DOE Award No. DE-SC0019383 Massachusetts Institute of Technology
Project Title: "Real-time Measurements of Complex Transition Metal Oxide Nanostructure Growth"
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The project, a collaboration between the Ross Lab at MIT and the Filler Lab at Georgia Tech, aimed to combine in situ microscopy and spectroscopy measurements to answer fundamental questions about the physics and chemistry governing the bottom-up vapor-solid-liquid (VLS) growth of one-dimensional (1-D) functional oxides. This work supported one PhD student and 1 postdoc. One paper has been published and 5 others are in preparation. To date, this work has been presented at 5 conferences.

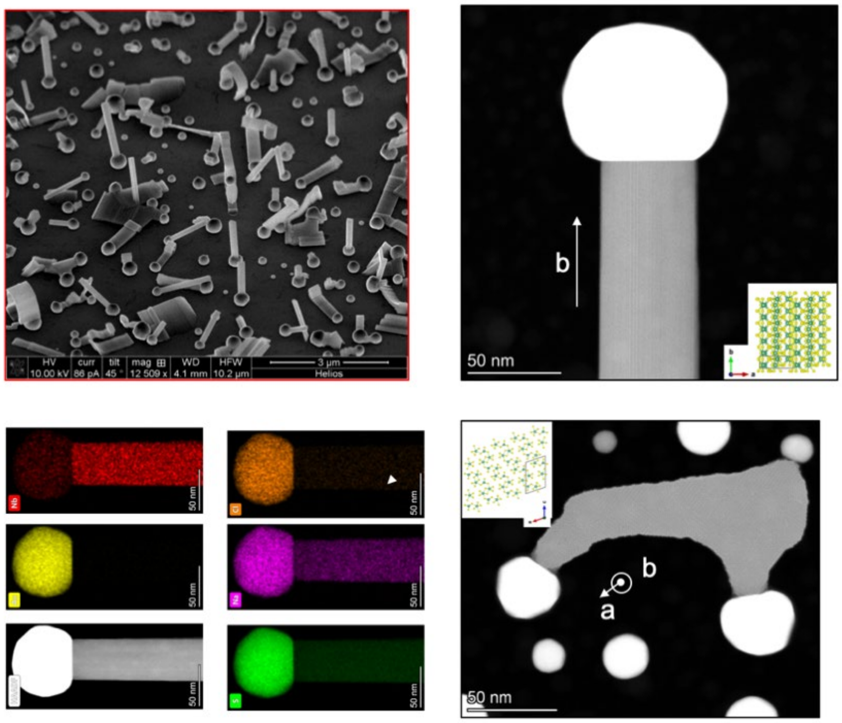
1. One-dimensional twisted and tubular structures of Zinc Oxide by semiconductor-catalyzed vapor–liquid–solid synthesis
Publication: T. Pham, S. Kommandur, H. Lee, D. Zakharov, M. A. Filler, F. M. Ross, Nanotechnology **32** 075603 (2020).

We studied the VLS growth of 1-D zinc oxide (ZnO) nanostructures catalyzed by a semiconductor (Ge). The growth showed two unexpected morphologies: twisted nanowires (NWs) and twisted hollow nanotubes (NTs), in addition to standard solid, straight NWs. While the twisting in the NWs can be explained by the Eshelby twist, the model cannot account for the large twist rate (up to ~ 9 degree/µm) in the hollow NTs. The combination of ex-situ and in-situ TEM (accomplished at MIT and at Brookhaven National Lab) is consistent with a competition between growing and etching processes at the Ge-ZnO interface, resulting in NTs with large hollow core (150-1000 nm diameter). The anomalous rate of twisting in the hollow NTs is attributed to the softening of elastic rigidity in the etch-induced hollow structures. This work shows there remains much to learn about bottom-up growth of oxides, including the ability of unconventional catalysts to generate novel structures.

2. Vapor-liquid-solid growth of transition metal trichalcogenide nanowires

Transition metal trichalcogenides (TMTs) are unusual among 2D materials because of their highly anisotropic electronic, optical, electrical, magnetic, superconductivity, and charge density wave transport properties relevant to applications in transistors, batteries and thermoelectric devices. Their properties derive from a structure composed of one-dimensional chains of metals and chalcogens in layers bonded via weak van der Waals (vdW) forces. Nanostructured forms of TMTs are not well explored due to the difficulty of synthesis and assembly.

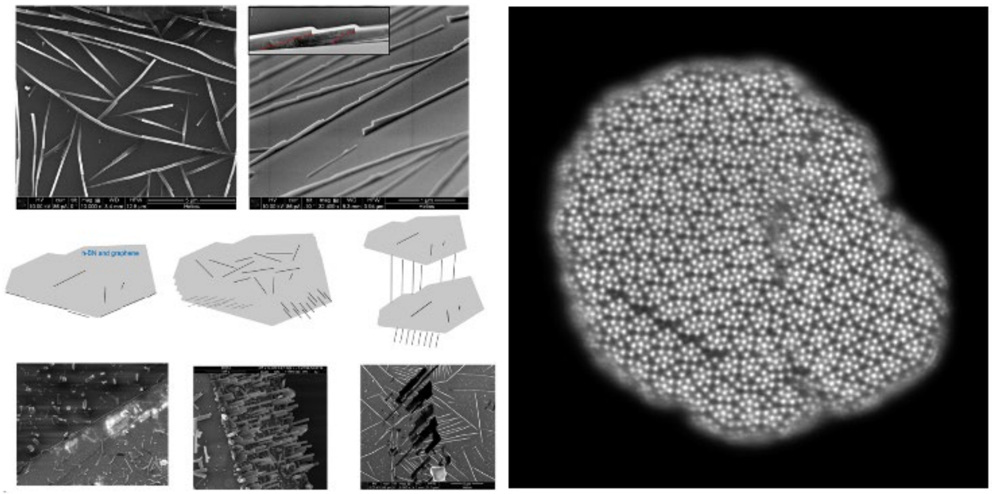
NbS_3 is one of the least studied TMTs, in part because of obstacles in synthesizing the material with a pure phase and controlled composition. In this work, we showed that NbS_3 can be synthesized in nanowire form via the vapor-liquid-solid (VLS) mechanism. We used a catalyst composed of an alloy of a metal (Au) and an alkali metal halide (NaCl). By varying conditions, we obtained distinct 1D morphologies such as wires, ribbons and walls, and two orientations in which the chain direction is parallel and perpendicular to the growth direction. We described the dimension and morphology of nanowires as a function of catalyst volume, growth time, and substrate. We also demonstrated synthesis of other TMTs ($NbSe_3$ and TiS_3) and two-step growth to show the potential of VLS to form heterostructures of 1D layered materials with prospects for tunable properties.



VLS-grown NbS_3 nanowires with mapping showing the elements present in the catalyst and nanowire, and images of two orientations where the b (chain) direction is parallel and perpendicular to the nanowire growth direction.

3. Synthesis and self-assembly of one-dimensional nanostructures of a transition metal trichalcogenide

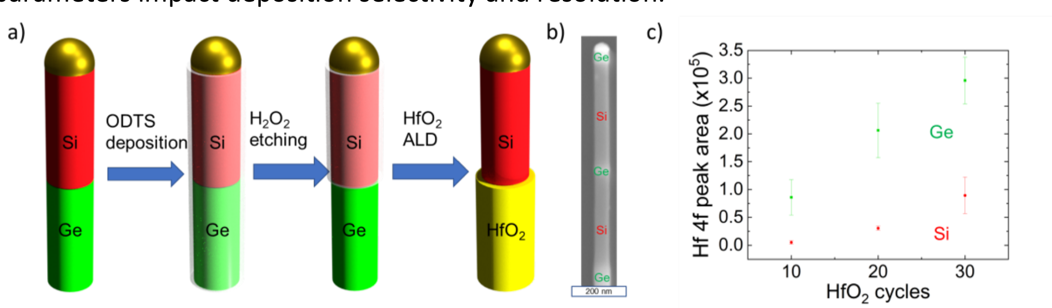
To fully realize applications of transition metal trichalcogenides, it is essential to develop synthesis and assembly techniques that are flexible and responsive to substrate patterning. In this work, we synthesized NbS_3 nanowires on substrates with amorphous or vdW-bonded surfaces via a vapor-solid (VS) mechanism. We first showed how to tune NbS_3 morphology via growth conditions and substrate chemistry. We demonstrated how NbS_3 nanowires can be grown epitaxially on certain vdW subtrates and along the boundary between different substrate materials, such as the step edge between a SiO_2 substrate and a 2D flake of h-BN or graphene. We also described an unusual synergistic growth mechanism in which chains of NbS_3 nanowire segments self-assemble to form sawtooth structures as long as tens of micrometers. These structures nucleated at step edges and grew to connect patterned contact areas consisting of 2D flakes. These growth mechanisms provide pathways towards integrating mixed-dimensional layered materials to build complex structures for quantum electronics and other applications.



(left) VS-grown NbS_3 nanowires in elongated chains with a sawtooth height profile, grown on an amorphous substrate and off the edge of a predeposited flake of a 2D material. (right) the structure of a VS-grown nanowire along the b (chain) direction.

4. Bottom-up nanopatterning of silicon/silicon-germanium heterostructure nanowires

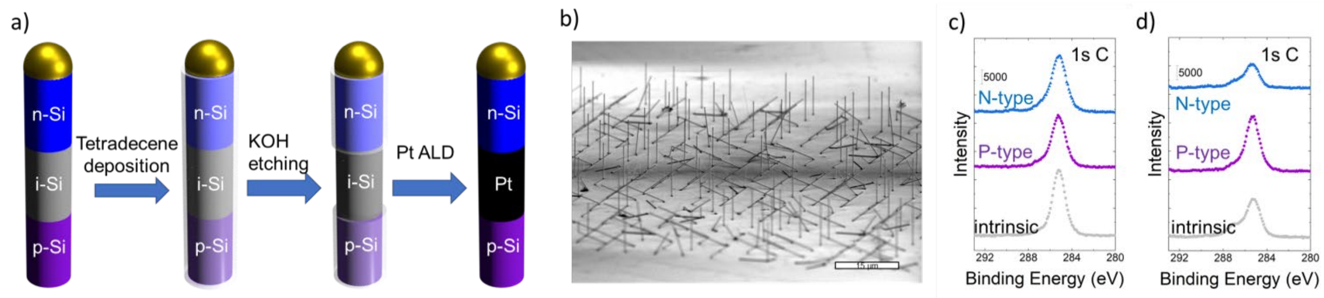
A long-standing challenge in nanoscience is the ability to bottom-up pattern the surfaces of nanoscale objects with nanoscale precision. Such a capability is crucial for building hierarchical materials or functional devices. To this end, we showed how to use self-assembled monolayers (SAMs) on Si and Ge surfaces as masks for directing the deposition of metal oxide films. Briefly, an octadecyltrichlorosilane (ODTS) monolayer is first applied to the entire surface. ODTS is then removed from only the SiGe regions, whose high Ge composition makes it susceptible to H_2O_2 etching. The ODTS remains on the Si regions and blocks the atomic layer deposition (ALD) of metal oxides such as HfO_2. We demonstrated the viability of this approach on planar substrates and Si-Ge nanowires as well as explored how different parameters impact deposition selectivity and resolution.



a) Overview of the nanopatterning process. b) SEM image of Si/SiGe heterostructure nanowires. c) Hf 4f XPS signal intensity on Si and Ge planar substrates for a 200°C HfO_2 deposition

5. Area selective metal deposition on dopant-modulated nanowires

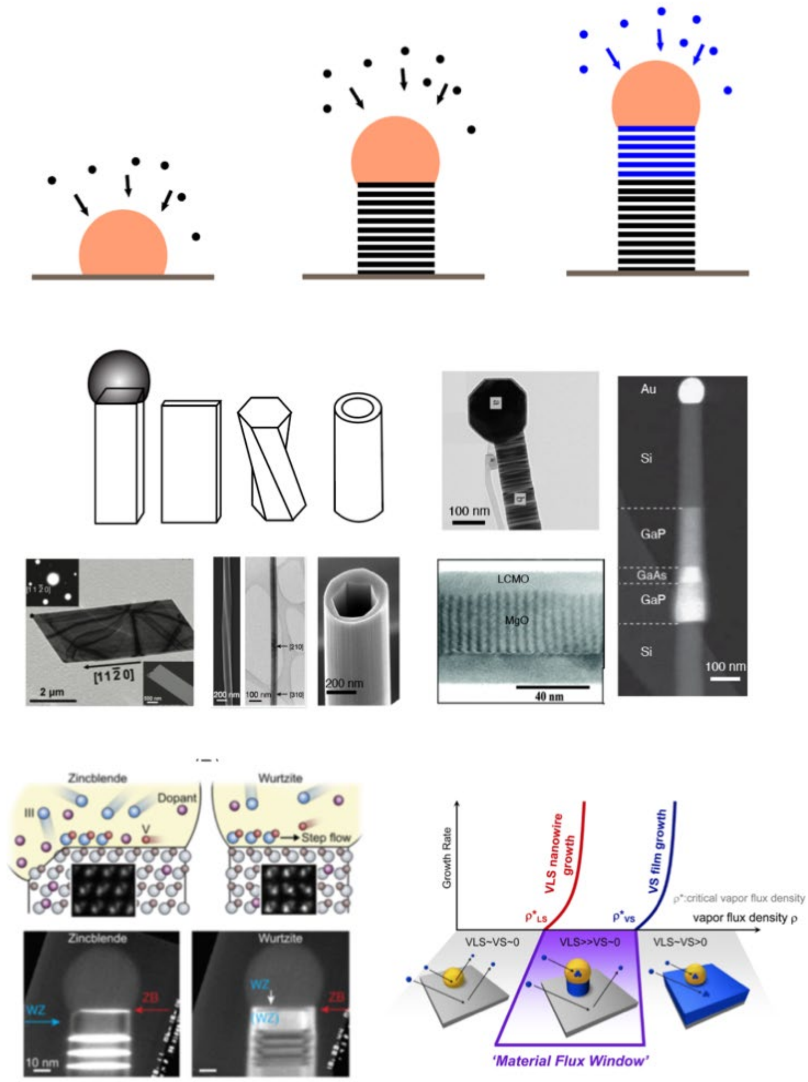
Selective metal deposition is useful for forming novel heterostructures or contacts to functional devices. We expanded the utility of the above described nanopatterning method to include metals. Dopant-modulated Si substrates and nanowires were used as a technologically relevant model substrate. A tetradecane SAM was applied to the entire surface and then removed only from the nominally intrinsic and n-type regions via KOH. The SAM was retained on p-type Si surfaces and can serve as a mask for metal deposition. Alloying of co-axial metal films with the underlying silicon to form silicide is being studied as a function of segment dimensions, film thickness, and annealing temperature. Such experiments hold promise for improving our understanding of alloying in confined regions on nanostructures and for making electrical contacts.



a) Overview of the process for selective metal deposition. b) SEM image of an array containing dopant-modulated Si nanowires. c) 1s C XPS of intrinsic, p-type and n-type substrates after a 3 hr tetradecene application. d) 1s C XPS of intrinsic, p-type and n-type substrates after a KOH etch showing retention of the SAM primarily on the p-type surface.

6. Growth mechanism and heterostructures of unconventional nanowires

A broad range of studies has established growth of group IV and III-IV nanowires using the VLS mechanism. But the same level of control over morphology, crystal phase and compositional modulation has not been developed in nanowires based on other classes of materials including oxides, carbides and chalcogenides, despite a range of predicted properties and applications. To this end, we completed an investigation of the literature of unconventional nanowire synthesis. We categorized the type of growth observed thus far, outlined possible reasons underlying the challenges with deterministic synthesis, and suggested approaches to close the gap. We anticipate that this literature review will serve as a guideline for deterministic synthesis and integration of complex one-dimensional nanomaterials.



The VLS growth mechanism; the range of morphologies that can be produced; control over heterostructures, crystal phase and morphology.