Self-assembly of semiconducting oxide nanowires, nanorods, and nanoribbons

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Received 8 October 2002; in final form 10 March 2003

Abstract

We have synthesized three-dimensional self-assembled ZnO-based nanoscale heterostructures through the addition of alloying elements (In or Sn) during the vapor phase transport and condensation deposition process. Each three-dimensional nanoscale heterostructure consists of a faceted nanowire core, with side branches (nanoribbons or nanorods) emanating from facets of the central nanowire core. The central nanowire core can be either ZnO, (ZnO)_{11}In_{2}O_{3}, or In_{2}O_{3}, depending on incoming flux composition ratio. The physical mechanism of branching stems from segregation of alloying elements to facets during the growth of the nanowire core, thus creating nucleation sites for side branches.

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Semiconducting oxides, such as ZnO, In_{2}O_{3}, SnO_{2}, and Ga_{2}O_{3}, are widely used as the base materials for transparent conducting oxide, photoelectronics, and gas sensors, etc [1–4]. Applications of these materials are by far, centered on two-dimensional films, and to a lesser degree, on zero-dimensional particle-like structures. More recently, it was reported that these semiconducting oxides materials could be synthesized through vapor transport into one-dimensional nanowires, nanorods, or nanoribbons [5,6]. These one-dimensional semiconducting oxide nanomaterials have generated tremendous interests in both the scientific and engineering community, which has visibly led to rapid and intense growth in research focus [7–9]. Current research in nanoscale semiconducting nanowires for devices applications span from field-effect transistors [10], bio/chemical sensors [11], ultra-violet lasers [12], light emitting diodes [13], and photo-detectors [14]. One of most critical nanomaterial issues is to create heterostructures in multi-component systems. This can be achieved by manually bringing nanowires with different composition into contact [15].

In this paper, we report the synthesis of self-assembled three-dimensional semiconducting oxide nanoscale heterostructures, which we believe, has never been reported. We can grow these self-assembled nanoscale structures in a highly controllable manner through the addition of alloying...
elements (In and Sn) using the simple vapor transport and condensation process. This novel method allows us to synthesize highly regular nanoscale heterostructures such as nanoribbons, nanocombs, and nanorotors (with 4- or 6-fold symmetry).

The growth of the ZnO-based nanostructures was carried out in a zone furnace, backed by a rotary pump. A mixture of desired oxide powders was positioned at the sealed end of an inner quartz tube. Graphite powder was added as reducing agent, and these powder mixture were reduced at 1000 °C in the zone tube furnace. The flux ratio of In (or Sn) alloying element to Zn in vapor phase was controlled by varying the proportion of In$_2$O$_3$ (or SnO$_2$) to ZnO powders. Evaporants, transported via vapor phase, was then oxidized near the open end of the inner quartz tube in presence of air, where flow-rate was controlled through a needle valve, and deposited onto a graphite foil. The temperature at graphite foil during deposition was maintained at 850 °C. All depositions were carried out for a fixed time of 30 min, followed by furnace cooling. The synthesized products were then characterized and analyzed by X-ray diffraction (XRD, Bruker D8-GADDS), scanning electron microscopy (SEM, JEOL 6340 with a field-emission gun), and transmission electron microscopy (TEM, JEOL 2010 with a field-emission gun, equipped with an energy-dispersive X-ray spectrometer (EDS) and a high-angle annular dark-field (so-called Z-contrast) detector).

Cross-sectional TEM along the core nanowire direction was introduced to observe the core structure and the orientation relationship between the arms and the core. Samples for cross-sectional TEM were prepared as follows: Given the brittle nature of the nanomaterials, we penetrated the films with M-Bond 610 epoxy resin (M-Line Accessories, Raleigh, NC) to provide mechanical stiffness. The hardened thin foils containing graphite substrate were then cut, glued together following the standard cross-sectional TEM sample preparation technique.

As a reference, specimens of pure ZnO nanostructure were first grown in the deposition system using ZnO powder as the only source material. We observed high purity and homogenous wool-like ZnO nanoribbons, which is in excellent agreement with previous result reported by Pan et al. [6]

In the presence of low In alloying flux, the deposited nanostructure consists of similar wool-like nanoribbons, with lengths and widths ranging from 10 to 20 μm and 50 to 200 nm, respectively (Fig. 1a). Cross-sectional TEM observations show that the width-to-thickness ratio of the ribbons ranges from 5 to 10. X-ray powder diffraction data indicates that the major phase in the product is ZnO with a hexagonal wurzite crystal structure. Diffraction contrast (Fig. 1b) and HRTEM (Fig. 1c) images show that all In-alloyed ZnO nanoribbons consist of a nanowire core with two adjacent nanoribbons, flanking the central nanowire core. It is important to note that this is not observed in pure ZnO nanoribbon specimens. Typical width of the nanowire core is 10–15 nm. Electron diffraction analysis indicates that the growth direction of nanowire core is along $\langle 0\overline{1}10 \rangle$ (the inset of Fig. 1c), it has the same length as the side nanoribbons. These side nanoribbons grew on $\langle 0001 \rangle (2\overline{1}0 \rangle$ facets of the nanowire core along the $\langle 0001 \rangle$ plane. EDS analysis showed that In content at the nanowire core is ~18 at.%, which is much higher than that of side nanoribbons (~3 at.%). Zn–In–O is a homologous layered compound which can be written as $(\text{ZnO})_k\text{In}_2\text{O}_3$ [16]. In our experiments, the nanowire core has the chemical composition of $(\text{ZnO})_{11}\text{In}_2\text{O}_3$.

With increasing In to Zn flux ratio, we start to observe the additional growth of nanorods in [0001] direction (perpendicular to the plane of nanoribbons), on both sides of central nanowire (Figs. 2a and b). These nanorods only nucleate and grow from the central nanowire core (not from the side nanoribbons), thus self-aligned to form a straight row of nanorods. EDS composition analyses show that the nanowires core and side nanoribbons have similar composition with those obtained Fig. 1 during deposition at low In to Zn flux ratios, whilst these new side nanorods are essentially pure ZnO growing along $\langle 0001 \rangle$ direction. Electron diffraction and image analyses show that the whole complex ZnO-based nanostructure has the same crystallographic orientation. This indicates that the nanorods and nanoribbons grew epitaxially on the nanowire core. A vast majority
of nanostructures (Figs. 2c and d) obtained under this exact condition have similar structure to Figs. 2a and b, with the visible absence in side nanoribbons. Due to its resemblance to a comb, we named the nanostructure shown in Figs. 2c and d as nanocombs. This suggests that the nanostructures shown in Figs. 2a and b correspond to the transition between nanoribbons (Fig. 1) and nanocombs (Figs. 2c and d).

At the highest In to Zn flux ratio employed, we observe rotor-like nanostructures with 4- and 6-fold (Fig. 3) symmetries as reported elsewhere [17]. The length of these nanorotors along the central core axis spans tens of micrometers, while the length of side nanorods ranges from 200 nm to

![Figure 1: SEM and TEM images of In-alloyed ZnO nanoribbons grown at low In:Zn flux ratio. (a) SEM image of the as-synthesized In-alloyed ZnO nanoribbons. The inset shows a schematic diagram of the synthesized nanoribbons. (b) Bright-field diffraction contrast TEM image of a ZnO nanoribbon showing the existence of a central nanowire core. (c) HRTEM image of the nanowire core shown in (b). The nanowire core grows along (01T0) direction as shown in the inset (selected-area electron diffraction pattern). The interfaces between side nanoribbon and nanowire core are atomically sharp and no misfit dislocations were observed.]

![Figure 2: SEM and TEM images of In-alloyed ZnO nanostructures grown at medium In:Zn flux ratio. (a) SEM image of a nanowire core with both side nanoribbons and nanorods. The growth of side nanorods is well-aligned and perpendicular to the growth of side nanoribbons. (b) TEM image taken along [0001] direction showing the well-aligned growth of nanorods only on the central nanowire core. (c) and (d) SEM images of nanocombs (ZnO side nanorods growing on (ZnO)11In2O3 central nanowire cores). The length of these side nanorods ranges from 100 to 3000 nm, while the width of nanowires core is ~10–20 nm.]

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Fig. 2. SEM and TEM images of In-alloyed ZnO nanostructures grown at medium In:Zn flux ratio. (a) SEM image of a nanowire core with both side nanoribbons and nanorods. The growth of side nanorods is well-aligned and perpendicular to the growth of side nanoribbons. (b) TEM image taken along [0001] direction showing the well-aligned growth of nanorods only on the central nanowire core. (c) and (d) SEM images of nanocombs (ZnO side nanorods growing on (ZnO)11In2O3 central nanowire cores). The length of these side nanorods ranges from 100 to 3000 nm, while the width of nanowires core is ~10–20 nm.
a few micrometers. EDS analyses identify the side nanorods as essentially pure ZnO. Diffraction analyses show all nanorods grow in [0001] direction and nanorods in the same row have the same crystallographic orientation. This can also be seen from the SEM image (Fig. 3c) since hexagonal end facets (with diameters ranging from 20 to 200 nm) at the end of nanorods are well aligned. Cross-sectional TEM observation shows that there is always a nanowire core in the nanorotors (Fig. 3e). TEM structural study by electron diffraction (Fig. 3f) and EDS composition analysis reveals that the core nanowire is In$_2$O$_3$ with a cubic lattice ($a = 10.118$ Å), which is a different phase from (ZnO)$_{11}$In$_2$O$_3$ as shown in Figs. 1 and 2. The symmetry of nanorotors is found to depend on the crystallographic orientation of In$_2$O$_3$ along core axis. For example, In$_2$O$_3$ core nanowire growing along [001] direction has four equivalent {100} facets as shown in Fig. 3e. These sides ZnO nanorods grow on each facets of the In$_2$O$_3$ core nanowire, forming 4-fold symmetry nanorotors. When the In$_2$O$_3$ core nanowire grew in [111] direction, the resulting nanorotors have 6-fold symmetry because the 6 equivalent {110} facets. Hence, by controlling the initial nucleation of In$_2$O$_3$, we can selectively manipulate the resulting nanorotors structure with either the 4- or 6-fold symmetry configuration.

The branched growth of nanoribbons, nanorods, and nanorotors are the common characteristic of semiconducting oxides in presence of alloying elements. For example, we also observed the growth of side nanoribbons in the presence of Sn as alloying element. The majority of the deposited nanostructure is ZnO nanoribbons with the lengths from 1 to 20 μm and the widths of around 1 μm. Width-to-thickness ratios are around 5. Each nanoribbon consists of a central core as can be clearly seen from high-resolution SEM image (Fig. 4a). TEM study shows nanowire cores grow along ⟨01T0⟩. Electron diffraction analyses
indicate that the nanoribbons are single crystalline and grow in the plane of (2\(\overline{1}0\)). EDS analyses show that the central core is essentially pure ZnO. Z-contrast imaging (Fig. 4b) reveals that there are two sharp Sn-rich interfaces (white contrast lines) between the nanowire core and side nanoribbons, since brighter regions in a Z-contrast image correspond to larger Z number. This is in agreement with EDS line-scans obtained using an ultra small probe size of 0.5 nm (the inset of Fig. 4b). EDS line-scans, acquired using a probe size of 2 nm, across nanoribbons show that Sn:Zn composition ratio increases from the center to the edges of the specimen (Fig. 4c). The Sn:Zn content ratio at the edge of the nanoribbon is around 8%.

Our TEM analyses suggest that the growth of the nanostructure is a vapor–solid rather than a vapor–liquid–solid process because we did not find any low melting-point phases at the growth front of both the central nanowire and the side branches. The composition of the central nanowire core, to first-order approximation (using the phase diagram), can be determined by the composition of incoming fluxes. This can explain the experimental observation of \((\text{ZnO})_{11}\text{In}_2\text{O}_3\) nanowire core in the case of low- and medium-In alloying content (see Figs. 1 and 2) and \(\text{In}_2\text{O}_3\) nanowire core at our highest In-alloyed specimen (Fig. 3) [18]. Similarly, the \(\text{SnO}_2–\text{ZnO}\) phase diagram can be used to explain the observation of ZnO core in the Sn-alloyed ZnO nanostructures.

An important feature of all nanostructures shown in Figs. 1–4 is all side branches are observed to be emanating only from facets of the central nanowire cores. The fact that side branching is observed only in the presence of alloying elements strongly suggests surface segregation may have played an important role. During growth of central nanowire, the alloying content is continuously segregated to the facets of the nanowire core. The alloy rich layer of the facets became the nucleation sites for the subsequent growth of side branches (Fig. 4d). During the side branches growth, its growth front will continually reject alloying atoms due to segregation; therefore, we can expect the tip of the branch to be rich in alloying element. The observations of Sn rich interfaces on the central nanowire core (Fig. 4b), and the increasing of Sn:Zn composition ratio from the center to the edges (Fig. 4c), therefore, strengthened our hypothesis that segregation is imperative in branching mechanism.

In summary, we can control the morphology and composition of ZnO-based nanoscale heterostructures by addition of alloying elements (Sn and In). The composition of central core during nanostructural growth can be inferred from the respective phase diagram while the physical mechanism of branching stems from surface segregation at growth front of the central axis, resulting in branch formation at the adjoining facets. The branching mechanism discussed in this paper is generic and, therefore, can be applied to other materials (e.g., Sn in \(\text{Ga}_2\text{O}_3\) and Cd in \(\text{SnO}_2\)), thus opening a new approach in synthesizing of similarly branched structures. These branched nano-
structures can potentially find diverse applications in nanoscale electronic, opto-electronic and photonic devices.

Acknowledgements

The authors gratefully acknowledge the financial support of NSF under Award No. CMS-0219836, and DOE under the Award No. DEFG02-91ER45439. This work is supported partly by the US Army Natick Soldier Systems Center under Grants DAAD16-00-C-9227 and DAAD16-02-C-0037, partly by the DOE under a Grant DE-FG02-00ER45805, and partly by the NSF under a Grant ECS-0103012. The authors also appreciated the use of facilities at the Center of Microanalysis of Materials at the University of Illinois at Urbana-Champaign.

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