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A Novel Method for the Formation of Ladder-like ZnO Nanowires

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ABSTRACT: This study introduces a simple approach for forming ladder-like nanowire arrays. The number of apparent steps of the ZnO nanowires could be increased by the number of vapor phase transport deposition processes. The growth of two diverse forms on different planes led to the ladder-like appearance of the nanowires: a coherent characteristic on ZnO$\{10\bar{1}0\}$ prismatic planes and epitaxial growth on ZnO(0002) planes. The $\{10\bar{1}0\}$ planes are much more stable than (0002) planes, and the $\{10\bar{1}0\}$ planes permit boundaries procreation.

1. Introduction

Zinc oxide nanomaterials that appear one-dimensional (1D) have attracted great attention in recent years because of their potential applications in both nanoscale electronic and optoelectronic devices.[1−4] Well-controlled growth of the nanomaterials is essential to the production of nanodevices. Some useful techniques for making vertical, well-ordered 1D ZnO nanomaterials arrays, such as using templates as supports,[5] the characteristics of catalysts in the vapor−liquid−solid (VLS) process,[6,7] and using buffer layers,[2,8−13] have been investigated. However, only a few studies, such as those of nanowire hybrid columnar film nanostructure, from nanowires to nanorotors structures and from nanowires to nanotubes structure, have addressed the changing of the morphology of 1D nanomaterials.[4,14,15] This study introduces a simple method to form ladder-like nanowires and discusses their mechanism of formation.

2. Experimental Section

Before ZnO nanowires were grown, a 100-nm-thick Ga-doped ZnO film was deposited directly on glass substrates by radio frequency sputtering. X-ray diffraction measurements showed the ZnO:Ga buffer layer was preferably oriented in the 0002 direction. Then, the ZnO nanowire was grown by vapor phase transport deposition (VPTD)[2,11] on buffered glass without a metal catalyst or other template. The VPTD process was repeated twice to renew the Zn metal powder and to ensure the vital Zn vapor supply, to generate a ladder-like appearance. The conditions of each VPTD process are as follows.

The zinc vapor source was Zn metal powder with a purity of 99.9%, obtained from Strem Chemicals. The substrates and zinc vapor source in an alumina boat were inserted into the quartz tube and placed close to the middle of the furnace. The distance between the Zn source and the substrate was only 30 mm, and the zinc vapor source was placed on the upstream side. A constant stream of argon flowed through the reaction system. A mechanical pump was used to evacuate the system to maintain the pressure inside the quartz tube at about 10 Torr. The heating ramp was set to 20 °C/min. The experiments lasted for 30 min after the furnace reached the reaction temperature (600 °C). Afterward, the power to the furnace was turned off, and the sample was cooled in the quartz tube until the temperature was below 100 °C.

A JEOL JEM-2100F high-resolution transmission electron microscope (HRTEM), operated at 200 kV, was then used to characterize the crystallography and structure of the nanowires. The morphologies of the samples were characterized using a JEOL JSM-6500F field emission scanning electron microscope (FESEM), operated at 5 kV.

3. Results and Discussion

Figure 1a shows an FESEM image of the nanowires grown by a single VPTD process. The diameters of the hexagonal-prism appearance of nanowires are about 70−200 nm, and the diameter of each single nanowire is uniform from the bottom to the top in Figure 1a. Figure 1b−d presents FESEM images of nanowires that were grown by two VPTD processes. Every nanowire has a two-step ladder-like appearance, in which the diameter of the bottom half exceeds that of the top half after the two VPTD processes.

Figure 2 presents HRTEM images of the sample that was grown by two VPTD processes. Figure 2a shows an HRTEM image of the area near the step of one of the ladder-like nanowires. The lattice images of the jog and core areas are similar, and the interface is difficult to identify. Figure 2b depicts a Fourier transformed pattern that corresponds to the area outlined by the white dashes in Figure 2a. Figure 2c exhibits a filtering lattice image revealing only the reciprocal lattice points between the two white arrows in Figure 2b (i.e., $\bar{g} = n \times 0001$, where n are integers). The filtering lattice image clearly reveals the interface along the misconnection of the (0002) planes, as outlined by the white dashed−dotted line. The interface of the jog and the core in Figure 2a exhibits a low-angle boundary. In fact, the relationship between the jog and the core is not epitaxial. The connection depends only on the coherence between their (0002) planes, the extent to which the axes of the jog and the core are parallel to each other, as shown in Figure 2a,d. Figure 2d shows an HRTEM image of another ladder-like nanowire in which the axes of the jog area and the core area are rotated through a large angle with respect to each other.

The surfaces of a hexagonal-prism ZnO nanowire are typically (0002) and $\{10\bar{1}0\}$ planes, and the areas of the $\{10\bar{1}0\}$ planes exceed those of (0002),[15,16] as shown in Figure 3a. This feature implies that these two planes have the lowest surface energy, and the surface energy of the $\{10\bar{1}0\}$ planes is much lower than that of (0002) under the conditions used for nanowire growth. For the second VPTD process, the ZnO grows on hexagonal-prism ZnO nanowires, which had been grown in the first VPTD process. Restated, the second ZnO grows on seven surfaces of the hexagonal-prism ZnO nanowire: one is the top (0002) plane, and the other six are $\{10\bar{1}0\}$ prismatic planes. The relationship between the first and the second growths on the $\{10\bar{1}0\}$ prismatic planes depends just upon the coherence of their (0002) planes at the interface. Their

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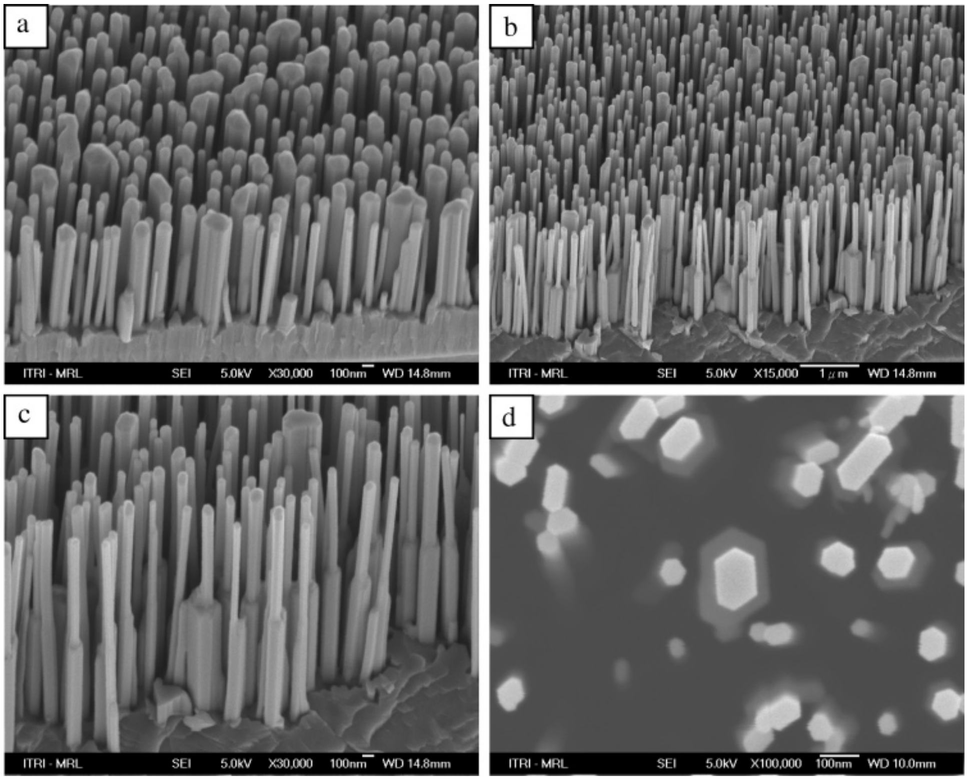

Figure 1. FESEM images of ZnO nanowires. (a) Nanowires with hexagonal-prism features grown by single VPTD process. (b−d) Two-step ladder-like nanowires grown by two VPTD processes. (a−c) Oblique view and (d) plane view.

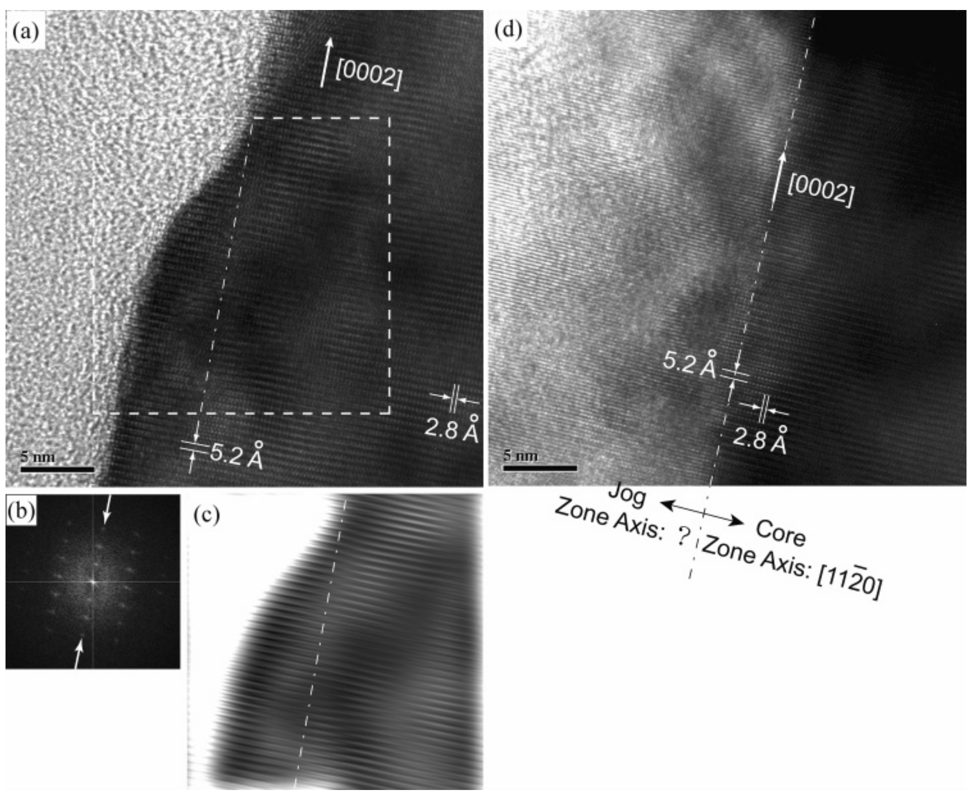

Figure 2. HRTEM analyses of two-step ladder-like nanowires. Panels (a) and (d) are HRTEM images of the jog/core interface area. (b) Fourier transformed pattern that corresponds to the area outlined by white dashed line in (a). (c) Filtering lattice image revealing only the reciprocal lattice points between the two white arrows in (b). The jog/core interfaces were outlined by white dashed−dotted lines in (a), (c), and (d) for ease of identification.

axes are rotated with an arbitrary angle, as shown in Figure 3b. The second growth on the {$10\bar{1}0$} prismatic planes prevents the crabwise extension of the second growth on the top (0002) plane. If the second growth on the top (0002) plane extends perpendicular to the axis, then a misfit intersection area proliferates on the top (0002) plane, as shown in Figure 3c, and the surface energy rises rapidly. HRTEM measurements indicate that the cores of the ladder-like nanowires are identically orientated such that the rotation of

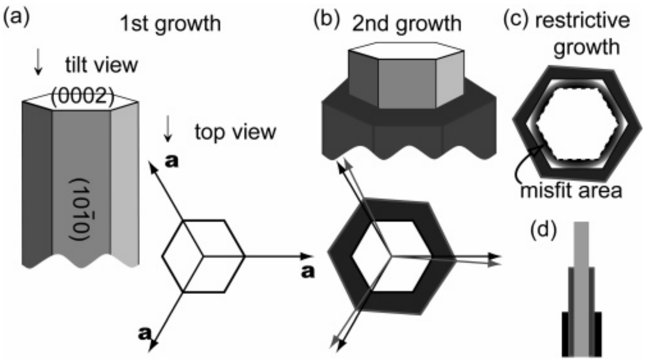

Figure 3. Sketches of first (a), second (b), and third (d) growth of the nanowires. (c) Restrictive growth in the second VPTD process.

the misfit area along the axis was not observed. Accordingly, the second growth on the top (0002) plane must follow the homogeneous epitaxy along the axis without crabwise extension. Two forms of growth on various planes result in the ladder-like appearance of the nanowires. Consequently, the nanowires have a three-step ladder-like appearance after three VPTD processes for the same reason (Figure 3d).

Figure 4 shows FESEM and cross-sectional TEM images of the nanowires that were grown by three VPTD processes. The three-step ladder-like appearance of the nanowires is clearly presented. The number of apparent steps of the ZnO nanowires could be increased by the number of VPTD processes on the same account.

4. Conclusion

This work reports a novel approach to preparing ladder-like ZnO nanowires arrays. Two diverse forms of growth on prismatic and (0002) planes result in the ladder-like appearance of the nanowires. The {10$\bar{1}$0} prismatic planes of ZnO are much more stable than the (0002) planes under the conditions in which the nanowires are grown. Interfaces present on the ZnO{10$\bar{1}$0} prismatic planes cause of a rotation of the crystal orientation through an arbitrary angle. However, a similar interface is not observed on ZnO (0002), even through the rotation is extremely small.

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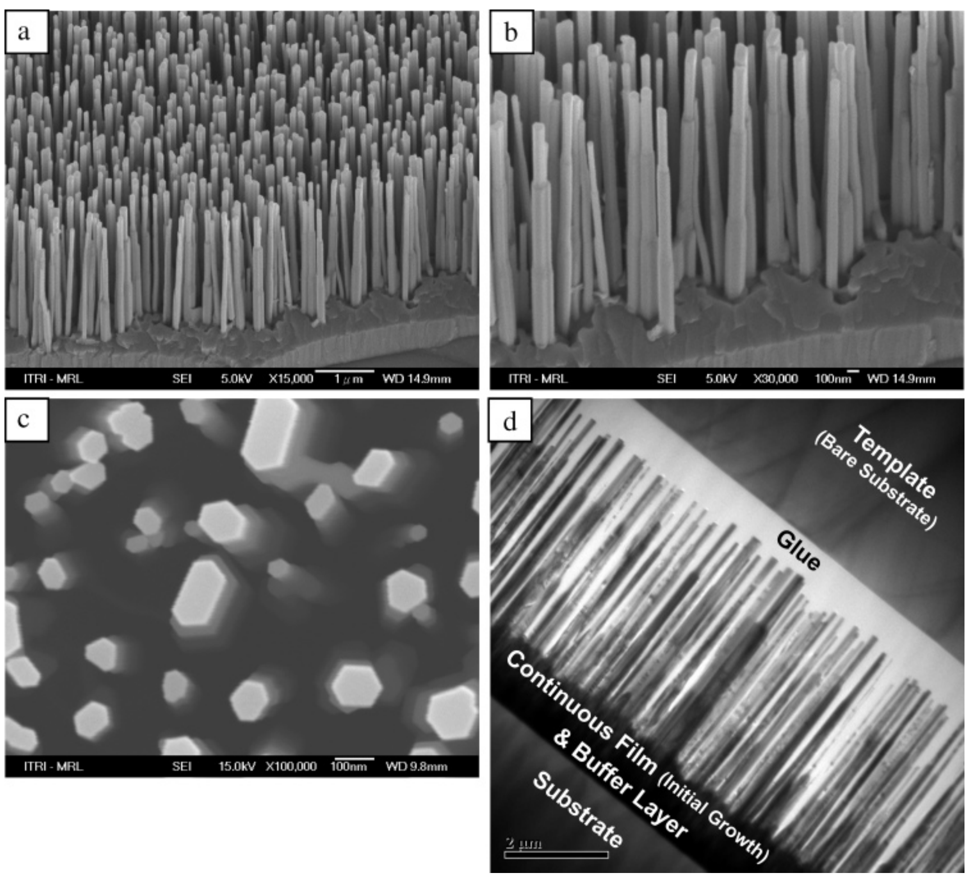

Figure 4. FESEM (a−c) and cross-sectional TEM (d) images of ZnO nanowires by three VPTD processes. (a), (b) observed obliquely; (c) plane view.