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Understanding nanomaterial synthesis with *in situ* transmission electron microscopy

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The vapor-liquid-solid (VLS) nanowire growth technique is a synthesis method widely used to grow high-quality, single-crystalline semiconductor nanowires [1-3]. First introduced in 1964 by Wagner and Ellis to grow silicon nanowires, this method has evolved to utilize many different metal catalyst materials to grow a wide variety of inorganic nanowires with facile control of diameter, length, and dopant concentration [1,4]. These inorganic nanowires have many applications, such as for Li-ion battery electrodes, gas sensors, and solar cell components [5-7]. While VLS is a ubiquitous growth method, understanding of the growth kinetics is limited, especially for binary and ternary crystal systems. Theoretical predictions suggest that the growth of such nanowires is governed by steady-state kinetics, and that the crystal chemistry of the reverse process may be different from that which governs the nanowire growth [8]. The use of *in situ* techniques has advanced the understanding of the VLS process and the kinetics of VLS growth [9]. By use of heating in a transmission electron microscope (TEM), we have developed a method to observe the Au-catalyzed VLS growth of metal oxide nanowires occurring *in reverse*; this nanowire dissolution is dubbed the solid-liquid-vapor (SLV) process.

All nanowires used in this study were grown *via* VLS synthesis using gold metal as the catalyst material. The as-grown nanowires were analyzed by powder x-diffraction (XRD) to determine crystal structure. The nanowires were then dispersed in high-quality methanol, and dropcast onto Protochips thermal E-chips for heating in the TEM. Nanowires of like-composition were heated using a consistent heating profile. Due to the ultrafast heating and cooling capabilities of the Protochips *in situ* TEM holder, nanowire dissolution can be quenched periodically throughout the SLV process in order to track the material content of the Au catalyst particle using energy dispersive x-ray spectroscopy (EDS), as the nanowire dissolves at the solid-liquid interface and evaporates at the liquid-vapor interface. High-resolution imaging is used to determine nanowire growth direction and its role in SLV dissolution.

This method of observing the reverse of the nanowire growth process should provide an experimental platform to explore features relevant to the VLS growth mechanism, such as saturation concentration of a reactant within a VLS catalyst droplet and the use of VLS catalyst metals for controlled etching of semiconducting materials. In addition, the use of *in situ* heating offers the ability to study nanowire heterostructure formation, such as evolution from a homogeneous nanowire to core-shell or peapod type nanowire. In the absence of advanced *in situ* TEM techniques, these processes would likely remain unstudied [10].

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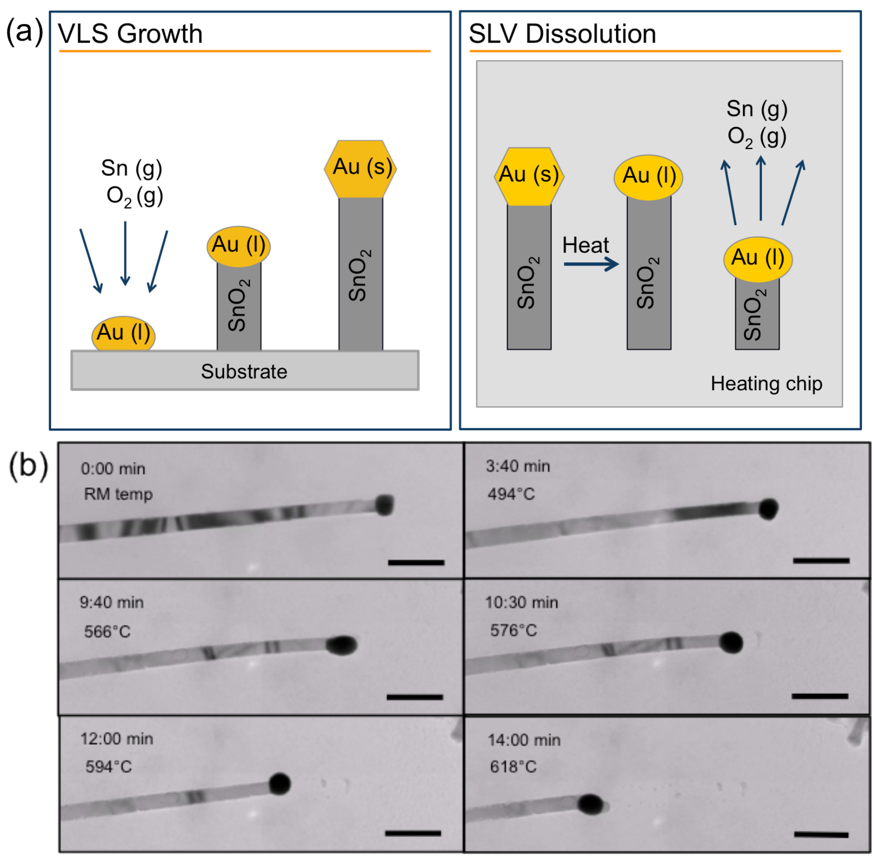

Figure 1. (a) Cartoon showing the relation between VLS nanowire growth and SLV dissolution of a SnO_2 nanowire. (b) Snapshots from a movie recorded during heating of a SnO_2 nanowire showing dissolution occurring at elevated temperature. Scale bar equals 0.2 µm.