

## Using *In situ* Gas Heating TEM to Investigate Compound Nanowire Growth Mechanisms

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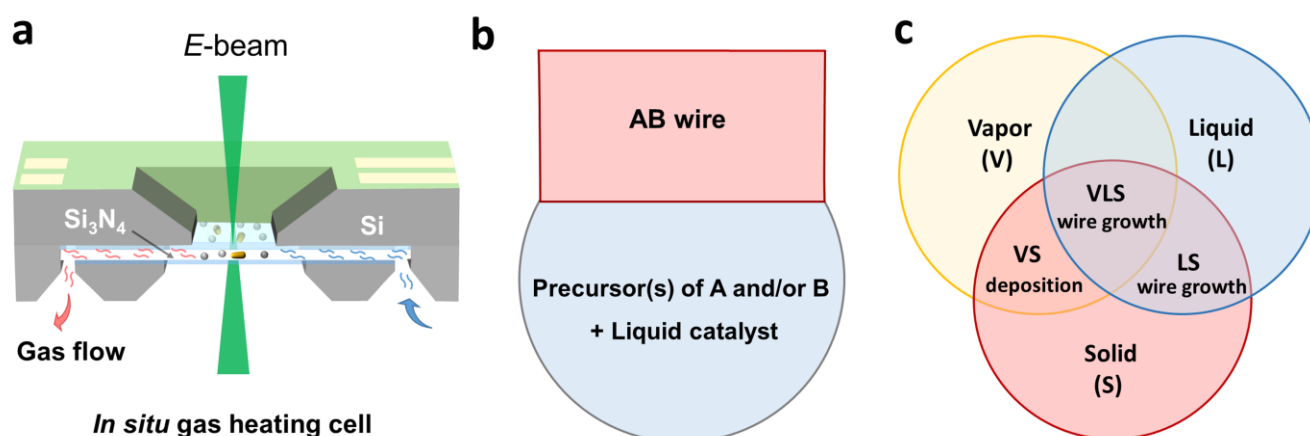
Vapor-liquid-solid (VLS) growth mechanism for nanowires has been extensively investigated. During VLS growth, vapor precursors are concentrated by a catalytic liquid droplet, allowing a solid crystalline nanowire to subsequently grow at the liquid-solid interface (L<sub>S</sub>) [1]. Nanowire VLS growth is generally considered to proceed by a mono-nuclear layer-by-layer process, during which one nucleation event occurs at VLS triple interface per added growth layer [2]. Recent advances in *in situ* transmission electron microscope (TEM) techniques have allowed atomic scale studies of the VLS growth process and provided insights into the heterogeneous interface structure [3] and interface kinetics [4]. Although investigations into growing nanowire structures have made great progress in controlling diameter [5], morphology [6], growth direction [7], and heterojunctions [3], the complete growth mechanism is not yet fully understood.

In addition, few *in situ* studies have focused on compound nanowires VLS growth, due to experimentally elusive, *i.e.*, it's difficult to carefully control the complicated reaction parameters such as temperature gradient [8] and precursor purity [9]. As special classes of IV-VI narrow-band-gap semiconductors that exhibit excellent quantum confinement at the nanoscale, lead sulfide (PbS) have been extensively investigated, including fundamental research [10] and practical applications [11]. Here, PbS were used as one of model system to investigate growth mechanisms of compound nanowires. The growth mechanisms include regular VLS and screw dislocation driven VSL, leading to two different branch structures. *In situ* gas heating high resolution TEM (HRTEM) and EDS were employed to explore the growth mechanisms and mass transport pathways of precursors during the course of crystal growth within a gas environment of 5 vol% H<sub>2</sub> in N<sub>2</sub> at  $\sim 5 \times 10^3$  Pa. On the other hand, in the *in situ* low magnification TEM experiment, a furnace heating holder (Gatan, USA) was used. The precursor powders were sandwiched by a TEM Si<sub>3</sub>N<sub>4</sub> chip and a TEM carbon grid and heated to target temperatures (575°C and 600°C) under the mixed gas conditions (5 vol% H<sub>2</sub> in N<sub>2</sub>) at a pressure of  $\sim 8 \times 10^2$  Pa. We hypothesize that growth kinetics are related to supersaturation of growth precursors in liquid catalyst droplet and the growth precursors of compound nanowires may be transported by different pathways. Our preliminary results demonstrate the strong correlation among supersaturation, mass transport pathways, and growth kinetics. Various mass-transport mechanisms may enable new controls over nanowire composition [12]. Further investigation is undergoing for understanding formation of various hyperbranched structures. [13]

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**Figure 1.** *In situ* gas heating TEM investigation of compound nanowire growth mechanisms. Schematic illustration of (a) *in situ* gas heating TEM setup, (b) a compound wire, (c) growth mechanisms and different mass transport pathways through vapor, liquid, and solid.