Synthesis, Microstructure, and Growth Mechanism of Dendrite ZnO Nanowires

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Received: March 31, 2003; In Final Form: June 9, 2003

High-purity ZnO nanowires, which possess branching structures, were prepared by evaporating metal zinc onto thermally oxidized Si wafer. The morphology and microstructure analyses of ZnO crystals were performed by scanning electron microscopy and high-resolution transmission electron microscopy. The nanowires possess hexagonal wurzite structure. The 1-D growth mechanism of ZnO nanowires corresponds to Sears theory. Multiply twinned ZnO fine particles deposited on silica surfaces serve as the growth centers of branching structure. The dendrite ZnO nanowires have potential for building optoelectronic nanodevices with special configurations or as building blocks in the construction of functionalized interfaces.

Introduction

Synthesis of one-dimensional (1-D) nanostructures (nanotubes, -wires, -cables, and -belts) with interesting hierarchical organization has attracted much attention in recent years because of fundamental curiosity as well as for practical reasons.[1−7] An anodic alumina template based CVD technique has been developed to fabricate Y-junction carbon nanotubes (CNTs). These Y-junctions of CNT have reproducible $I-V$ rectifying characteristics at room temperature and may be used as the building blocks in the construction of nanoelectronics, such as three-terminal nanoscale transistors.[1] Furthermore, a variety of oxide semiconductors with fascinating structures have also been reported, such as, e.g., ZnO arrays,[2] ZnO nanobridges, and nanonails,[3] hierarchically organized ZnO−In_2O_3 nanorods,[4] tadpole-like ZnO arrays,[5] SnO_2 nanoribbon networks,[6] ZnO tetrapods,[7] and MgO fishbones.[8] These complex structures of 1-D oxide semiconductors are expected to have potential applications in building functional nanoelectronics devices with special architectures and distinctive optical and electrooptical properties.

Here we report a branching structure of ZnO nanowires, so-called dendrite ZnO, that consist of a branched joint similar to that of Y-shaped CNTs. The microstructure and morphologies of the dendrite ZnO nanowires were studied by high-resolution transmission electron microscopy (HREM). By summarizing the results of HREM analyses, both the mechanism of 1-D growth and the formation of branching structure were discussed in detail.

Experimental Section

Dendrite ZnO nanowires were synthesized on thermally oxidized Si substrate by a simple vapor deposition method. In a typical synthesis, about 2 g of pure metal Zn (99.999%) was put in a small alumina boat to serve as source material. A SiO_2 layer of 300 nm was achieved on the Si wafer through means of rapid raising annealing (RTA). And the oxidized silicon wafer was placed above the source at a vertical distance of ∼5 mm with its smooth side facing downwardly. Then, the alumina boat was transferred into the center of an alumina tube furnace. Afterward, the chamber was set to 750 °C with a heating rate of 10 °C/min at a constant flow of argon (99.9%, 200 sccm) and held for 3 h. The resulting products were collected on the oxidized surface of Si wafer. The as-deposited products were characterized by scanning electron microscopy (SEM) [Amray FEG-1910], high-resolution transmission electron microscopy

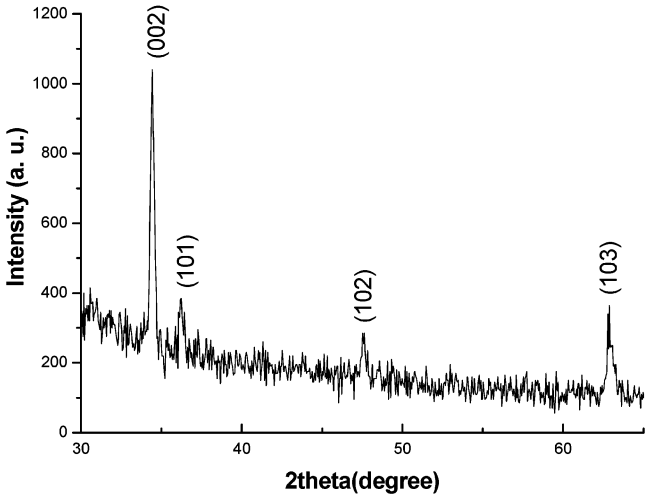

Figure 1. X-ray diffraction of dendrite ZnO nanowires.

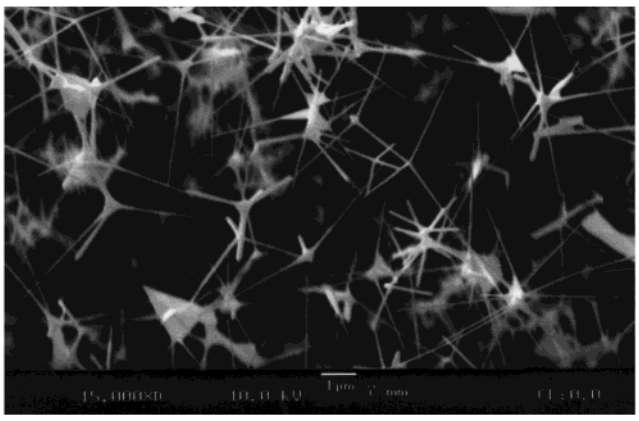

Figure 2. SEM image of ZnO nanowires.

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10.1021/jp034834q CCC: $25.00
Published on Web 07/23/2003

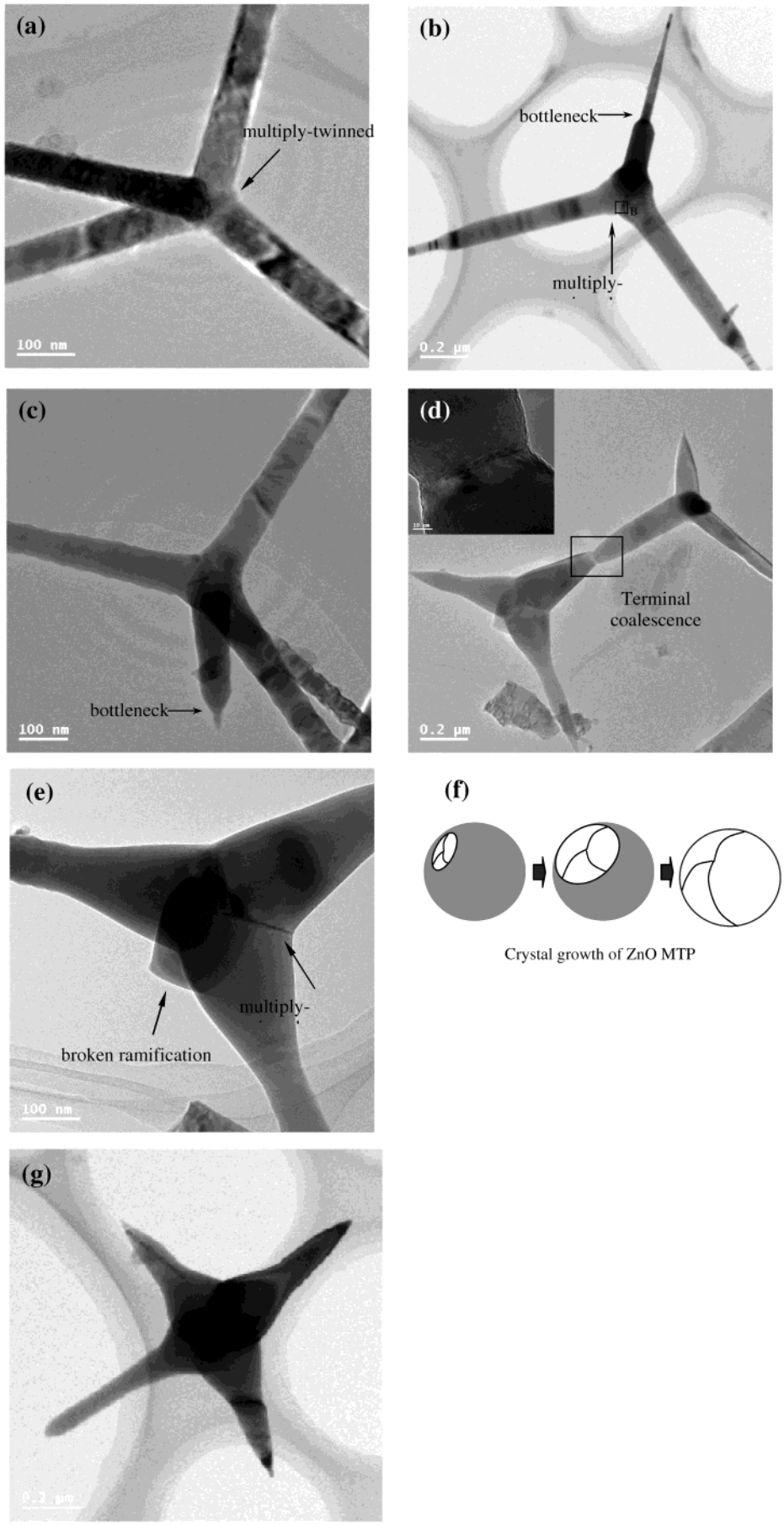

Figure 3. TEM images of ZnO nanowires at low magnifications. (a) Four ramifications. (b) Three ramifications. (c) Showing terminal-bottleneck phenomena. (d) Terminal-coalescence of two nanowires resulting in a "neck". Inset: high-magnification image of the "neck". (e) Multiply twinned joint. (f) A model for crystal growth of ZnO MTP. (g) Multiply twinned nucleus at early growth stage.

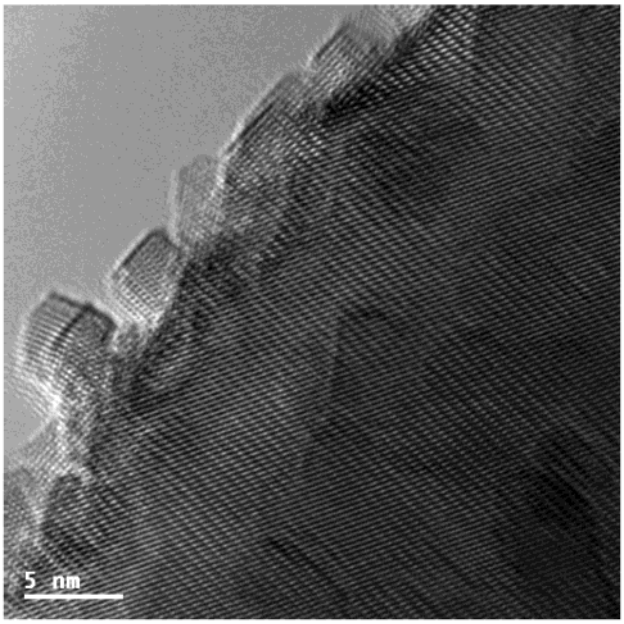

Figure 4. Typical HREM image showing that ZnO nanowires are single crystalline and free from dislocation and defects.

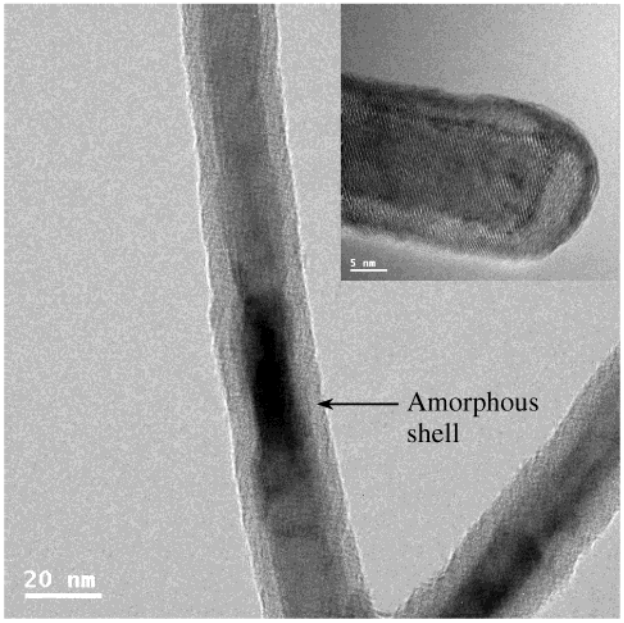

Figure 5. Core−shell structure of nanowire.

(HREM) [Tecnai F30], nanosized beam energy-dispersive spectroscopy (EDS) [Tecnai F30], and X-ray diffraction (XRD) [X'pert MRD-Philips diffractometer]. Specimens for HREM and EDS were prepared under an ultrasonication process as follows: ZnO nanowires were ultrasonically dispersed in ethanol, and then drops of ethanol suspension were deposited onto carbon-coated holy Cu grids. After ethanol evaporated, those specimen were used for TEM observations.

Results and Discussion

X-ray diffraction measurement (Figure 1) and energy-dispersive spectrometry identify that the as-synthesized products are hexagonal wurzite ZnO crystals with lattice parameters of $c = 5.21$ Å, which is consistent with the reported value of ZnO crystals.[9]

Figures 2 and 3 show scanning electron microscopy and transmission electron microscopy images of ZnO morphologies at low magnifications, respectively. It is visualized that the products are composed of dendrite structured nanowires. The branching structure of ZnO nanowires resembles hypaethral antenna, which typically consist of four or three ramifications, as shown in Figure 3a,b. In rare case, some ramifications were found broken, as illustrated in Figure 3e, which might be caused by our TEM specimen preparation process. The diameters of nanowires are ∼100 nm and the lengths vary from hundreds of nanometers to several micrometers. It is worth mentioning that a terminal-bottleneck phenomenon (Figure 3b,c) was visible at the ends of some nanowires. In other words, diameters of some nanowires were frequently found to become narrow abruptly at terminal sections of those nanowires, most of which possess a sharp tip. Another interesting phenomenon was observed, as shown in Figure 3d: The terminals of two nanowires, which belonged to two ramifications of different dendrite units, crystallographically coalesced. As discussed in the following sections, these two phenomena, viz. terminal-bottleneck and terminal-coalescence, have implications for the evolved 1-D growth mechanism of ZnO nanowires. The microstructure of ZnO nanowires was further analyzed by HREM. The HREM images (Figure 4) of nanowires confirmed the single crystalline feature of nanowires and showed no defects or dislocations. In addition, several nanowires had a thin amorphous shell with a thickness of ∼4 nm, as indicated in Figure 5.

Because none of the metal catalyst is used during our synthesis process, the 1-D growth of ZnO nanowires cannot be dominated by the vapor−liquid−solid (VLS) mechanism.[10] Moreover, it is also unlikely to be explained by screw-dislocation evolved growth mechanism[11] because most of ZnO nanowires are free from defects and dislocations, as evidenced by HREM observations. In view of the above-mentioned terminal-bottleneck and terminal-coalescence phenomena, it is reasonable to consider that the 1-D growth process follows Sears' law.[12] Sears proposed a vapor−solid (VS) whisker growth model for the impingement of atoms onto a whisker side surface, temporary adsorption of impinging atoms, and diffusion of atoms along the lateral surface to a sink at the whisker tips. And those atoms not reaching the tip, being energy unstable, were removed by reevaporation.[12] According to Sears' theory, the 1-D growing process happened at the tip of a nanowire where there were enormous atom sinks. So the observed terminal-bottleneck phenomenon can be looked at as a frozen state of dynamic growth process. When the ends of two nanowires met occasionally during the growth, they could easily crystallographically coalesce together perfectly (Figure 3d). Incidentally, in the case of VLS, it is unlikely to find such phenomenon, because the crystal growth always takes place at the SL interface between the liquid alloy droplet and solid crystal.

The microstructure of the branching joint region, which might provide important information to understanding the nucleation and growth of dendrite structures, was characterized by TEM. The joint region of the branching structure was found to be multiply twinned, which showed a 3-fold symmetry (Figures 3 and 6a). Two sets of selected-area electron diffraction patterns shown in Figure 6b possess the zone co-axis of ZnO and are superposable by rotating, which reveals the twinned feature of the joint. In previous literature, various kinds of multiply twinned particles (MTP), such as decahedral MTPs and icosahedral MTPs, were usually found in preparation of fine crystalline particles (e.g., Si, Ge, and face-centered cubic metals) by a gas evaporation method.[13−15] The formation of MTPs is a consequence of minimization of surface energies of the par-

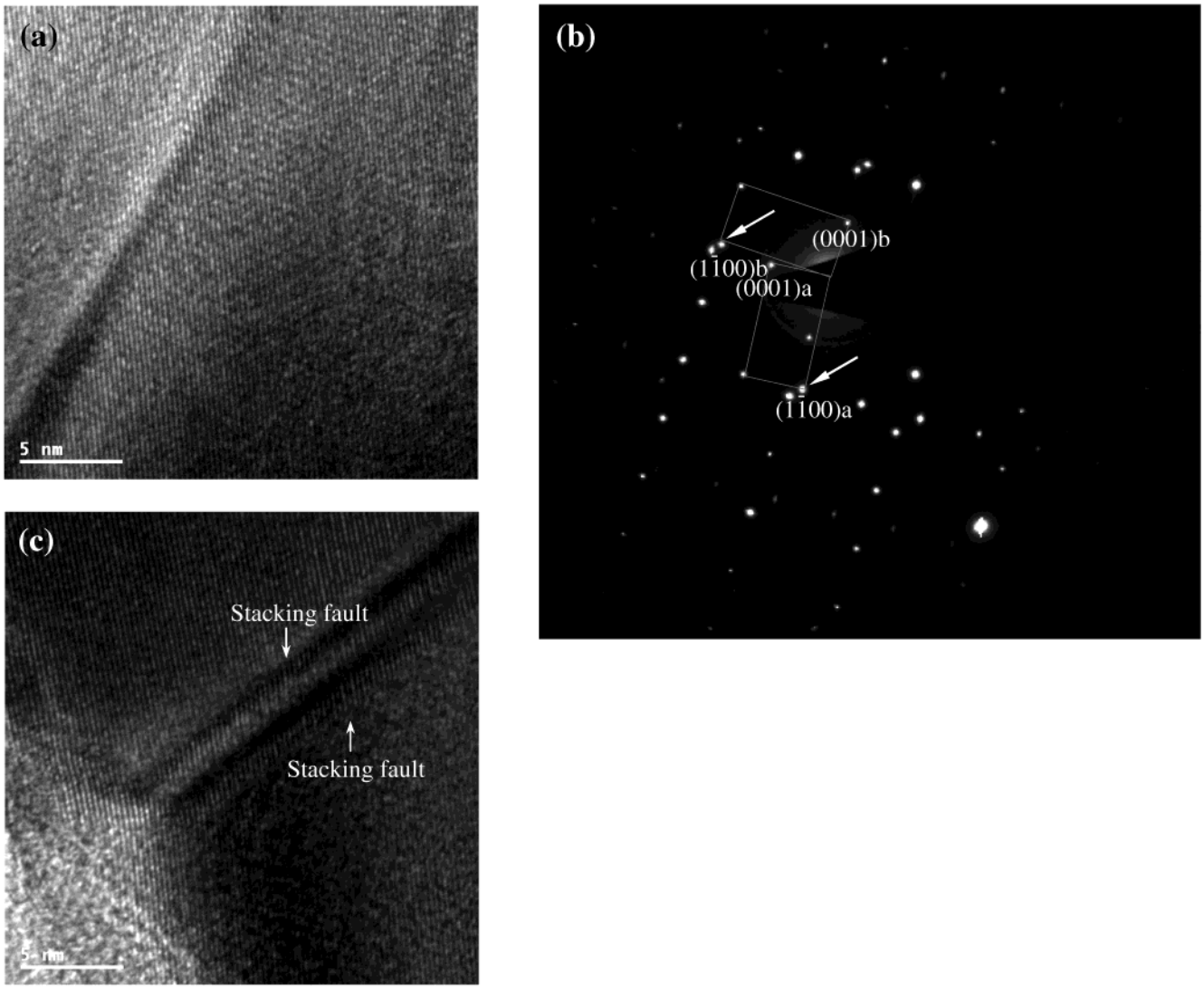

Figure 6. (a) Typical HREM image of the multiply twinned joint of the branching structure (an enlargement of the region B in Figure 3b). (b) Selected-area electron diffraction patterns of (a). Two sets of diffraction patterns corresponding to two grains within the multiply twinned joint were labeled as *a* and *b*. (c) HREM image of a pseudotwin plane.

ticles.[16] Based on the above TEM observations, it is reasonable to consider that deposited ZnO MTPs on a silica surface act as the nucleation centers for 1-D growth of the branching structure. ZnO MTPs are formed via evaporation and condensation of zinc vapors in the Ar ambient (Figure 3f). The O element of ZnO crystals might originate from residual oxygen in the apparatus. Instead of developing to faceted particles, these deposited ZnO MTPs grow to the branching structure. Namely, each grain within a ZnO MTP will develop to one ramification of the branching structure. Another Sears' crystal growth theory can be used to explain the initialization of the growth of the above branching structure: if the supersaturation is below the value required for forming the euhedral morphology of the crystal of some certain materials, anisotropic 1-D growth in specific crystal directions could occur.[12] Correspondingly, we speculate that the supersaturation in our case is expected to be below that required for forming the euhedral morphology of the ZnO crystal and then in favor of preferential 1-D growth in ZnO MTPs. Thus, the branching structure was formed. Such a process is illustrated as Figure 3g, which shows a ZnO multiply twinned nucleus at the early 1-D growth stage.

It is worth pointing out that the interface of the joint, in a rare case, is observed to be not twinned but separated by a group of stacking faults (Figure 6c). These phenomena of stacking-fault-related pseudotwin planes are similar to those observed in the Si decahedral MTPs by Iijima.[13] He pointed out that MTPs of Si sometimes incorporate small angle grain boundaries (SAG) or stacking faults to accommodate tetrahedron packing mismatch or to release lattice strain.[13]

In conclusion, high-purity dendrentic wurzite ZnO nanowires were synthesized on a thermally oxidized Si substrate by a simple physical vapor deposition method. The non-metal-catalyst approach guarantees the high purity of the products. ZnO nanowires are highly crystalline and free from defects. The 1-D growth mechanism of ZnO corresponds to the Sears model. The branching structures typically possess three or four ramifications. The formation of multiply twinned ZnO particles on silica surfaces and at a lower supersaturation than required for forming euhedral morphology is responsible for the formation of the branching structure. The joint-center multiply twinned ZnO nanowires carry information on the inherent anisotropic traits of the wurtzite ZnO crystal.

Acknowledgment. We gratefully acknowledge financial support from the National Natural Science Foundation of China (Grant No. 50025206), the Research Fund for the Doctoral Program of Higher Education (RFDP) of China, and the Jun-

Zheng Fund of Peking University, China. Y.Z. and H.J. contributed equally to the work.

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