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Fabrication and green emission of ZnO nanowire arrays

ZHANG Bin, ZHOU ShaoMin[†], LIU Bing, GONG HeChun & ZHANG XingTang

Key Lab for Special Functional Materials of Ministry of Education, Henan University, Kaifeng 475004, China

Well-aligned single-crystalline wurzite zinc oxide (ZnO) nanowire arrays were successfully fabricated on a Si substrate by a simple physical vapor-deposition (PVD) method at a relatively low temperature of about 500℃. The as-fabricated nanowires were preferentially arranged along the [001] direction of ZnO. The photoluminescence spectrum of ZnO nanowire arrays showed two emission bands: a strong green emission at around 500 nm and a weak ultraviolet emission at 380 nm. The strong green light emission was related to the existence of the oxygen vacancies in ZnO crystals. Corresponding growth mechanism of the ZnO nanowires was briefly discussed.

II-VI semiconductor, nanostructures, photoluminescence

One dimensional (1D) and zero dimensional ZnO semiconductor nanomaterials have been extensively studied for their potential applications in the fields such as the cerams, piezoelectric sensors, catalysts and luminescence apparatus[1−24]. As contrasted with the macrodisordered 1D nanostructures, the well-aligned 1D nanostructures (W1DN) in large area provide opportunities for fabricating nanodevices in a macroscopic way because the W1DNs have advantages of 1D nanostructure and are controllable. Since Huang et al.[1] reported room-temperature ultraviolet nanowire nanolasers, many techniques have been proposed to form ZnO nanowires arrays such as chemical vapor deposition (CVD), metal organic CVD (MOCVD), pulsed laser deposition (PLD), sol-gel-template method, and wet chemical method[2−6]. However, these techniques always involve expensive equipment, complex procedures, and harmful environment. The PVD technique is a good approach to fabrication of various films because the process of making samples is simple, composition of products can be controlled, and there is no pollution such as drain water, discharge gas, and waste slag. Recently, the technique has been used to fabricate ZnO nanowires[7−10]. For example, Pan et al.[9] have synthesized ZnO nanowires and nanobelts through directly thermal evaporation of ZnO powders at a high temperature of 1400℃. The obtained ZnO nanowires or nanobelts were of high purity and high-crystalline structure, but the high-temperature vapor-phase processes was expensive and energy-consuming. Wang et al.[10] reported vertically well-aligned ZnO nanowires arrays on sapphire substrates at 750℃ using PVD method, but a complex pulsed lasing deposition was involved before ZnO nanowires were grown. In this paper, based on a simple PVD method at a relatively low growth temperature of 500℃, we demonstrate fabrication of a high quality single-crystalline ZnO nanowire arrays on the Si substrates. The optical investigation shows that the ZnO nanowires are of high crystal quality and have attractive optical properties. Therefore, we believe that as-synthesized ZnO nanowire arrays have potential applications in manufacturing optoelectronic nanodevices.

1 Experimental

In a typical experiment, all the reagents used in this experiment were of analysis reagent grade. P-type Si substrates were first ultrasonically cleaned in acetone and

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[†]Corresponding author (email: smzhou@henu.edu.cn)

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a solution (0.02 M) of nickel nitrate and ethanol was dropped onto the wafers. Subsequently, the as-obtained wafers were dried and annealed at 400℃ in the atmosphere, a thin NiO film was evenly formed on the Si substrate. High-purity Zn powders as source material were put in a ceramic boat located at the center of a horizontal tube furnace. The silicon substrates were placed on the top of boat to collect the products. The system was quickly heated to 500℃ under 50 sccm nitrogen gas flowing at a pressure of about 10^{-3} torr for 1 h and then cooled to room temperature. Large-scale white-colored filmlike products were newly formed on the whole substrate. In sample characterizations, scanning electron microscopy (SEM, JEOL JSM-5600LV), and transmission electron microscopy (TEM, JEOL 2010), high resolution TEM (HRTEM), and selected area electron diffraction (SAED) were used to investigate the corresponding morphologies and microstructures. The sample phases, crystal structures, chemical compositions, and element valences of the ZnO nanowire arrays were detected by X-ray diffraction (XRD, Phillips X' Pert Pro MPD), energy dispersive X-ray spectroscopy (EDS, OXFORD ISIS) and X-ray photo-electric spectrum (XPS, KRATOS AXIS ULTR), respectively. Room temperature photoluminescence (RTPL) measurement was carried with a fluorescence spectrophotometer [SPEX F212 (USA)] with an Xe lamp as the excitation light source (330 nm). Optical absorption spectra were measured using a CARY5000 spectrophotometer (VARIAN).

2 Results and discussion

Two typical SEM images of the as-synthesized ZnO array nanostructures are shown in Figure 1(a) and (b), which reveal that the sample is composed of large quantities of high quality long wire-like nanostructures with the typical length up to several microns and the uniform diameter of about 100 nm. Further, microstructural characterization of the ZnO nanowires was performed by TEM and HRTEM. As shown in Figure 2(a), TEM image with a general morphology of a single ZnO nanowire reveals that the ZnO nanowire has a diameter of about 100 nm where no catalyst particles are observed in the tip of the nanowire. A HRTEM image with a clear lattice plane and SAED patterns with regular electron diffraction patterns demonstrate that the nanowire has a

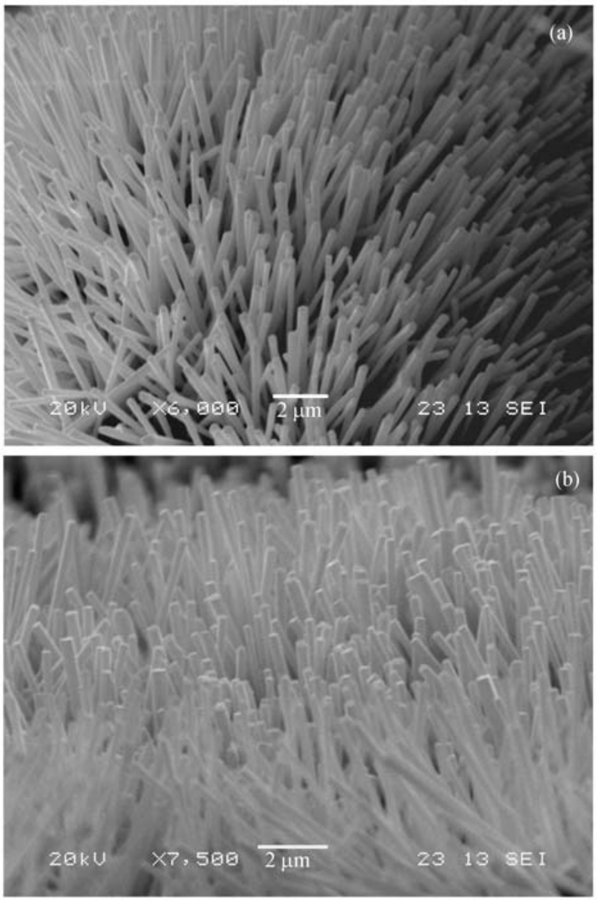

Figure 1 Two SEM images of aligned ZnO nanowires on the Si substrate. (a) The top view of ZnO nanowires; (b) the side view of ZnO nanowires.

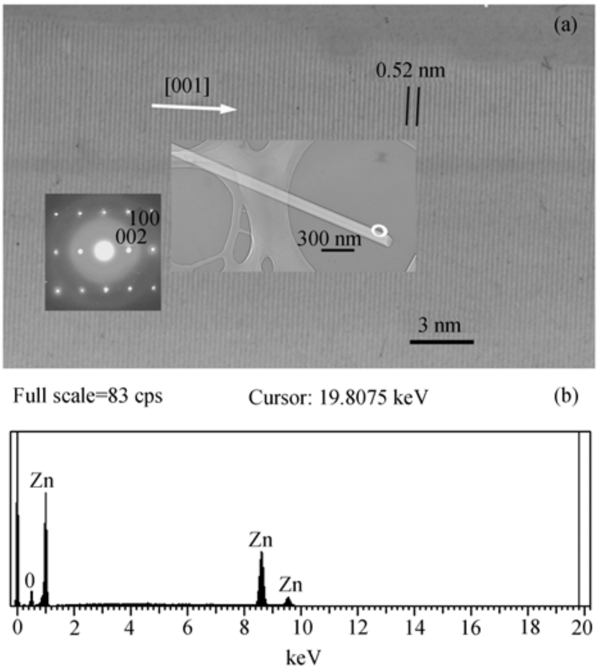

Figure 2 A typical HRTEM and TEM image, as well as the corresponding SAED patterns taken from the white loop (a) and EDS spectra (b).

single crystalline structure. In addition, based on these analyses of HRTEM image and SAED pattens, we know that the growth direction of the nanowire corresponds to [001] direction. Spectrum of EDS from the single nanowire is shown in Figure 2(b). EDS analysis demonstrates that the nanowire consists of both Zn and O. Moreover, according to the quantitative analysis of EDS, the ratio of Zn to O is 0.52:0.48 Zn/O composition, which is consistent with stoichiometric ZnO. The XRD patterns of the as-synthesized products are shown in Figure 3, where all Miller indices of peaks are presented. The whole diffractogram can be indexed in peak positions to a crystalline ZnO phase and a typical hexagonal (hexagonal wurtzite with lattice parameters of a = 3.2 Å and c = 5.2 Å) is indicated, which is consistent with that of a bulk ZnO crystal (JCPDS Card File, No. 89-511). Moreover, no diffraction peaks from other impurities have been found in Figure 3.

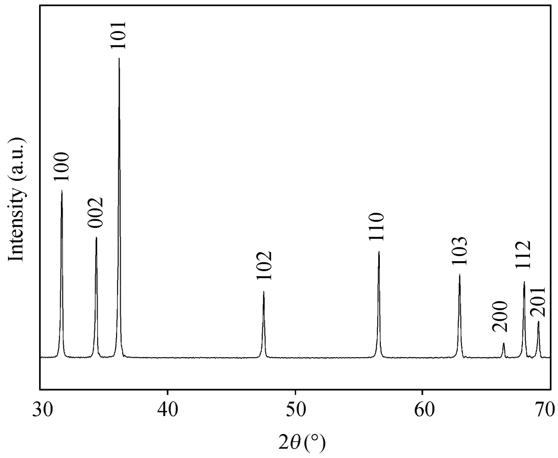

Figure 3 XRD patterns of the as-synthesized ZnO nanowires with a wurtzite (hexagonal) structure.

Corresponding chemical compositions of the synthesized ZnO nanowires were determined by XPS. Figure 4(a) shows that Zn2p has two peaks at 1022.2 and 1045.3 eV, which respectively correspond to 2p3/2 and 2p1/2 peaks of Zn from ZnO. The two peaks clearly separate, indicating that all Zn in zinc oxide is Zn (II). As indicated in Figure 4(b), the main binding energy peak of O1s with relative lower binding energy value of 531.2 eV is believed to be the lattice oxygen, while the satellitic peak (532.7 eV) is the absorbed oxygen. All data of XPS show that the as-prepared products are high-quality ZnO, which is compatible with the results from HRTEM, SAED, EDS and XRD.

Figure 5 shows the RTPL spectra (hollow dots) and absorption (solid dots) spectra of the as-obtained ZnO nanowire arrays. As shown in Figure 5, a UV emission peak centered at about 384 nm and a strong broad green emission band centered at ~506 nm were observed. The UV emission corresponds to the recombination of free excitons between conductive band and valence band and is called near-band-edge emission (NBE)[11−14]. This UV peak, with the full width at half maximum as narrow as 18 nm, is much sharper than the result given by ref. [15], indicating the high purity and similarity of our nanowires. The deep-level (DL) emission (the green emission of about 500 nm) is considered to relate to the oxygen vacancy, interface defects and donor-acceptor complexes. The absorption spectrum of the ZnO nanowire arrays was obtained at room temperature (see solid dots in Figure 5). The onset of the absorption spectrum at about 380 nm corresponds to the band gap of ZnO (3.23 eV), which is consistent with the result of RTPL measurements.

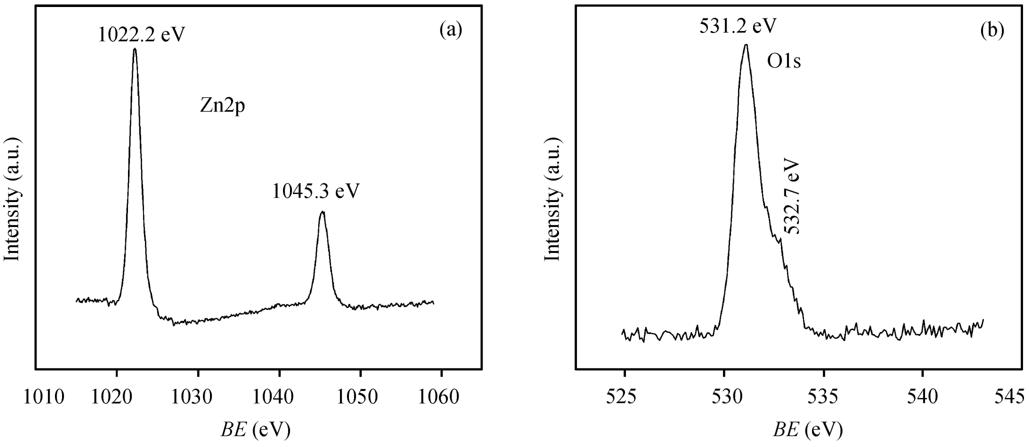

Figure 4 High resolution XPS spectra of ZnO samples. (a) The Zn2p; (b) the O1s.

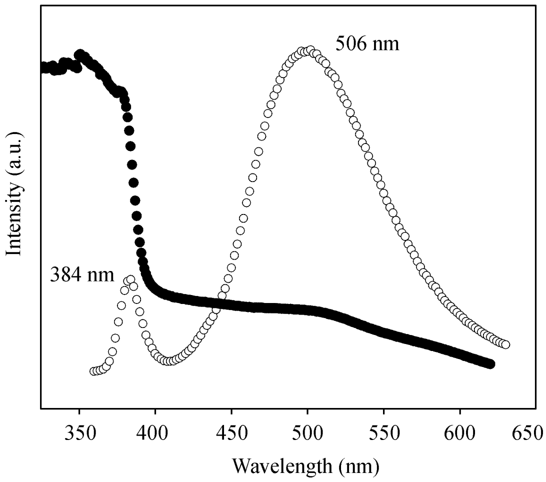

Figure 5 RTPL (hollow dots) and absorption (solid dots) spectra of the as-obtained ZnO nanowire arrays.

To understand the observed behaviors of ZnO nanowire arrays, it is necessary to study the counterpart growth mechanism. As far as we know, as a wurtzite-structure, ZnO belongs to the P63mc space group, which has a highly anisotropic structure along the *c*-axis. The plane (001) (terminated with zinc) of ZnO has the maximum surface energy, while the (00$\bar{1}$) plane (terminated with oxygen) has the minimum surface energy[16]. As a result, the growth along the [001] direction has a faster rate than that along other directions and is much more favorable. So 1D wire-like nanostructures of ZnO are easily formed. There have been reported transition metal oxides such as NiO and FeO, have a similar catalytic effect on the vapor-liquid-solid (VLS) growth of semiconductor nanowires as well as metal catalysts[17]. But in our work, the TEM images show that no catalyst particles are in the tip, stem, or bottom of ZnO nanowires. Therefore, we suggest that the high-orderly nanowires follow a vapor-solid growth mechanism[2,18−20] and our additional transition metal oxides are not as catalysts but to offer favorable nucleation sites. In an additional metal catalyst assisted process, the nanowires grow from the supersaturated metal—Zn alloy droplet, the additional metal droplet remaining at the tip of each nanowire. Unlike the additional metal catalyst, our NiO thin film acts only as the nucleation site. As the Zn species have taken an active part in the formation of ZnO 1D nanowires they could not be termed as catalyst in the true sense but in analogy with the catalytic action the term “self-catalyzed” has been used here[21]. Therefore, it is believed that the formation of 1D nanowires undergoes the VS growth mechanism. The eutectoid metal Zn acts not only as the reactant but also as the catalyst to provide an energetically favored site for the absorption of oxygen gas. The ZnO nucleus functions as a wire seed, which further grows up to a wire-like nanostructure in the presence of eutectoid metal Zn (l) and O_2 (g), and the size and shape of wire-like nanostructure are predecided by the size of the eutectoid metal Zn droplet.

3 Conclusions

Based on a simple PVD technique, well-aligned single-crystalline wurzite ZnO nanowire arrays have been fabricated at low temperature. The morphologies, structures, composition and optical properties of ZnO samples were detected by SEM, XRD, TEM, HRTEM, EDS, SAED, XPS and RTPL, respectively. Their corresponding growth mechanism and RTPL were discussed. The nanowires with high density of oxygen vacancies we report here are optically active, indicating that the wire-like nanostructures are promising candidates as electron nanoconductors in nanooptoelectronic devices. They could therefore offer opportunities for further fundamental research and technological applications in optoelectronic, biochemical sensing and nanoscale electrics.

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