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A novel self-catalytic route to zinc stannate nanowires and cathodoluminescence and electrical transport properties of a single nanowire

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ABSTRACT

A simple chemical vapor evaporation (CVD) method has been employed to fabricate zinc stannate (Zn_2SnO_4) inverse spinel nanowires without using any catalyst. It is found that the Zn_2SnO_4 (ZTO) nanowires are single crystals and their average length is up to several tens of micrometers. Based on the results of X-ray photoelectron spectroscopy and energy dispersive X-ray spectroscopy, and transmission electron microscopy, the mechanism in the formation of the Zn-rich ZTO nanowires has been deduced, and it is found that the growth of the wires follows a self-catalytic vapor–liquid–solid (VLS) mechanism. The cathodoluminescence (CL) spectrum of a single nanowire contains a strong and broad red emission, which is originated from the disordered spinel structure induced by the substitution of excess Zn ion for the sites of the Sn ions. The electrical transport measurement of a single ZTO nanowire reveals that it is an N-type semiconductor behavior. The calculated resistivity without gate voltage is *ca.* 1.6 Ωcm^{-1} at 300 K. The gate-dependence plot shows a distinguish gate control for the voltage ranged between −10 and 30 V, and the resistance decreased almost linearly with increasing gate voltage.

1. Introduction

Low dimensional semiconductor nanostructures have attracted considerable attention due to their unique physical and chemical properties [1–20]. Many of the ternary oxides with a general formula of AB_2O_4 are both fundamental interesting and technological importance due to their unique spinel structures [21–25]. Among these spinel compounds, Zn_2SnO_4 (ZTO, with space group *Fd3m*) is an interesting semiconductor due to its unusual inverse spinel structure. It has a rather wide band gap of 3.6 eV [26–28]. Some of its Zn^{2+} ions occupy the tetrahedral A-sites, and the rest of Zn^{2+} and Sn^{4+} ions occupy the octahedral B sites. This inverted order of Zn^{2+} and Sn^{4+} is an important structural parameter of inverse ZTO spinel [29–31]. The A and B cations can occupy the octahedral sites in the stable inverse spinels, which results in the disorder spinel structure which accommodates a larger deviation from stoichiometry. These non-stoichiometric spinels with high cation-related point defect concentration possess various excellent chemical and physical properties such as high electron mobility, high electrical conductivity and low visible absorption [32,33]. Recently, considerable efforts have been focused on the synthesis and properties of the ZTO films and nanoparticles [34–36]. In some reported works, it is found that ZTO thin films have good optical and photoacoustic transparency [37–39] and can be used as buffer layers to improve performance of CdS/CdSe solar cells [40]. The ZTO nanoparticles are found to be promising materials and can be used as electrodes in dye sensitized solar cells [41,42], photocatalysts [43–45] and anodes for Li-ions batteries [46–48]. While the reports on fabrication and study of ZTO thin films and nanoparticles are readily available, those related to ZTO in the form of nanowires are less common. In generally, ZTO nanowires are produced by the Au-assisted chemical vapor deposition (CVD). The photoluminescence (PL) property of the nanowires are usually investigated in a large area containing many nanowires [49–52]. In this work, we have developed a facile

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catalyst-free CVD route to synthesize ultra-long single-crystalline ZTO nanowires. The structure properties and growth mechanism have been studied in detail. Moreover, the cathodoluminescence (CL) and electrical properties of individual nanowire were investigated. These results give exact insight in optical and electrical properties of the ZTO nanowires.

2. Experimental

ZnO powder was placed in the center of an alumina boat located in the center of an alumina tube. SnO powder was placed at a position 10 cm away from the ZnO powder. A quartz tube with an inner diameter of 3 cm was placed in the alumina tube at the downstream end from the ZnO and SnO powders. The entire system was inserted in a horizontal tube furnace. The temperature of the furnace was ramped to 1250 °C and held for an hour while argon was allowed to flow into the system at 100 sccm. After annealing, the system was cooled to room temperature, and a layer of white products was found on the inner surface of the quartz tube.

The morphologies of the as-prepared products were characterized by a field-emission scanning electron microscopy (SEM; FEI QF400). The crystal structure of the products were analyzed by the X-ray diffractometry (XRD; RU-300, Rigaku) with the Cu-K_α radiation (λ = 1.5405981 Å). The composition of the products was determined by The X-ray photoelectron spectroscopy (XPS, VGESCALAB MKII X-ray Photoelectron Spectrometer) by using a non-monochromatized Mg-Kα X-ray as the excitation source. The microstructure of the products were investigated by the field emission transmission electron microscopy (FE-TEM; Tecnai 20ST) equipped with the energy-dispersive X-ray spectroscopy (EDS). The room-temperature CL spectra of the products were performed via the scanning electron microscopy (SEM, LEICA Cambridge) equipped with an Oxford Instruments MonoCL2 spectrometer. The focused electron beam was scanned across the areas of interests, and the emitted X-ray was collected with a parabolic aluminum mirror and guided to the slit of a grating monochromator with a focal length of 20 cm. The measurement was conducted at an accelerating voltage of 10 kV and probe current of 200 pA. Electron beam lithography (EBL) was conducted to produce the electrode-like pattern with individual Zn_2SnO_4 nanowire, and for their subsequent Ti/Au deposition. The Ti adhesive layer was made to 50 nm thick and is coated with a 70 nm Au layer resulting with a Ti/Au contact. The electrical measurements were conducted by the four-point measuring method at room temperature.

3. Results and discussion

The as-prepared products were collected from the quartz tube located in the downstream end of the system. The products were characterized by SEM. The SEM image (Fig. 1a) shows that the product was nanowires, and their length was up to several tens of micrometers. The enlarged SEM image in Fig. 1b indicates that the diameter of the nanowires was about. 80–120 nm, and each of them has smooth surface. Fig. 2 shows the XRD pattern of the nanowires. All the diffraction peaks in the pattern were indexed and the lattice parameter was determined to be a = 8.647 Å. The peak positions matched to those of standard cubic Zn_2SnO_4 (JCPDS No. 24-1470). This result indicated that these nanowires were pure cubic spinel Zn_2SnO_4. The chemical composition of the nanowires was further confirmed by using XPS measurement in a range of binding energies from 0 to 1100 eV (Fig. 3). The core levels of the Zn2p, Sn3d and O1s are clearly identified XPS as shown in Fig. 3a, and no other species were detected. The spectra of the Zn2p, Sn3d and O1s were displayed in Fig. 3b–d, respectively. The binding energies $Zn2p_{3/2}$, $Sn3d_{5/2}$, $Sn3d_{3/2}$ and O1s were centered at 1022.375, 487.75, 496.125 and 531.75 eV, respectively. This result was in good agreement with those of ZTO reported in other papers [53]. Quantification of the Zn2p and Sn3d peaks also revealed that the Zn/Sn atomic ratio was 2.134:1, indicating that there were slight excess Zn atoms in the nanowires. Thus, our XRD and XPS results indicated that these nanowires products were pure ZTO with cubic spinel structure.

To characterize the basic microstructures and the growth process of the as-prepared ZTO nanowires, we had carried out an extensive study on the ZTO nanowires by TEM and HRTEM. As shown in Fig. 4a, the bright TEM image reveals that the ZTO

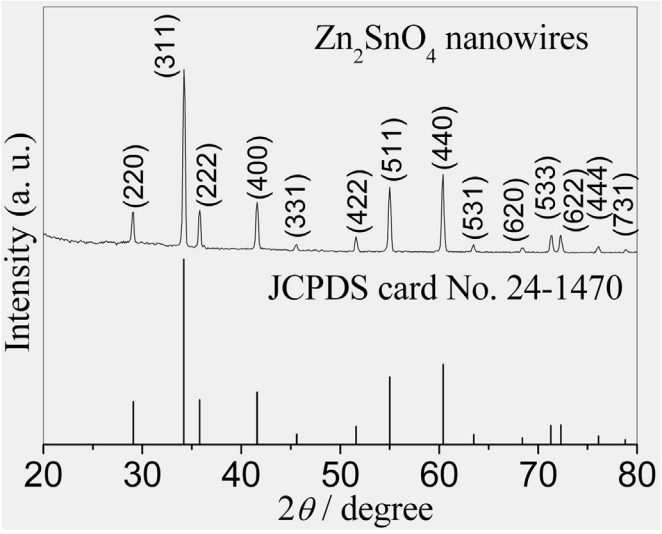

Fig. 2. XRD patterns of the ZTO nanowires.

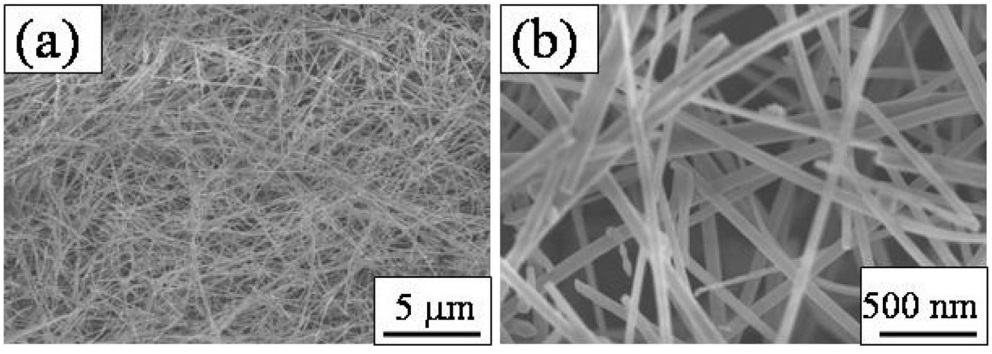

Fig. 1. (a) SEM image of the ZTO nanowires. (b) Enlarged SEM image of the ZTO nanowires.