

Characterization of semiconductor nanowires by HRTEM and *in-situ* TEM

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In order to better control the morphology and atomic structure of semiconductor nanostructures, we have systematically investigated the formation mechanisms of various semiconductor nanowires (e.g. Si, III-V and II-VI compounds) [1] by high-resolution transmission electron microscopy (HRTEM). Among the various techniques so far developed for synthesizing 1D nanostructures, the metal catalytic growth (also known as the vapor-liquid-solid (VLS) reaction) shows many advantages and has been widely used in growing nanowires of different materials because the nucleation sites and the diameters of the nanowires can be well-controlled by the pre-formed metal catalysts.

In this talk, we show our recent studies on the growth of ultrathin semiconductors nanowires, particularly the nucleation and initial growth of II-VI compound (e.g. ZnSe and ZnS) nanowires by molecular beam-epitaxy (MBE) technique via Au-catalyzed VLS reaction [2]. Since the impurity of the source materials, surface structures of the substrate and growth condition can be well controlled by MBE, interesting growth phenomena of ultrathin II-VI nanowires such as diameter-dependent and temperature-dependent growth directions and growth rates have been revealed. Due to the presence of metal catalysts, the geometry and structure of the interface between the catalyst and the nanowire have been found to be very critical to the growth velocity and growth direction or crystal orientation and the formation of defects. The sizes of the catalysts, the interfacial structures and the surface or interfacial energies mainly determined the growth morphologies and directions of ZnSe nanowires (FIG. 1). On the other hand, the growth temperature largely influenced the nanowire growth direction [3] and resulted in structural transformation from cubic to hexagonal phases. Different from the classical VLS mechanism (the growth rate is determined by the supersaturation in the catalyst droplet), we present that ultrathin nanowires show an interesting growth behavior of diameter-dependence of growth rates. The smaller the nanowire diameter, the faster is its growth rate, and the growth rate is mainly controlled by surface and interface diffusion and incorporation of the source atoms.

The growth behavior of ultrathin nanowires has been investigated using *an in-situ* TEM. We have observed the nucleation and initial growth of nanowires catalyzed by Au particles (FIG. 2). The interface structures and chemical composition at the catalysts varied with temperature. The electrical transport properties and cathodoluminance of individual as-grown nanowires have been studied *in-situ* by a nano manipulation and measurement system in TEM (FIG. 3). For example, the Au-catalyst at the ZnSe nanowire tip shows a Schottky barrier. Electron-beam irradiation at the catalyst interface can effectively eliminate this barrier, and the resistivity of the nanowires are measured to be about $1 \times 10^2 \Omega \text{cm}$. Ultrathin ZnSe nanowire surfaces are extremely active to capture hydrocarbon forming core/shell structures and thus changing the nanowires electrical properties. By applying a large current through a single core/shell nanowire, we observed material transportation through the nanowire and the structural changes from nanowires to nanotubes (FIG. 3(c)). The advantages of *in-situ* TEM in studying semiconductor nanowire formation and their properties will be discussed.

References:

- [1] N. Wang, Y. Cai and R.Q. Zhang, *Mater. Sci. Eng.* R60 (2008) 1.
- [2] Y. Cai, S. K. Chan, I. K. Sou, *et al.*, *Adv. Mater.* 18 (2006) 109.
- [3] Y. Cai, S.K. Chan, I.K. Sou, *et al.* *Appl. Phys. Lett.*93 (2008) 233107.
- [4] Acknowledgement: this work was financially supported by the Research Grants Council of Hong Kong (N_HKUST615/06; G_HK021/07).

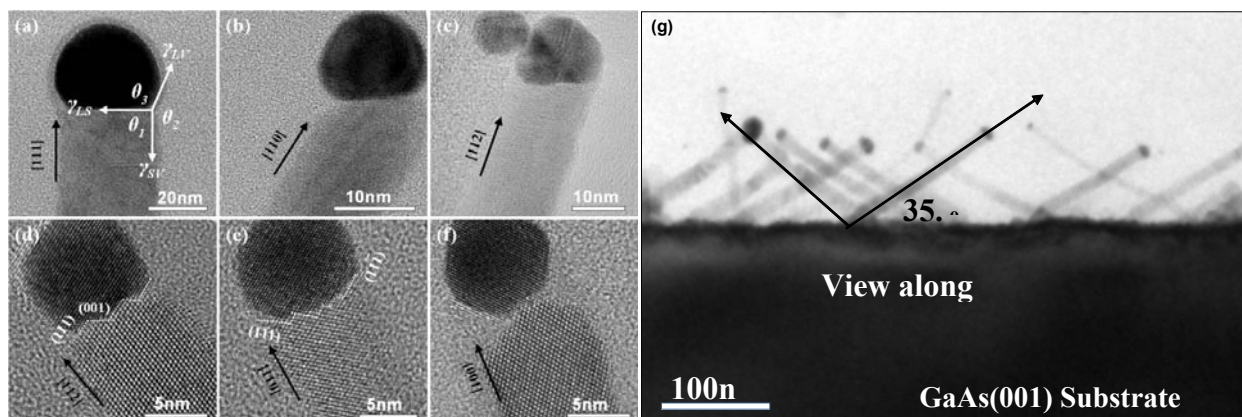


FIG. 1. ZnSe nanowires grown along (a) [111], (b) [110] and (c) [112] directions. The interfaces between the catalysts and the nanowires are always (111). (d) , (e) and (f) are HRTEM images showing the interface structures of nanowires grown along different directions. (g) The nanowire growth direction is temperature- and diameter-dependent, but independent of the substrate surface.

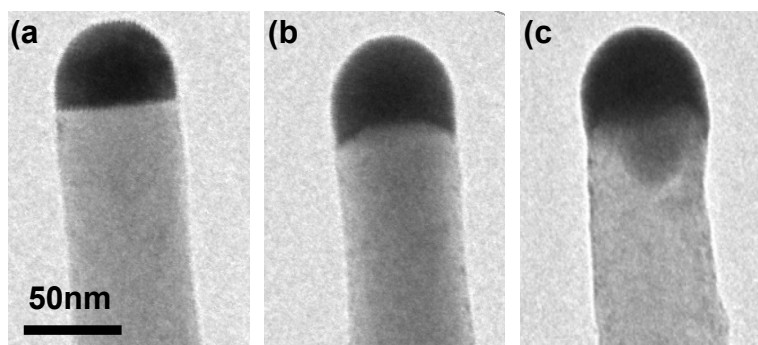


FIG. 2. (a) Sharp interface at low temperature. (b) Interface changing with increasing temperature. (c) Inter-diffusion at the interface of the catalyst.

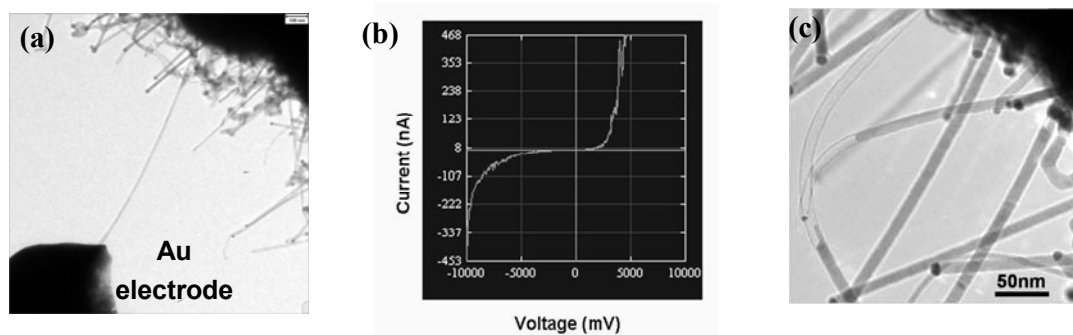


FIG. 3. (a) *In-situ* I-V measurement of a ZnSe nanowire. (b) I-V curve obtained from the nanowire shown in (a) indicating a Schottky barrier. (c) Structural changes from nanowires to nanotubes.