SCREW DISLOCATION DRIVEN NANOWIRE GROWTH AND ITS POTENTIAL APPLICATIONS

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Nanowire (NW) and other one-dimensional (1-D) nanomaterials have found many applications in electronics, photonics, chemical and biological sensing, and renewable energy applications. The fundamental understanding of their rational growth is critical important to their applications. I will discuss a “new” nanowire formation mechanism that is different from the well-known metal catalyzed vapor-liquid-solid (VLS) mechanism. Axial screw dislocations provide the self-perpetuating steps to enable 1-dimensional crystal growth, unlike previously understood mechanisms that require metal catalysts. This mechanism was first found in hierarchical nanostructures of lead sulfide (PbS) nanowires resembling “pine trees” that were synthesized via chemical vapor deposition.

We first synthesized hyperbranched nanowire clusters of PbS and PbSe via an in situ vapor-liquid-solid (VLS) nanowire growth (Fig. 1).[1] Metallic lead reduced from the lead chloride precursor by the co-flowed H_2 in the CVD reaction induced the formation of multiple generations of branches in an epitaxial fashion to result in very dense networks of “dendritic” NWs.

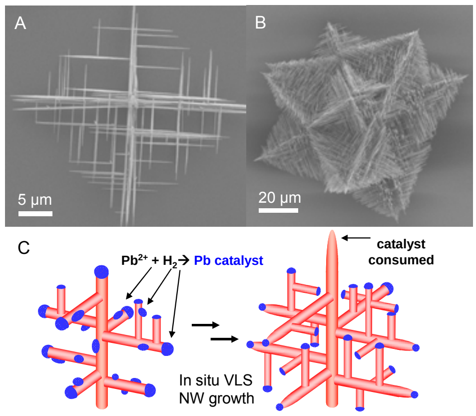

Fig. 1. Hyperbranched PbS nanowire clusters generated by the in situ VLS growth mechanism.

Furthermore, under slightly different conditions of hydrogen flow, we have further made some fascinating “Pine-tree” like NWs of PbS (Fig. 2A) and discovered a fundamentally different NW growth mechanism that is driven by axial screw dislocations (Fig. 2B, C).[2] Structural characterization reveals a screw-like dislocation in the nanowire trunks with helically rotating epitaxial branches. The cone-shaped nano “trees” are the result of simultaneous fast dislocation-driven trunk nanowire growth and the slower VLS driven branch growth while the helical rotation of the branches are the consequence of the stress and strain of the axial dislocation called “Eshelby twist”.

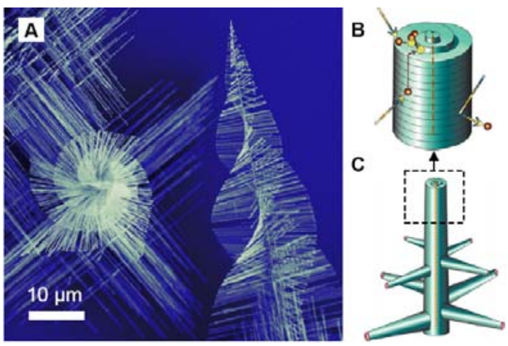

Fig. 2. “Pine tree” nanowires of PbS; **B)** Screw dislocation driven nanowire growth; **C)** screw dislocation combined with VLS branch driven growth.

The basic characteristics of screw dislocation driven nanowire growth were further investigated systematically.[3] The effects of various growth parameters, such as hydrogen flow, temperature, pressure, and the growth substrates employed, were investigated. Statistical survey showed that the dislocation-driven trunk has a constant growth rate of about 6 μm/min and the VLS driven branch nanowire has a growth rate of about 1.2 μm/min under the typical reaction conditions at 600 ^{o}C and 900 Torr and a hydrogen flow rate of 1.5 sccm. The onset of hydrogen flow plus the presence of fresh silicon have been identified as the critical ingredients for generating PbS nanowire trees reproducibly. To explain the experimental findings in the context of classical crystal growth theory, the former is suggested to create a spike in supersaturation of the actual sulfur precursor H_2S and initiate dislocations with screw component that then propagate anisotropically to form the PbS nanowire trunks. Maintaining suitable hydrogen flow provides a favorable low supersaturation that promotes dislocation-driven trunk nanowire growth and enables the simultaneous VLS nanowire growth of branches. Furthermore, thermodynamic consideration and experiments showed that silicon fortuitously controls the supersaturation by reversibly reacting with H_2S to form SiS_2 and SiS_2 can also be a viable precursor for PbS nanowire growth. The key requirements of screw dislocation driven nanowire growth are summarized and will provides general guidelines for further nanowire growth driven by screw dislocations.

Dislocation-drive nanowire growth is a fundamental advance that promises to create a new dimension in the rational design and synthesis of 1-D nanomaterials because dislocation-driven growth is underappreciated in modern literature on 1-D nanomaterials. It is a general method applicable to many materials including ZnO, GaN, InN, SiC, and others grown from both solution and vapor phase. It can also explain other 1-D nanomaterials morphology. Our fundamental study of dislocation driven nanowire growth will also enable the large scale synthesis of practical nanowire materials for diverse applications.

The complex hierarchical nanostructures shown here can have advantages in solar energy harvesting and nanoelectronics.[4] Nanowires are interesting because they have a long axis to absorb incident sunlight yet with a short radial distance to separate the photogenerated carriers. We further suggest that more "complex" branching/hyperbranching nanowire nanostructures are potentially even more interesting for solar energy harvesting and conversion because the enhanced light scattering and absorption and efficient pathway for carrier collection. Unconventional heterostructures between dissimilar materials that would have been impossible in bulk thin films can also be formed in nanoscale heterostructures. For example, we have demonstrated the epitaxial growth of PbS nanowires on single crystal rutile surface.[5] In order to realize the potential of these complex nanostructures, we need to develop potential strategies for their incorporation into solar conversion devices and investigate some fundamental issues.

REFERENCES

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