text{TiTe}_2)_y$ superlattices and are in the process of measuring thermal conductivity as a function of repeat spacings. This will complement thin film

measurements that indicate that thermal conductivity is reduced in a superlattice relative to that of a random alloy.

These studies will provide a fundamental understanding of solid state reaction kinetics and mechanisms which has many implications both in basic science and technology. The ability to prepare new compounds and superlattices with designed structure will permit structure-function relationships to be understood and tested on a more detailed level than previously possible. Novel and unique properties may be found as modulation lengths are decreased and interfacial properties become more important. Many technologies depend on the ability to prepare thin films of materials with particular properties. The next generation of microelectronic devices will incorporate both new low and high dielectric materials to replace currently used field and gate oxides respectively. Thin film reactions will need to be controlled to prepare thin film silicides for contacts. Understanding and controlling reactions at buried interfaces to yield desired structures will provide important insight into the development of new processing conditions for these new films. Understanding the evolution of properties in nanocomposites as a function of the constituents in and the length scale of the nanocomposite is also significant. Applications from magnetic materials to structural coatings will benefit from the ability to tailor properties via design of nanostructure.

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