Heterostructures of ZnO–Zn coaxial nanocables and ZnO nanotubes

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The heterostructures of Zn–ZnO coaxial nanocables and ZnO nanotubes with an average diameter of 30 nm have been synthesized by simple pyrolysis of zinc acetylacetonate. High-resolution transmission electron microscopy analyses reveal that the Zn core and the ZnO sheath of the nanocables have an epitaxial relationship with their longitudinal axis oriented along the $\langle 001 \rangle$ direction. ZnO nanotubes with a wall thickness of 4 nm possess a single-crystal structure and appear to be the extension of the ZnO sheath of the coaxial nanocables. It is suggested that the ZnO nanotubes are formed by partial evaporation of Zn core of the Zn–ZnO coaxial nanocables. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1499512]

Since the discovery of carbon nanotubes,[1] one-dimensional (1D) nanometer-sized materials have attracted much attention owing to their great potential for fundamental studies as well as for applications in nanodevices and functional materials.[2] In addition to nanotubes, nanowires and nanorods, other interesting 1D nanostructures such as nanocables,[3] nanoribbons,[4] and nanobelts[5] have been demonstrated recently. ZnO is a versatile material and has been used considerably for its catalytic, electrical, optoelectronic, and photochemical properties.[6] As a gas sensing material, it is one of the earliest discovered and an important oxide semiconductor sensitive to many sort of gases with satisfactory stability.[7] ZnO also has been demonstrated as a promising material for a dye-sensitized oxide semiconductor solar cell.[8] Moreover, due to its wide direct band gap of 3.37 eV and large exciton binding energy of 60 meV at room temperature, ZnO is recognized as a promising photonic material in the blue-UV region.[9] It is predicated that the gas sensing, photon-to-electron conversion efficiency and photonic performance would be enhanced by reducing the dimensions of ZnO structures because of surface area increase and quantum confinement effect. Growth of 1D ZnO nanostructures including nanowires,[10] nanorods,[11] and nanobelts[5] have been demonstrated recently. In this letter we report on the synthesis of the heterostructures of ZnO–Zn coaxial nanocables and ZnO nanotubes by simple pyrolysis of zinc acetylacetonate. The tubular ZnO nanostructures, providing a different shape and higher surface area, might exhibit some interesting physical and chemical properties unattainable by other nanostructures.

Heterostructures of ZnO–Zn coaxial nanocables and ZnO nanotubes were synthesized in a two-temperature-zone furnace. Zinc acetylacetonate hydrate $[\mathrm{Zn}(\mathrm{C_5H_7O_2})_2 \cdot x\mathrm{H_2O}$, Lancaster, 98%] placed on a cleaned silicon suscep-tor was loaded into the low temperature zone of the furnace which was controlled at 130–140 °C to vaporize the solid reactant. The evaporated gaseous species were carried by a 500 sccm $\mathrm{N_2}$ flow at a total pressure of 200 Torr into the higher temperature zone of the furnace which was set at 500 °C. Black products were formed on the wall of the quartz tube in the region down stream out of the higher temperature zone with a temperature of 230 °C. The morphology and size distribution of the products were examined using scanning electron microscopy (SEM) (Hitachi, S-4200). The microstructures of the nanostructured materials were analyzed using transmission electron microscopy (TEM) (JEOL, JEM-4000EX, and JEOL 2010). Energy dispersive spectrometry (EDS) equipped on a TEM (JEOL 2010) was employed to perform the elemental analyses of the nanostructured materials.

Uniform nanowire-like morphology of the black products is observed from SEM, as shown in Fig. 1(a). The average diameter of the 1D nanostructures is around 30 nm. The low-magnification TEM image illustrated in Fig. 1(b) shows that some tubular and very few nontubular hollow nanostructures (as indicated by an arrow in the bottom left region of the micrograph) are observed among the nanowires. Further magnified TEM image, as shown in Fig. 1(c), provides a clearer view of these 1D nanostructures. It reveals that the solid 1D nanostructure possesses a coaxial structure, that is, a thin sheath with lighter contrast is formed outside the surface of nanowire-like structure of dark contrast. Moreover, some of the tubular nanostructures are connected with the coaxial nanocables. As shown in Fig. 1(c), the tubular structures and the sheath material have the same thickness and similar contrast. It appears that the tubular nanostructure is the extension of the outermost layer of the coaxial nanocable.

Figures 2(a) and 2(b) show the EDS spectra of the coaxial nanocable and the nanotube, respectively. They reveal the presence of the Zn, O, Cu, and C. Copper and carbon

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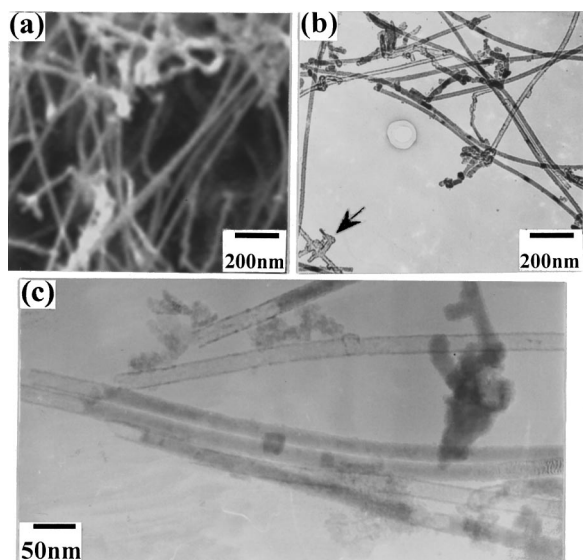
FIG. 1. (a) SEM image of the black products by pyrolysis of zinc acetylacetonate. (b) Low-magnification TEM image of the black products by pyrolysis of zinc acetylacetonate. (c) TEM image of the heterostructures of the coaxial nanocables and the nanotubes.

FIG. 3. (a) High-resolution TEM image of the heterostructure of the coaxial nanocable and the nanotube. (b), (c) The corresponding diffraction patterns of the nanotube and the nanocable, respectively.

signals should be contributions of the copper grid coated with porous carbon film for supporting samples. Thus, the coaxial nanocables and nanotubes heterostructures are composed of zinc and oxygen only. Quantitative analyses of these EDS spectra show that the atomic composition ratios of Zn/O are 86:14 and 57:43 for the coaxial nanocable and the nanotube, respectively.
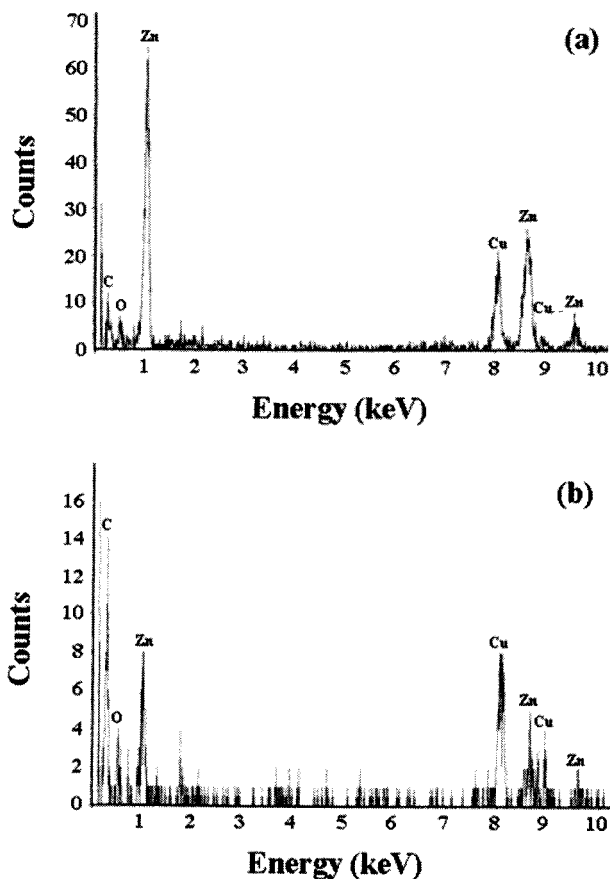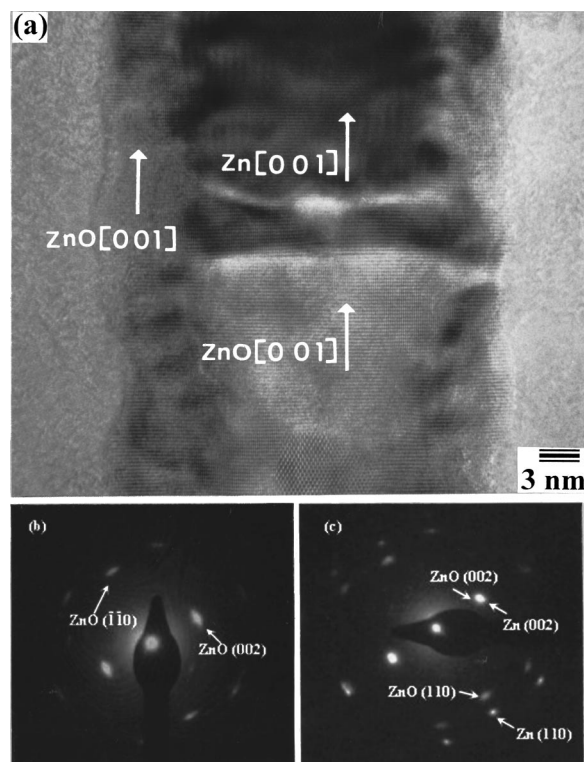

FIG. 2. (a), (b) The EDS spectra of the coaxial nanocable and the nanotube, respectively.

A high-resolution TEM (HRTEM) image of the heterostructure of nanotube and coaxial nanocable as well as the corresponding diffraction patterns are shown in Fig. 3. The HR image reveals that both the sheath and the core portions of the nanocable and the nanotube exhibit clear lattice images, indicating well crystallized structures. The thickness of the sheath of nanocable and the wall of nanotube are both around 4 nm. With the quantitative EDS result, the diffraction pattern of the nanotube is identified to be the hexagonal ZnO with zone axis $[1\bar{1}0]$, as shown in Fig. 3(b). The darker contrast on the edge and appearance of lattice image in the central region typically observed in the HRTEM image of the ZnO nanotube are consistent with simulation results of HRTEM images of a multiwall nonhelical (achiral) carbon nanotube calculated by a MAC TEMPAS program.[12] The diffraction pattern of the coaxial nanocable, as shown in Fig. 3(c), is composed of two sets of single crystal diffraction patterns with epitaxial relationship. The two sets of diffraction patterns are indexed as the hexagonal Zn and ZnO with zone axis $[1\bar{1}0]$ by referring to the quantitative EDS analysis also. We suggest that the sheath and the core of the coaxial nanocable are ZnO and Zn, respectively, due to the low diffraction intensity of ZnO in the nanocable diffraction pattern and the consistency of the lattice spacings of the nanotube with the sheath of the nanocable in the HRTEM image. Furthermore, the HRTEM image indicates that both ZnO–Zn nanocable and ZnO nanotube are grown along the $\langle 001 \rangle$ direction. Therefore, we conclude that the 1D heterostructures, which are composed of Zn–ZnO coaxial nanocables and ZnO nanotubes with longitudinal axis along the $\langle 001 \rangle$ direction, are formed by simple pyrolysis of zinc acetylacetonate. It should be noted here that no additional metal is

present in this process, indicating that ZnO nanostructures were grown by a nonvapor-liquid-solid method. A possible mechanism for the formation of the heterojunction of Zn–ZnO coaxial nanocables and ZnO nanotubes is proposed as follows. Zn nanowires with longitudinal axis along the $\langle 001 \rangle$ direction were formed by pyrolysis of zinc acetylacetonate at a temperature lower than 500 °C. Under catalyst-free environment, the nanowire morphology is presumably a result of the growth rate being highly anisotropic along different crystal orientation. Due to the low oxygen concentration in the N_2 ambient from decomposition of $Zn(C_5H_7O_2)_2$, the surface of the Zn nanowires could be oxidized to form a thin oxide sheath. Both Zn and ZnO exhibit a hexagonal structure, and a ZnO layer around a Zn nanowire was therefore epitaxially formed. While passing through the 500 °C zone with N_2 flow, Zn metal with low melting point (410 °C in bulk) was vaporized out of the nanocable, resulting in partial evacuation of the core of the nanocable. Since the structure of the ZnO shell would not be destroyed at a temperature of 500 °C, the Zn liquid that remained in the nanocable would crystallize epitaxially with the ZnO shell. Therefore, the heterojunction of the Zn–ZnO coaxial nanocable and the ZnO nanotube was formed finally. In contrast to the conventional anodic alumina template assisted method for forming nanotubular structures within the pores of the anodic alumina membranes,[13] the present study demonstrates a spontaneous formation of single crystalline ZnO nanotubes from Zn nanowires templates. An alternative speculation on the formation of the heterojunction structure is that the ZnO nanotube is simply formed at a high temperature zone as an extension of the ZnO shell portion of the Zn–ZnO coaxial nanocable. However, the formation mechanism of the nontubular hollow ZnO structure as shown in Fig. 1(b) is unclear.

In summary, we have demonstrated the formation of the heterostructures of Zn–ZnO coaxial nanocables and ZnO nanotubes by simple pyrolysis of zinc acetylacetonate. ZnO nanotubes possess single crystal structure and appear to be the extension of the ZnO sheath of the coaxial nanocables. The Zn core and the ZnO sheath of the nanocable have epitaxial relationship with their longitudinal axis oriented along the $\langle 001 \rangle$ direction. It is suggested that the ZnO nanotubes are formed by partial evaporation of the Zn core of the Zn–ZnO coaxial nanocables. The Zn nanowires could be considered as the templates for subsequent spontaneous formation of single crystalline ZnO nanotubes.

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