ZnO nanowires and nanobelts: Shape selection and thermodynamic modeling

Hong Jin Fan
Department of Earth Sciences, University of Cambridge, Cambridge CB2 3EQ, United Kingdom
and Max Planck Institute of Microstructure Physics, Weinberg 2, 06120 Halle, Germany

Amanda S. Barnard
Department of Materials, University of Oxford, Oxford OX1 3PH, United Kingdom

Margit Zacharias
Department of Physics, University of Paderborn, Warburger Straße 100, 33098 Paderborn, Germany

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The authors show that, during a steady-state vapor phase growth of ZnO nanomaterials, indium doping causes the structural change from usual [0001]-axial short nanowires to [1120]-axial nanobelts of much larger aspect ratio. They used an analytical thermodynamic model based on geometric summation of the Gibbs free energy to predict the dimension dependence of the nanowires and nanobelts for both pure and In-doped ZnO. The calculation result agrees with the experiment observation that in situ indium doping influences the nucleation and supports the dominating growth of a-axial nanobelts over c-axial nanowires. © 2007 American Institute of Physics. [DOI: 10.1063/1.2720715]

Tailoring the crystallographic orientation of semiconductor nanowires (NWs) is one of the key points of the growth control. It has been shown experimentally that the growth direction can be changed by, e.g., applying corresponding lattice-matching substrates for wurtzite NWs, or using small-sized catalyst for Si NWs, or changing growth temperature for ZnSe NWs. Theoretical calculations have been conducted to describe the thermodynamics and kinetics of semiconductor NWs and predict the size dependent behavior.

Vapor-liquid-solid (VLS) is a widely used mechanism for controlled growth of semiconductor NWs, including ZnO. There is also great interests in doping ZnO NWs to enhance the electric conductivity or ferromagnetic ordering. Depending on the doping elements and/or concentration, the ZnO nanostructure can be dramatically different. For example, the In-doped ZnO NWs by Xu et al. have an unusual zinc blende crystal structure with periodically twinning, whereas in many other cases the indium doping causes a wurtzite-type belt structure.

Recently we found that, in the carbothermal reduction experiments routinely for ZnO NW growth, introducing an additional indium oxide source causes a transition from usual c-axial NWs to a-axial nanobelts (NBs). The growth kinetics that has been proposed for oxide NBs by high-temperature decomposition and crystallization might not be applicable to explain the variation of shape and crystallographic orientation in this relatively low temperature VLS case. Instead, it can be reasoned that it is correlated to the indium doping.

In this letter, we present more experiment evidence that the transition of ZnO nanostructures from c-axial wires to a-axial belts is caused by indium doping. A thermodynamic model is applied to predict the dimension dependence of the structure/orientation selection. The result of the modeling supports the hypothesis that indium, even in a trace amount, plays the essential role in the nucleation of NBs and supports its growth.

The ZnO nanostructures were synthesized inside a double-tube furnace via VLS mechanism. Details of the fabrication setup can be found elsewhere. For the growth of NBs an indium-contaminated small tube was used (contaminated after the experiments where an additional In2O3 source was used), while for the growth of NWs, the tube was indium-free. All the rest conditions were identical. During the whole process, the Ar gas flow rate and total pressure were kept constant by using a gas flow controller, an electronically controlled needle valve, and an oil-free pump station, so as to establish a quasiequilibrium environment.

The scanning electron microscopy images in Fig. 1 give a comparison of the result. When a clean ZnO source was used, the result is ordered arrays of pure ZnO NWs oriented vertical to the GaN surface. The mean diameter of the ordered NWs is 50 nm. The NWs have [0001] long axis and hexagonal cross sections bounded with equivalent \{11\bar{2}0\} planes. However, if the growth chamber has indium contamination (trace amount), the substrate surface is dominated with ultralong NBs together with a small amount of irregular-shaped structures. These NBs are randomly oriented and have no alignment relative to the initial gold nan-

![FIG. 1. Comparison of the sample surface structure when different source types were used. (a) Pure ZnO+C source and (b) ZnO+C source in a indium-contaminated alumina tube.](image)

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**References**

1. Electronic mail: hfan05@esc.cam.ac.uk
2. Electronic mail: amanda.barnard@materials-ox.ac.uk
In: Zn
ated by gold, since no growth was observed at places without
widths of 100–220 nm. Growth of the NBs was also initi-
tations, the growth kinetics can be dramatically different, e.g.,
side surfaces. This is likely due to an effect of the surface-
planes, a fast growth in [0001] is thermodynamically fa-
lower limits of the NBs observed, e.g., by Jie et al. 
Figure 2, all changes are response to extension along the prin-
We can see from Fig. 3(a) that at large volume sizes, pure ±[0001] oriented ZnO NWs are clearly thermodynamically pre-
was not included in our model.

The morphology of the most common one-dimensional ZnO structures is geometrically defined in Fig. 2, assum-
ing hexagonal and rectangular cross sections for NW and NB, respectively. Type A1 represents the NW observed herein, type A2 represent an alternative NW structure oriented in the ±[0001] direction but enclosed by {1010} facets, types B1 and B2 represent the upper and lower limits of the NBs re-
ported here, and types C1 and C2 represent the upper and lower limits of the NBs observed, e.g., by Jie et al. 
In each case, the model was used to calculate the total free energy as a function of total volume (in terms of the number of ZnO formula units) in Fig. 3(a) and aspect ratio in Fig. 3(b). In

FIG. 2. (Color online) Schematic representations of the A1, A2 nanowires, B1, B2 nanobelts, and C1, C2 nanobelts. L refers to length, W to width, T to thickness, and D to diameter.

FIG. 3. (Color online) Free energy of the nanowire and nanobelt shapes as a function of (a) the total volume in terms of the number of ZnO formula units and (b) the aspect ratio. The change of aspect ratios is made by lengthen-
ing along the corresponding principle axis.
Fig. 4. (Color online) Free energy of the nanowire and nanobelt shapes as a function of the aspect ratio for dominated growth (a) along (0001) and (b) along (1120). The estimated values for In-doped nanostructures are also shown, with 5% In incorporated preferentially into the (1120) and (10\(\bar{1}0\)) nonpolar surfaces.

getically preferred over the NWs and their growth would be thermodynamically encouraged in the absence of In. However, if the [0001] growth dominates, the morphology predicted for pure ZnO nanostructures disagrees with observations in our In-doping experiment. High aspect-ratio pure ZnO NBs are metastable with respect to a morphological transformation to a NW. The crossover occurs at a NB thickness of 31 nm, much larger than those observed in our experiments (≈10 nm). Therefore, the results of the theoretical modeling indicate that, in order for the large aspect ratio NBs to be thermodynamically preferred over the NWs, indium has promoted the growth in the [1120] direction and inhibit the [0001] growth.

As an estimate of the impact that indium incorporation may have on the relative stability of these nanostructures, the above modeling was repeated with substitutional In defects included artificially in the pure ZnO surface energies. The “defect energy” was approximated by comparing known values for the Zn–O and In–O bond enthalpies and the free atom enthalpies, and by accounting for the fact that Zn or In atoms at the surface will form three bonds with surrounding oxygen atoms and have one dangling bond (taken as half of a Zn–O or In–O bond). Assuming that In atoms incorporate preferentially into the nonpolar {1120} and {10\(\bar{1}0\)} surfaces and that the defect density is approximately 5% (as determined by energy dispersive x-ray spectroscopy), we can estimate the free energy of In-doped nanostructured surfaces. Results are also shown in Fig. 4 for extensions in both [0001] and [1120] directions. We can see that the artificial In defects have a greater impact on the free energy of the NWs than that of the NBs, and in Fig. 4(a) the crossover between the In-doped nanostructures occurs at an aspect ratio of ~410, which is consistent with the experimental observations. In general, although this result supports the formation of high aspect ratio NBs over NWs due to indium incorporation, a more definite verification requires explicit, accurate data of surface energies of In-doped ZnO.

In conclusion, we show that in situ indium doping (with a 4–6 at.%) causes the structural change of the ZnO from usual c-axial NWs to a-axial NBs. An analytical thermodynamic model was used to predict the dimension dependence of the shape by comparing the total Gibbs surface energies. The modeling result corroborates our hypothesis that In doping influences the nucleation and supports the growth of a-axial NBs over c-axial NWs.

Future work is to model how the atomic arrangement is disordered by indium doping, and how much indium is needed for a crystallographic transition during nucleation.