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On the fabrication of resistor-shaped ZnO nanowires

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Abstract

A novel morphology of zinc oxide (ZnO) consisting of resistor-shaped nanowires connected “in-series” has been synthesized by a vapor phase transport method in the presence of water and copper. Scanning electron microscopy showed that the diameter of nanowires changes abruptly from ~200 to ~20 nm and forms a resistor-shaped nanostructure. Transmission electron microscopy and selected-area electron diffraction revealed a grain boundary at the thicker center (200 nm) and the nanowires were composed of a pair of crystallites of wurtzite ZnO growing along $\pm[0001]$ directions. A growth mechanism is proposed which takes into account the crystal growth conditions, the catalytic effect of water and copper, as well as the inherent polarization of the wurtzite structure along its c-axis.

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Keywords: Zinc oxide; Vapor phase transport; 1D nanostructure; Transmission electron microscopy

1. Introduction

The fabrication of novel nanostructures based on important basic materials featuring more complex attributes is crucial for the fundamental understanding of structure–physical properties relationships as well as for the development and optimization of existing devices as well as for the creation of new functional devices. Zinc oxide (ZnO), a II–VI semiconductor of wide direct bandgap (3.37 eV) and large exciton binding energy (60 meV at room temperature) [1] is an excellent material for ultraviolet/blue optoelectronic applications, with low threshold UV lasing action observed in oriented arrayed nanostructures [2–4] as well as in microparticulate thin films [5]. Meanwhile, one-dimensional (1D) nanostructures have attracted great attention for their potential applications as key building-blocks and materials, in nanodevices [6], interconnect integration [7], and nano-biotechnology [8,9]. Vapor phase transport (VPT) appears as the most commonly used method for growing oxide nanostructures of various morphology and aspect ratio, for instance, wires, tetrapods, tubes, belts, disks, combs, and walls [2,4,10–14]. To some extent, the shape- and size-control of the nanostructures is achieved by controlling the growth parameters, such as carrier gas flow rate, the partial pressure of reactive gases, the vapor flow direction, as well as the temperature and the choice of substrate materials [12,15]. In

addition, the formation of nuclei and subsequent growth behavior can be largely influenced in the presence of metals, metal ions and water [14,16,17]. For instance, ring-shaped nanostructure have been fabricated by adding indium and/or lithium to the precursors [16]. Triboulet et al. [17] have reported the growth of ZnO single crystals using water as growth “activator”. In a recent study by Huang et al. [14], ZnCu₂ alloy was used as Zn source, with water vapor introduced into the system by carrier gas. They found that Cu and water vapor resulted in a modified growth behavior of ZnO nanobelts.

The stable crystallographic phase of ZnO is wurtzite and occurs in nature as the mineral zincite (although scarcely as natural single crystal). Its ionic and polar structure can be described as a hexagonal close packing (HCP) of oxygen and zinc atoms in point group 3m and space group P6₃mc with zinc atoms in tetrahedral sites. The occupancy of four of the eight tetrahedral sites of HCP arrays controls the structure. The hexagonal unit cell contains two formula units and the crystal habit exhibits basal polar planes (oxygen terminated (0 0 0 1) faces and tetrahedron corner-exposed Zn face (0 0 0 $\bar{1}$) as well as two types of low-index faces consisting of non-polar faces ($\bar{1}$ 0 0 0) and C_{6v} symmetric ones). The low-symmetry non-polar faces, with three-fold coordinated atoms are the most stable ones. Additionally, there is no center of inversion in the wurtzite structure and thus, an inherent asymmetry along the c-axis is present, allowing the growth of anisotropic crystallites and nanostructures. In addition to the inherent anisotropy along the c-axis, the wurtzite structure shows piezoelectric activity, which is currently being studied for building nano-scale electro-mechanically coupled sensors and transducers [18] due to a large and permanent electric dipole moment, which have been observed experimentally to scale with the volume of the nanocrystal [19]. The unique polar surfaces in ZnO, the basal plane, $\pm(0\ 0\ 0\ 1)$, as well as $\{0\ 1\ \bar{1}\ 1\}$ planes, induce such a dipole moment and spontaneous polarization, as well as a divergence in surface energy. The spontaneous polarization dominated by $\pm(0\ 0\ 0\ 1)$ polar surfaces was the main driving force in forming nanosprings and nanorings, while $\{1\ 0\ \bar{1}\ 1\}$ -type polar surfaces have been observed in a nanohelical structure [18]. Due to the absence of inversion symmetry in wurtzite structure, second-order dipole moments are of even greater amplitude compared to other (homo)polar crystals [20].

Based on such a unique structural characteristic, resistor-shaped ZnO nanowire (RSNWs) nanostructures are fabricated by a VPT method in the presence of water and copper. The morphology and structural characteristics and a growth mechanism are discussed. This new ZnO morphology, analog to the shape of electrical resistors connected in series is characterized by an abrupt diameter change at the junction, which is similar to the step-shaped Bi nanowires [21], (Ga,Mn)As nanowires [22], and Y-shaped CNTs [23] reported previously.

2. Experimental

The ZnO RSNWs were synthesized via a VPT method using a high-temperature tube furnace [24]. The mixture of ZnO and graphite power (0.5g, 1:1 in wt%) was placed at the end of a slender one-end sealed quartz tube. One piece of a 10 cm long copper wire (0.2 mm in diameter) placed on a wet silicon strip was inserted into this slender quartz tube at a downstream area. A volume of 0.2 ml water was intentionally spread on the silicon strip. The furnace was then heated from room temperature to 1090 °C at a rate of 30 °C/min. Once the temperature reached 650 °C, the quartz tube was inserted into the furnace. When the source temperature reached 1070 °C, a constant flow of vapor in the quartz tube could be observed. The quartz tube was then pulled out and cooled down to room temperature when the temperature reached 1090 °C. The Si substrate and copper wire were covered with a silk-like powder near the open-end of the quartz tube. To study the effect of water and copper on the nanostructure morphologies, the experiment was also carried out with absence of (1) water, (2) copper wire, and (3) both water and copper wire, separately.

The crystal structure of the as-prepared product was characterized by powder X-ray diffraction (XRD) using a Siemens D5005 XRD diffractometer with Cu $K_{\alpha 1}$ line operated at an accelerating voltage of 40kV. Morphological and structural analyses were carried out by scanning electron microscopy (SEM; JSM-5910LV), as well as transmission electron microscopy (TEM; JEM-2010, operated at 200 kV). Chemical composition analysis was obtained by energy-dispersive X-ray spectroscopy (EDX) attached to the SEM.

3. Results and discussion

Fig. 1 shows the powder XRD pattern of the as-synthesized product. All peaks as labeled match the hexagonal ZnO nanostructure well with lattice constants of $a = 3.249 \text{ \AA}$ and $c = 5.205 \text{ \AA}$. No diffraction peak originated from copper, silicon (used as substrate) or any of their compounds can be found in the XRD data. Further examination by EDX shows that the atomic ratio of O:Zn is close to 1. The copper signal is below the detection limit of EDX, which indicates that concentration of copper is too low to be detected.

Fig. 2(a)–(c) shows SEM images of the as-synthesized nanostructures at various magnification. Abundant RSNWs are clearly observed, which consist of a thick nanorod in the center with diameter ranging from 150 to 200 nm, and length of about 2 μm . Fine nanowires grow from both ends of the thick nanorods. The length of nanowires ranges from tens of nanometers up to tens of micrometers, and their diameter is only about 10–20 nm. In comparison, the as-grown product (1) without water, (2) without copper wire, and (3) without both are shown in Fig. 2(d)–(f), respectively, where no RSNWs but (1) nanocombs growing only on Cu wire, (2) powder of submicron needle-like rods, and (3) powder of submicron tetrapods are found, respectively. It is clear that Cu itself (without water) does not induce the growth of RSNWs. In the presence of both water and Cu, the density of RSNWs ($2.56 \times 10^{16} \text{ mm}^{-3}$) and morphology are close to that of needle-like rods ($2.59 \times 10^{16} \text{ mm}^{-3}$, Fig. 2(e)); however, the diameter is much reduced by around 10 times.

It is noted that many RSNWs are connected to each other forming “in-series” structures as shown in Fig. 3(a). The enlarged “in-series” structures are clearly shown by TEM images in Fig. 3(b) and (c). Their diameter is on average around 200 nm for the rods and around 10–20 nm for the wires, with sharp reduction in diameter at the nanorod–nanowire junctions. In-depth investigation revealed that they were formed by attachment of several RSNWs. The TEM caption images inserted in Fig. 3(b) and (c), taken from the dot-circled parts at the nanowire junction between two RSNWs, present a clear evidence of the connection in-series of the RSNWs.

In Fig. 3(b) and (c), the grain boundaries of the RSNWs can be observed from the contrast near the center of the thick nanorods. Typical bright-field and dark-field TEM images taken from the rectangle-selected area of the thick nanorod (Fig. 3(b)) are shown in Fig. 3(d) and (e), respectively. The grain boundary was further studied by high-resolution TEM (HRTEM). Fig. 4(a) shows a low-magnification TEM image of a single RSNW and the selected-area electron diffraction (SAED) patterns taken from the circled regions near the grain boundary to examine the crystal structure of the thick nanorods. It is worth mentioning that, the SAED patterns shown in Fig. 4(a) were obtained without tilting the sample. Both SAED patterns are the same except a relative intensity difference of diffraction spots, indicating the same crystal orientation of these two grains. Fig. 4(b) shows a higher magnification TEM image recorded from the grain boundary at region A in Fig. 4(a), and the inset is the corresponding HRTEM. A grain boundary can be clearly seen. Fig. 4(c) and (d) shows the HRTEM images taken from region B (near nanorod-nanowire junction) and region C (thick nanorod) in Fig. 4(a), respectively. All the HRTEMs show clear lattice fringes indicating that the RSNWs are formed from two single-crystallites with a grain boundary at region A (Fig. 4(a)) separating them. As shown in Fig. 4(c), the

spacing of 0.26 nm between adjacent lattice planes corresponds to the d-spacing of (0 0 0 2) planes, indicating $\langle 0\ 0\ 0\ 1 \rangle$ as the growth direction for the RSNWs. It is worth mentioning that the surface of the nanostructure is rough (Fig. 4(b)), which might be due to electron beam irradiation in TEM [25].

According to the electron microscopy observations and analysis, a possible growth mechanism is proposed by considering the $\pm(0\ 0\ 0\ 1)$ polar surfaces of ZnO. A corresponding schematic diagram is displayed in Fig. 5. The formation of the RSNWs can be depicted as a three-stage process, as illustrated in Fig. 5(a)(c). In Fig. 5(a), growth species of ZnO_x and Zn are formed due to the thermal reactions of ZnO and graphite, and the growth of ZnO 1D nuclei and nanorods involves adsorption/desorption of growth species. Following the argument proposed by Huang et al. [14], the addition of Cu and water can control the supply of Zn and oxygen, and thus modify the crystal growth kinetics. Our present work supports such assumptions. The following chemical reactions between water vapor and growth species at high temperature could be [14]:

where water is a source of O_2 and H_2 . The chemical reactions (1)–(3) between water vapor and growth species probably confine the growth of ZnO nuclei in c-axis by lowering the surface energy of $\{0\ 0\ 0\ 1\}$ [26]. On the other hand, according to Haugrud [27] and Fujikawa and Yoshikawa [28], Cu can be easily oxidized by water vapor at high temperature according to the following reactions:

Therefore, production of hydrogen from water vapor can be enhanced. More H_2 can increase the desorption speed of growth species on the growing surface through reductive reactions, and consequently reduce the growth speed, in comparison with the case where only water is present.

In Fig. 5(b), the formation of the paired-crystal structure can be understood from electrostatic interaction at both ends of nanorods with sharp tips. It is well known that the chemically active facet (0 0 0 1) of wurtzite-structured ZnO is Zn^{2+} -rich and the inert facet (0 0 0 $\bar{1}$) is O^{2-} -rich. When (0 0 0 1) facet comes close to (0 0 0 $\bar{1}$) facet, they will be connected due to electrostatic attraction with well-matched lattice [18]. Although the purity of RSNWs is high (Fig. 2), we can still find some needle-like nanorods in TEM, which are just half the length of the thick nanorod. We can also find small amount of paired-nanorods with two grains connected in a random orientation (TEM images not shown here). Such observations are in agreement with the proposed growth mechanism.

Fig. 5(c) shows the formation of single and “in-series” RSNWs. The diameter of nanowires decreases drastically at this stage, due to the substantial decrease in the vapor pressure. Similar to Fig. 5(b), the floating RSNWs attract each other and connected together to form RSNWs “in-series”. It is worth mentioning that, fine nanowires grow in both $\pm[0\ 0\ 0\ 1]$ directions from thick nanorod and the growth rates in both directions are close.

4. Conclusion

In conclusion, a novel nanostructure of ZnO, that is the “resistor-shaped” nanowires, has been synthesized using a VPT method in presence of water and Cu, which adjusted the growth kinetics, enabling therefore the growth of such a unique complex morphology. The RSNWs are built up by thick nanorods and fine nanowires, bridged with abrupt junctions, morphologically, and of wurtzite paired-crystalline nanostructures. The formation of paired-crystalline structure and series RSNWs are attributed to the electrostatic force induced by the spontaneous polarization of ZnO $\pm(0\ 0\ 0\ 1)$ polar facets at different growth stages. The RSNWs are potentially useful for building and connecting electrical nanodevices as well as building blocks in the fabrication of functionalized interfaces.

Acknowledgments

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5