Phase Selection Enabled Formation of Abrupt Axial Heterojunctions in Branched Oxide Nanowires

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Supporting Information

ABSTRACT: Rational synthesis of nanowires via the vapor—liquid—solid (VLS) mechanism with compositional and structural controls is vitally important for fabricating functional nanodevices from bottom up. Here, we show that branched indium tin oxide nanowires can be in situ seeded in vapor transport growth using tailored Au—Cu alloys as catalyst. Furthermore, we demonstrate that VLS synthesis gives unprecedented freedom to navigate the ternary In—Sn—O phase diagram, and a rare and bulk-unstable cubic phase can be selectively stabilized in nanowires. The stabilized cubic fluorite phase possesses an unusual almost equimolar concentration of In and Sn, forming a defect-free epitaxial interface with the conventional bixbyite phase of tin-doped indium oxide that is the most employed transparent conducting oxide. This rational methodology of selecting phases and making abrupt axial heterojunctions in nanowires presents advantages over the conventional synthesis routes, promising novel composition-modulated nanomaterials.

KEYWORDS: Vapor—liquid—solid growth, indium tin oxide, branched nanowire, phase selection, heterojunction

In the nanowire growth via the vapor—liquid—solid (VLS) process and its variants,1–3 the complex interactions between vapor, liquid and solid phases give rise to rich phenomena,4–10 often going beyond the general conception that nanowires are merely a miniature form of their bulk counterpart sharing the same crystalline phase. In VLS synthesis of nanowires, liquid-phase catalyst nanoparticles play pivotal roles by collecting vapor-phase precursors, and their dynamic supersaturation drives the precipitation of crystalline nanowires.1,11 Therefore, the nanoparticles serve as tiny nanoscale reactors, making the VLS growth depart from the conventional synthesis routes. Chemical pressures and the associated thermodynamic equilibrium in catalyst nanoparticles can be dynamically tailored to control the nucleation at the nanoparticle/nanowire interface.12 Recently, there have been notable advances in VLS synthesis propelled by the needs in constructing nanowire-based functional devices. In particular, the dynamics of catalyst nanoparticles and modulation of the vapor-phase reactants during VLS growth have been harnessed in synthesizing complex nanowire-based architectures, such as branched nanowires,4,13–16 abrupt heterojunctions,7,17–20 superlattices,6,13,21,22 and kinked superstructures.23 These structure and composition tailored nanostructures are promising for applications in nanoelectronics, photonics, and energy harvesting. But the experimental realizations of such interesting VLS-grown nanostructures with epitaxial interfaces have been limited to a few material systems such as silicon, germanium, III–V compounds, and some oxides.

Regarding the growth of branched nanowires, ex situ seeding were grown first and the subsequently decorated catalyst nanoparticles seed the growth of nanowire branches. As a drastically different approach, in situ seeding was reported recently for silicon nanowires.15,24 It relies on controllably destabilizing the catalyst nanoparticles at the end of primary growth so that the derived nanoparticles can migrate along the primary nanowire trunks and seed the subsequent growth of branches. The in situ seeded growth process is illustrated in Figure 1A. The onset of catalyst migration depends on various factors such as growth temperature and pressure, and what matters is the overall change of chemical potentials when the catalyst starts to migrate from the nanowire tips onto the
crystalline structures are common in the bulk and thin film in oxide nanowires although functional oxides with compatible modulation and epitaxial interfaces has not been reported so far fabrication of abrupt axial heterojunctions with compositional oxide phase within individual nanowires. Overall, instead of axial heterojunctions with the conventional tin-doped indium phase in the nanowires. This cubic indium tin oxide phase is nanoparticles and selectively stabilize a cubic indium tin oxide dynamically tune the chemical potentials in the catalyst sequential inputs into the growth process, we were able to reduction temperatures of tin and indium sources and their Furthermore, utilizing the variation of the carbothermal surface contamination or oxidation which often happens in the nanowire trunks. This approach effectively avoids undesirable growth process without ex situ depositing nanoparticles on the nanowire branches, and generally the thicker ones show higher growth rates, which is consistent with the Gibbs effect (see Supporting Information Figure S5C).

In the stage II, disintegration and migration of catalyst particles accomplish the in situ seeding process and reliably lead to the growth of branched nanowires (Figure 1D, also see Supporting Information Sections II and III). This in situ seeding process hinges on the dynamic changes of the growth conditions as well as the lower melting point and probably the enhanced mobility of the AuCu alloy. The branched nanowires exhibit a 4-fold symmetry, reflecting the expected crystallinity and the epitaxial growth. Moreover, as shown in Figure 1E, the average length of the nanowire branches can reach 400 nm and be well controlled by adjusting the duration of growth stage II. We surveyed many nanowire branches, and generally the thicker ones show higher growth rates, which is consistent with the Gibbs–Thomson effect (see Supporting Information Figure S5C).

In our experiments, the abrupt pressure change between the growth stages I and II presumably breaks up the original nanoparticles into much smaller ones (see Supporting Information Section III), and the enhanced mobility of Au–Cu alloys facilitates the migration of the generated nanoparticles that seed the subsequent growth of branches. Importantly, our synthesis strategy also brings about the stabilization of a rare cubic phase, demonstrating the advantages of our approach of using bimetallic Au–Cu alloys in the VLS synthesis, which will be the focus of following discussions.

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**Figure 1.** Growth of branched In–Sn–O nanowires using Au/Cu alloys as catalyst. (A) Schematic illustration of the in situ seeded growth of branched nanowires. In step 1, Au alloys with Cu forming bimetallic droplets that then initiate the growth of primary nanowire trunks in step 2. In step 3, the nanoparticles are disintegrated into much smaller ones that subsequently migrate and seed the growth of nanowire branches in step 4. (B) Diagram of a typical growth process. The three stages serve to (I) grow the primary nanowire trunks, (II) seed the branches, and (III) terminate the growth. (C) SEM image of aligned ITO nanowires grown on a YSZ substrate without in situ seeding. Scale bar, 1 μm. (D) SEM image of branched ITO nanowires after the grown process shown in panel B. Both growth stages (I and II) last for 45 min. Scale bar, 1 μm. (E) Dependence of the branch length on the duration of the growth stage II.
The bright-field transmission electron microscopy (TEM) image in Figure 2A shows a nanowire branch, forming a perpendicular single crystalline junction with the trunk. Interestingly, the annular dark-field scanning TEM (ADF-STEM) image in Figure 2B shows a clear boundary at the waist of the nanowire branch. The high-resolution TEM (HRTEM) image in Figure 2C suggests that the lower part of the branch adopts the conventional ITO bixbyite phase, while the upper part exhibits a different crystalline structure, giving rise to an abrupt defect-free heteroepitaxial interface. The electron diffraction (ED) patterns (insets of Figure 2C) confirm the existence of two distinct structures within the nanowire.

The energy dispersive X-ray (EDX) spectrum taken at the upper part of the nanowire (Figure 2D, upper panel) indicates that the new structure we observed is indium tin oxide with a Sn/In ratio close to 1, which is much higher than that of the conventional ITO (<10%). On the other hand, the spectrum of the lower part of the nanowire gives a normal low Sn concentration (Figure 2D, lower panel). This new indium tin oxide phase is denoted herein as ISO. Comparing the electron energy loss spectroscopy (EELS) spectra of the ISO phase with the references of ITO, In₂O₃, and SnO₂ in Figure 2E provides more clues about the ISO phase. As expected, the spectra of ITO and In₂O₃ are quite similar due to the well-known limited solubility of Sn in In₂O₃ (≤6 atom %). On the other hand, the ISO spectrum shows distinct features. First, the intensity ratio between the two subspeaks of the oxygen K-edge around 540 eV is different from that of ITO, second the ISO spectrum shows a lower contribution of the In M-edge around 500 eV. The fine structure of the oxygen K-edge for ISO resembles the SnO₂ data, suggesting that the valence state of Sn in the ISO is 4+. Thus the chemical formula of the ISO phase is In₁₋ₓSnₓO₃₋ₓ(3+2)/2 with x close to 0.5. Although ITO is the most studied and utilized transparent conducting oxide, the cubic ISO phase stabilized here is not part of the conventional ternary In–Sn–O phase diagram. The HRTEM images and the selected area electron diffraction (SAED) patterns (inset of Figure 2C) suggest a cubic structure with a lattice constant about half that of the bixbyite ITO structure (a₁TO = 10.12 Å), which gives a perfect lattice match with ITO. Detailed electron diffraction analysis along different zone axes (Figure 2F) further revealed that the ISO phase possesses a fluorite structure (Figure 2G) with space group (SG) of Fm3m and the distribution of In and Sn atoms in the lattice is completely random. Such a fluorine indium tin oxide phase has been reported only in the form of nanosized precipitates with ITO grains in polycrystalline samples synthesized at high temperatures (e.g., 1600 °C). Diffuse scattering can be observed in electron diffraction as a result of short-range order of the oxygen-vacancy sublattice and it is characteristic of oxygen deficient fluorite structures found in cubic stabilized zirconia of the type (1 – x)ZrO₂-xLnO₁.₅ where the shape and sharpness of the diffuse scattering depend on the Ln ion. Such a fluorite structure is actually quite unusual in ITO at low tin doping (less than 6%) the bixbyite structure is preserved while the InₓSn₉O₁₂ phase usually appears at higher doping levels.

We further carried out first-principles calculations to shed more light on the crystal structure of the ISO phase. The projector augmented wave potentials were used to simulate the electron-ion interactions while exchange-correlation effects were treated within the generalized gradient approximation (GGA). The calculated results confirm the existence of the oxygen deficient fluorite structure with a cohesive energy of 4.42 eV per atom. The calculated lattice constant of this cubic ISO phase is 5.12 Å, matching well the experimental value. Furthermore, the obtained electronic structure suggests that ISO is metallic, which makes this material a potential less-indium alternative to the common ITO as a transparent conducting oxide (see Supporting Information Section IV). On the basis of the experimental observations and the theoretical calculations, a schematic of the simplified fluorite structure...
The actual cationic sublattice is disordered, that is, In and Sn atoms take random positions while keeping the overall stoichiometric ratio. Another important aspect of this structure is that one-eighth of the oxygen sublattice is vacant (represented by the unconnected red dot in Figure 2G).

To understand the formation mechanism of the ISO phase, we took a close look at the catalyst nanoparticles. Figure 3A shows a high-angle annular dark-field scanning TEM (HAADF-STEM) image of the interface area between the Au–Cu catalyst nanoparticle and the ISO nanowire. Inset: SAED pattern showing the epitaxial relationship between the ISO nanowire segment and the Au–Cu catalyst nanoparticle. Scale bar, 2 nm. (B) HRTEM image taken at the area near the nanowire/nanoparticle interface. Inset is the FFT pattern of the SnO$_2$ shell. Scale bar, 10 nm. (C) Enlarged HRTEM image of the marked area in B, showing the epitaxial relationship between the catalyst particle and the SnO$_2$ shell. Scale bar, 2 nm.

Figure 4. Mechanism of phase selection and epitaxial growth. (A) Calculated difference in formation energies $E_f$ per In/Sn atom for the fluorite ISO and the bixbyite ITO structures as a function of the oxygen chemical potential and the atomic Sn/(In + Sn) ratio. (B) Phase diagram calculated at a particular value of $\Delta \mu_{\text{ITO}} - \Delta \mu_{\text{ISO}}$ showing the separated growth domains favoring the growth of ITO or ISO as a function of $\Gamma_{\text{ISO}}/\Gamma_{\text{ITO}}$ and $\Delta \mu_{\text{ITO}}$ (see Supporting Information Section VI). (C) Schematic illustrating the stepwise formation of the axial nanowire heterostructure and the core/shell nanoparticle. The conventional ITO phase grows in the step 1, while the Sn content surges in the catalyst nanoparticles and the nucleation of the ISO phase occurs in the step 2. In the final step, the excess Sn in the catalyst nanoparticles precipitates out to form the crystalline SnO$_2$ shell when the growth is terminated during cooling down. The light and the dark blue sections represent ITO and ISO phases, respectively. The orange sphere in the step 2 represents the Sn-rich catalyst nanoparticle. (D) Summary of the various epitaxial relationships involved at the AuCu–ISO and the ISO–ITO interfaces within the heterostructured nanowire branch.
nanophotonics and nanolasmonics. Furthermore, the presence of the SnO$_2$ shell suggests that the catalyst nanoparticle is Sn rich during the branch growth, which we believe is the prerequisite to the formation of the cubic ISO phase.

In the VLS mechanism, nanowire growth takes place in a layer-by-layer fashion with series of ledge nucleation events. In a simplified model, nucleation at the liquid–solid interface involves the interplay of the enthalpy change in forming the solid phase and the energy cost in creating the new liquid–solid interface. In a simplified model, the nucleation barrier can be written as a function of $\Delta \mu$ (the variation of chemical potential involved in the transition from the liquid to the solid phase) and $\Gamma$ (the effective surface energy due to the formation of the nucleus) (see Supporting Information Section VI). The minimization of the effective surface energy may favor the growth of single-phase nanowires, that is, the homogeneous nucleation, that is, ITO on ITO. However, as the Sn concentration surges in the catalyst particles during the growth stage II, $\Delta \mu_{\text{ITO}}$ and $\Delta \mu_{\text{ISO}}$ will change accordingly, and the competition between the nucleation barriers $\Delta G_{\text{bar,ITO}}$ and $\Delta G_{\text{bar,ISO}}$ enables the phase selection. Indeed, as shown in Figure 4A, our first-principles calculations suggest that forming the ISO phase takes less energy than the ITO phase when the Sn/In ratio is high enough. Note that the first-principles calculations only give the ground state properties at 0 K, but we expect similar behaviors at the growth temperature as the thermal energy is relatively small (<0.1 eV).

On the basis of the general nucleation model, we constructed a schematic phase diagram as a function of the relevant surface, interface, and bulk free energies (Figure 4B), and this phase diagram contains a boundary separating the domains favoring the growth of the ITO and the ISO phases. An increase of $\Delta \mu_{\text{ITO}} - \Delta \mu_{\text{ISO}}$, that is, an increase of the Sn concentration in the catalyst nanoparticles, enables the phase selection across the boundary, giving rise to the nucleation and growth of the ISO phase.

The nucleation of the ISO phase and the subsequent growth process is schematically illustrated in Figure 4C, including the formation of the ITO/ISO heterojunction as well as the Au–Cu/ITO core/shell nanoparticle. In the VLS synthesis, the Au–Cu alloy catalyst nanoparticles play important roles well beyond serving as a collector for the metal vapors. They in situ seed the growth of nanowire branches; they help to selectively stabilize different phases in the In$_x$Sn$_{1-x}$O$_2$ nuclei. This research was supported in part by the Singapore National Research Foundation. S.T. gratefully acknowledges the financial support from the Fund for Scientific Research Flanders (FWO). The Titan microscope used in this study was partially financed by the Hercules Foundation. T.W. thanks Professor Z. L. Wang of Georgia Institute of Technology for stimulating discussion and reading the manuscript.

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