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钢掺杂氧化锌-氧化硅纳米电缆芯-壳异质结构的制备及表征

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摘要: 利用碳热还原反应气相沉积法制备了钢掺杂氧化锌-氧化硅纳米电缆芯-壳异质结构. X 射线衍射(XRD)、透射电子显微镜(TEM)及 X 射线能谱(EDS)研究表明, 纳米电缆内芯为结晶完好的单晶纤锌矿结构, 外壳包覆一层氧化硅非晶层. 纳米电缆直径为 30–60 nm, 长径比大于 100. 掺杂纳米异质结构的生长机理与传统的金属晶种辅助气-液-固(VLS)机理有所不同. 这种掺杂纳米异质结构有望作为理想的结构单元应用于纳米器件领域.

关键词: 纳米结构; In-掺杂; 氧化锌; 纳米电缆; 生长机理
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Fabrication and Characterization of In/ZnO-SiO_x Core-Shell Nanocable Heterostructures

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Abstract: Indium doped ZnO-SiO_x core-shell nanocable heterostructures were successfully fabricated by introducing In ions into the raw material *via* a simple thermal evaporation process. X-ray diffraction (XRD), transmission electron microscopy (TEM), and energy dispersive X-ray spectroscopy (EDS) were used to investigate the structure of the In/ZnO-SiO_x core-shell fibers. Results indicated that the core zone of ZnO nanocables is single crystalline In/ZnO with a wurtzite structure and the shell zone is a SiO_x amorphous layer. The nanocables have high aspect ratio of more than 100 with widths of 30–60 nm. The growth mechanism of the nanocable heterostructures is different from the commonly reported metal-seeded vapor-liquid-solid (VLS) mechanism. The synthesis of core-shell structures reveals the general potential of radial heterostructure growth for the development of nanowire-based devices.

Key Words: Nanostructure; In-doping; ZnO; Nanocable; Growth mechanism

As a II-IV compound, zinc oxide is an important semiconductor with a wide band gap and large exciton binding energy of 60 meV which is much higher than those of other materials, such as ZnS (40 meV) and GaN (25 meV). Moreover, ZnO has also been investigated as transparent conducting materials with piezoelectricity, and has wide range of applications including photoelec-

tric devices, sensors, catalysts, composites, etc. In the past several years, one-dimensional (1D) ZnO nanostructures have attracted considerable attention for their fascinating physical-chemical properties and potential applications for nanodevices^[1-5]. The understanding on the subjects of fabricating, characterization, and utilities for various ZnO nanostructures have made great progress^[6-9].

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Several research groups have demonstrated that nanoscale electronic and optoelectronic devices can be built up based on ZnO nanostructures which are intensively promptive for actual applications^[10–12].

In order to enhance the properties of ZnO nanophase materials, it is feasible for producing ZnO nanostructures with controlled dimension and morphology as well as doping using groups III, IV, and V elements. Recently, various doped ZnO nanostructures with different elements (e.g., Al, Ga, In, Sn, and Sb) have been achieved^[13–18]. It is demonstrated that the properties of ZnO nanostructured materials, such as photoluminescence, field emission, and magnetic properties, can be modified by doping. In previous study, In was considered as one of the most important doping elements for improving the piezoelectric properties of ZnO^[19–21]. However, up to now, little progress has been made on the preparation of In-doped ZnO nanocable heterostructures, which have potential applications as building blocks in electrical/optical nano-devices. In this paper, In-doped ZnO-SiO_x core-shell nanocable heterostructures were successfully fabricated by a simple thermal evaporation process. The structure of the In/ZnO-SiO_x core-shell nanocables was investigated. A possible growth mechanism was also discussed.

1 Experimental

In-doped ZnO nanocable heterostructures were fabricated by thermal evaporation under controlled conditions. The mixture of zinc (purity 99.9%, 50 μm in size), In₂O₃ (purity 99.9%, 50 μm in size), and graphite powders (purity 99.9%, 40 μm in size) with the mole ratio of 3:1:2 was placed in an Al₂O₃ boat inside a quartz tube as the evaporation source. A silicon substrate coated with a thin layer of H₂AuCl₄·3H₂O was then positioned on the top of the source boat fixed by a brass wire. Ar was used as carrier gas, and O₂ was the reaction gas. The total flow rate of Ar (98%) and O₂ (2%) was about 300 cm³·min⁻¹. The synthesis process was conducted at 930 °C for 15 min.

The morphologies and structures of the products were investigated by X-ray diffraction (XRD) (Rigaku DMAX-RB, Japan), high-resolution transmission electron microscopy (HRTEM) (JEOL-2010, Japan, operating at 200 kV), and energy dispersive X-ray spectroscopy (EDS) (Oxford, England).

2 Results and discussion

A typical XRD pattern of the as-grown In/ZnO fibers is

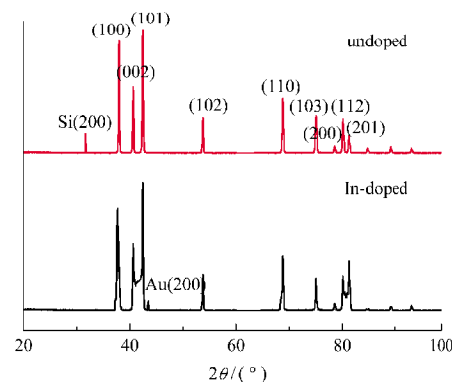


Fig.1 XRD patterns of undoped and In-doped ZnO fibers synthesized by thermal reduction reaction

Si comes from the substrate, and Au comes from the catalyst.

shown in Fig.1. Compared with the XRD pattern of ZnO, all main diffraction peaks of the In/ZnO fibers can be perfectly indexed to the hexagonal wurtzite structure of ZnO (JCPDS 75-576) with lattice constants corresponding to $a=b=3.242$ nm and $c=5.194$ nm, and no other peaks were clearly detected.

TEM analysis was employed to further investigate the structure of the product. Fig.2(a) presents the TEM micrograph of a typical single synthesized fiber, clearly demonstrating the core-shell structures from the obvious contrast variations between the outer part and the inner part. The diameters of the fibers are about 30–60 nm with high aspect ratio above 100. The core diameter and the sheath thicknesses are about 20 and 10 nm, respectively. The HRTEM image taken with the electron beam along the fiber (Fig.2(b)) further confirms the core-shell (or coaxial cable) structure. It can be seen that the core zone shows clear lattice fringe, while the shell zone looks like amorphous. Combined with the XRD results, it is inferred that the core zone is single crystalline wurtzite ZnO structure and the shell zone is amorphous layer.

The compositions of the outer shell and the inner core were checked using EDS generated with an electron nanoprobe (5 nm), as shown in Fig.3. Fig.3(a) shows the presence of Si and O (the Cu signal comes from the TEM grid), corresponding to the amorphous layer in the outer part of the fiber. Fig.3(b) indicates that the inner fiber mainly contains Zn, In, and O. Combined with the results above, it is suggested that an In doped ZnO fiber confined within the SiO_x amorphous shells. These results clearly confirm the formation of In/ZnO-SiO_x core-shell structures.

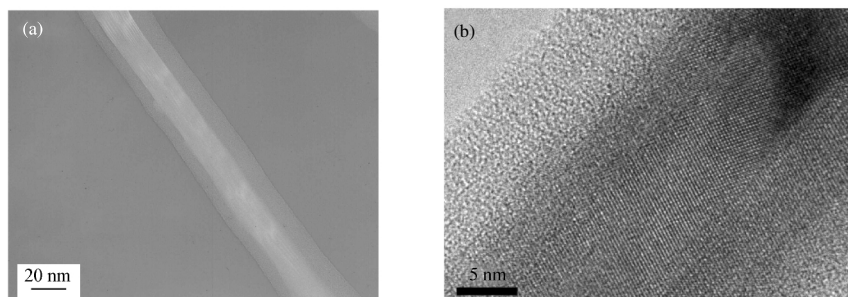


Fig.2 TEM (a) and HRTEM (b) images of the synthesized In/ZnO-SiO_x fibers

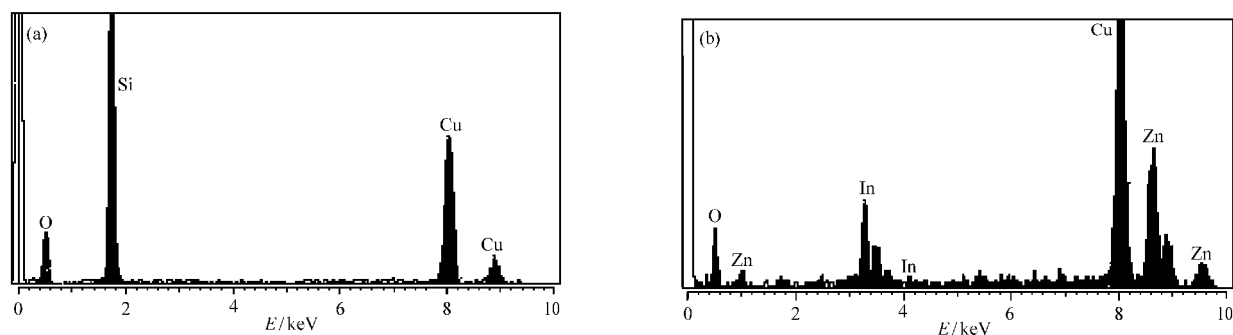


Fig.3 EDS spectra of the core-shell nanostructures from the outer part (a) and the inner part (b)

Cu peaks come from the Cu grid used for TEM measurement.

It is suggested that the self-assembling of core-shell In/ZnO-SiO_x nanowires may be used as a new type of ideal building blocks for nanodevices. Amorphous silicon oxide shows stable and highly bright blue light emission and is widely used as passivation or insulation layers in integrated circuits^[22]. These core-shell In/ZnO-SiO_x nanowires may have a potential application in mechanical-optical information coupling and conversion and act as cables for nanoelectronics.

Here we propose the possible growth mechanism of the self-assembling of the heterostructures. No metal particles were found at the tip of the nanocables in our TEM investigations, which suggested that the growth of the In/ZnO-SiO_x nanocables was not governed by the commonly reported metal-seeded vapor-liquid-solid (VLS) mechanism^[2,23]. Fig.4 describes a schematic illustration of the growth processes. Although the melting point of pure gold and silicon is 1063 and 1412 °C, respectively, the eutectic temperature of the Au-Si system is known to be only 370 °C^[24]. During the reaction process, the eutectic reaction between gold thin layer and the silicon substrate occurred firstly at 370 °C and formed Au-Si eutectic alloys before zinc vapors beginning to release at approximately 400 °C. At higher reaction temperature, zinc vapors were generated. At the same time, In₂O₃ reacted with graphite *via* the reaction $\text{In}_2\text{O}_3 + \text{C} \rightarrow \text{In} + \text{CO}$. The Au-Si liquid alloy began to absorb the generated zinc and indium vapors and silicon atoms from the substrate to reach equilibrium condition. When the liquid alloy became supersaturated, In/ZnO-SiO_x nanocables precipitated out and kept on growing from the supersaturated surface, possibly through the oxidation reactions: $\text{In(l)} + \text{Zn(l)} + \text{O}_2 \rightarrow \text{In/ZnO(s)}$ and $2\text{Si(l)} + \text{O}_2 \rightarrow 2\text{SiO}_2(\text{s})$. The growth process

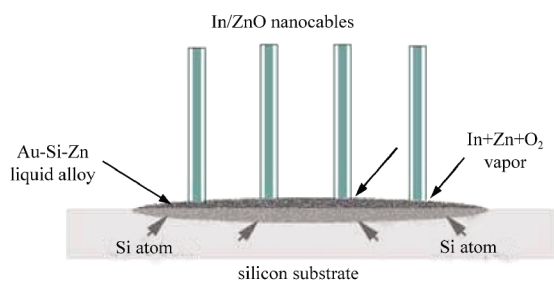


Fig.4 Schematic illustration of the formation mechanism of coaxial In/ZnO-SiO_x core-shell nanocables

of the nanocable heterostructures is some-what different from the commonly reported metal-seeded VLS mechanism. Indium ions incorporated into the lattice of ZnO by substituting parts of Zn atoms forming a single wurtzite structure. During the growing process, the core and the shell were formed simultaneously.

3 Conclusions

We synthesized coaxial In/ZnO-SiO_x core-shell nanocable heterostructures by introducing In ions in the raw material *via* a simple thermal evaporation process. A eutectic and reduction reaction growth mechanism was proposed. The synthesis of core-shell structures indicates the general potential of radial heterostructure growth for the development of nanowire-based devices.

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