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Letters

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Structural and optical properties of ZnO nanotower bundles

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ZnO nanotower bundles have been grown on the electrochemically deposited ZnO thin film by a simple hydrothermal process. The influence of surface/interface defects on the structural and optical properties is studied by x-ray diffraction, selected area electron diffraction, and photoluminescence techniques. The formation of ZnO nanotowers and defects may be attributed to kinetic confinement and thermodynamic processes. A wide visible emission band covering nearly the entire visible region is related with the surface/interface defects. By controlling the surface area-to-volume ratio and the width change of the single ZnO nanotower, the emission properties of ZnO nanotowers can be well modified. © 2006 American Institute of Physics. [DOI: 10.1063/1.2188386]

ZnO is currently attracting increasing attention because of its electronic properties, i.e., a semiconducting bandgap of about 3.3 eV and a large exciton binding energy of 60 meV, and the possibilities for an application in optoelectronic devices. Furthermore, the intrinsic anisotropy and the higher surface energy in the polar surface for ZnO promote the preferential growth along the [0001] direction. As a result of this, one-dimensional (1D) ZnO can be obtained under appropriate conditions.^{1,2} In general, the 1D structure can naturally provide a directed path for electron transport, which makes 1D ZnO become one of the ideal materials for the study of quantum confinement effects and nanodevice physics. Accordingly, extensive research has been focused on 1D ZnO nanostructures including ZnO nanowires,3 nanobelts,4 nanorods, and nanotubes.^{5,6} The traditional approaches to synthesize 1D ZnO nanostructures are the template-assisted growth, ⁷ vapor phase deposition and wet chemical method.^{8,9} Some defects such as stacking faults, twins, bicrystals, dislocations, and point defects can be observed in nanostructures.^{10,11} These defects have a significant effect on the structure and properties of 1D ZnO. However, the formation mechanism of defects and their influence on the structure and properties of 1D ZnO nanostructures were less discussed in previous publications. In fact, the chemical bonds around the defects differ from those of the bulk, which often dramatically changes the structural, thermodynamic, optical and electronic properties of the materials, which in turn can provide some novel properties for new potential applications in nanotechnology.¹² In this aspect, an example includes pentagon-heptagon defects in carbon nanotubes,13 which makes carbon nanotubes exhibit nonlinear transport characteristics resembling those of rectifying diodes in siliconbased microelectronics. Huang et al. recently reported a novel phenomenon that periodic defects located at ZnO wellfaceted fibers with periodic junctions produced periodic enhanced green-light emissions.¹⁴ This can be used as nanoscale light-emitting arrays and barcodes for biotechnology and electronics. Further, understanding the influence of the local defects on the overall material properties and controlling the defect structures is one of the greatest challenges in order to manipulate these materials to an industrial application.

In this paper, we have fabricated 1D ZnO nanotower bundles by the hydrothermal process. The hydrothermal technique has several clear advantages: a high reaction rate, good dispersion in liquid, almost pollution free, low cost, simplicity, and energy conservation.¹⁵ We investigated the effects of defects on the structural and optical properties of ZnO nanotower bundles and explained the broadening of a visible emission band by developing the model for the visible emission mechanism, as proposed by Dijken *et al.*¹⁶ Further, by controlling the size and shape of ZnO nanotowers to control surface/interface defects, the optical properties can also be well controlled, indicating a large potential for the fabrication of nanoscale devices.

ZnO nanotower bundles were grown on cleaned ITO glass via a two-step process. In the first step, a thin ZnO seed layer was deposited electrochemically on the ITO substrate to minimize the interfacial energy between crystals and substrates increasing seed number density and promoting the nucleation process. Without the first step, only a small quantity of ZnO nanotower bundles can be obtained because of the low nucleation rate on the substrate at the initial stage. The aqueous solution used for deposition contains 0.005 mol/L zinc chloride and 0.1 mol/L potassium chloride. A platinum wire was used as the counterelectrode and the Ag/AgCl electrode was employed as the reference electrode. The reaction was performed at a constant potential of -0.6 V versus the reference electrode. After deposition at 60 °C for 0.5 h, the substrate was vertically immersed into

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FIG. 1. (a) SEM images of ZnO nanotowers; (b) XRD pattern of ZnO nanotower bundles.

the aqueous solution of 0.025 mol/L zinc nitrate and 0.025 mol/L methenamine in an autoclave. Subsequently, sealed and heated at 90 °C for 3 h, the autoclave was cooled to room temperature.

Figure 1(a) shows the scanning electron microscope (SEM) images of ZnO nanostructures. It is clearly illustrated that the grown nanostructure is like a tower, i.e., a nanotower. The width at the top of the single nanostructure is smaller than the width of the nanotower bottom. At the bottom, several tens of the individual nanotowers are jointed together. These characteristics imply that ZnO nanoparticles in solution had selectively aggregated onto the surface of the substrate at the initial stage and then the nanotower structures grew into bundles from the nucleation sites in various directions. Each ZnO nanotower has a regular hexagon cross section with typical length of 1 to 4 μ m, originating from the sixfold symmetric structure of ZnO c plane. The single ZnO nanostructure has an uneven diameter along its entire length, which can be understood based on kinetics. Since the (0002) plane of ZnO has a highest surface energy as the most instable plane, zinc or oxygen atoms tend to be adsorbed to the (0002) surface resulting in the growth of ZnO nanostructure along [0001] direction. The tower-like growth pattern may originate from the fast growth rate. The fast growth rate makes Ostwald ripening only affect the ZnO crystal morphology slightly and the kinetic confinement results in the presence of steps on the side surface of ZnO.¹⁷

The x-ray diffraction (XRD) result is illustrated in figure 1(b). The obtained ZnO nanotower bundles are of the hexagonal wurtzite structure with lattice constants of a=3.243 and c=5.196 Å. All diffraction peaks of ZnO nanostructures shift toward larger angles compared with standard bulk ZnO data,¹⁸ suggesting a decrease of the interplane distance. The observation may be attributed to the existence of compressible stress in the lattice. As discussed below, transmission electron microscope (TEM) measurement confirms the presence of the local strain.

Figure 2 is the TEM image of the individual ZnO nanotower. A selected area electron diffraction (SAED) pattern corresponds to the region as marked by the circle in Fig. 2. The inset in the down left corner of Fig. 2 shows an enlarged SAED pattern with a compound diffraction image, where there are two cross lines at a very small angle along c axes to form two group lattice diffractions, indicating the existence of two crystal phases. The finding further suggests that the individual ZnO nanotower is not a single crystal but an assembly of single crystals. Between two adjacent single crystals, there are many edge dislocations to parallel to the (0002) plane, leading to the formation of the interface layer. When the local strain is beyond the structural endurance, a plastoelastic deformation in the lattice occurs. As a result, the



FIG. 2. TEM image and SAED pattern for the individual ZnO nanotower.

edge dislocations will be formed to release elastic energy created by strain and thereby to decrease the system energy. As for the formation mechanism of the edge dislocations, the relatively rapid growth rate in a unequilibrium system may be the reason of the formation of the defects in the growth process of the free-standing nanotowers to lower the system energy. The edge dislocations, in turn, may play an important role in the growth of a 1D tower-like structure. From the kinetics point of view, the aggregation may be naturally facilitated near the dislocation, which dramatically accelerates the growth process of ZnO nanostructures and affects the shape of nanostructure.

By changing substrates and growth temperatures, ZnO nanostructures with different sizes and shapes can be well controlled and their photoluminescence (PL) spectra are measured using a 325 nm He–Cd laser. Figures 3(a)-3(c), respectively, show the SEM images of ZnO nanostructures grown on a Si substrate at 90 °C, the ZnO seed layer coated ITO substrates at 90 °C, and powder collected in solution at 150 °C. It is interesting that the single nanotower grown on



FIG. 3. SEM images of ZnO nanotowers (a) grown on a Si substrate at 90 °C. (b) Grown on the seed layer coated ITO substrate at 90 °C. (c) Powder collected in solution at 150 °C; (d)–(f) PL spectra of ZnO nanotowers, respectively, corresponding to different ZnO nanostructures in (a)–(c).

Si substrates always shows a shape more similar to a hexagonal prism and the side facets are very smooth. If the growth temperature is higher (150 °C), the ZnO nanotowers show a larger sidewall angle compared with those obtained at lower temperature. The corresponding PL spectra are given in Figs. 3(d)-3(f). All spectra are composed of the ultraviolet (UV) emission peak and the visible emission band. The UV peak is known due to the exciton emission. In general, the visible emission ranging from 440 to 600 nm is associated with structural defects. In the current PL measurements, the visible emission of ZnO nanotower bundles has a much broader band from 440 to 800 nm. This observation differs from the reported data in most literature but it is similar to the results obtained by Yang et al.¹⁹ We think that the visible emission is correlated with the surface/interface defects of ZnO nanotower bundles. Dijken et al. have proposed that upon photon excitation, the created valence band holes can be trapped by surface states and then tunnel back into oxygen vacancies containing one electron (V_{Ω}^{*}) to form a V_{Ω}^{**} recombination center, leading to the visible emission by the recombination between a shallowly trapped electron and a deeply trapped hole in a $V_{\rm O}^{**}$ center.¹⁶ In the current experiments, abundant surfaces/interfaces in ZnO nanostructures will introduce a fairly high density of surface/interface defects to form defect energy bands, which can trap free carriers from the bulk. Accordingly, the trapped photogenerated holes in surface/interface states tunnel back not only into $V_{\rm O}^*$ to form a V_0^{**} visible emission center, but also a deeply trapped hole in the interface defect band combined with a shallowly trapped electron to cause visible emission. As a result, the broadening of visible emission is obtained.

Since the optical properties are related to surface/ interface defects, the optical properties should be modulated and controlled by the control of surface and interface features of ZnO nanostructures, as shown in Fig. 3. For the single ZnO nanostructure, the size decreases gradually and the width changes more obviously from samples (a)–(c). A smaller size implies a larger surface-to-volume ratio and the more obvious width change from the end of the single ZnO nanostructure to its top indicates more interfaces existing in the ZnO nanostructures. Therefore, more surface/interface defects will cause the decrease in the intensity ratio of UV peak to visible emission band, as shown in Fig. 3.

We have synthesized ZnO nanotower bundles on the ZnO thin film by the simple hydrothermal process at a mild temperature of 90 °C without using any catalyzers or tem-

plates. The shifts in the XRD spectrum and the twin lines in the SAED pattern indicate the existence of a high level of surface/interface defects in nanotower structures. The broadening of the visible emission band may also be related to the surface/interface defects. The size and shape of ZnO nanostructures can well control surface/interface defects, and hence can control their optical properties. This indicates the important application in manipulating the ZnO material for nanoscale electronic and optoelectronic devices.

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