

The growth and optical properties of ZnO nanowires at the junctions of nanowalls

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Abstract

Highly pure ZnO nanowires at the junctions of nanowalls have been successfully prepared via a simple vapor phase route at relative low temperature in the absence of catalyst. SEM, TEM, Raman scattering and PL were employed to characterize as-grown samples. The nanowires have average diameter of 10 nm with [001] growth direction. Raman scattering shifted from higher frequency to lower frequency and the enhancement of PL intensity of the green emission to the UV may be attributed to smaller nanowires and thinner nanowalls. This nanostructure may have important applications in batteries, light-emitting and energy conversion devices and other fields demanding high surface area materials.

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1. Introduction

Zinc oxide is of much interest as a result of its intriguing optical functions based on its wide gap of 3.37 eV. A prominent feature of ZnO is its large excitonic binding energy (60 meV) at room temperature, which leads to extreme stability of excitons [1], and enables devices to function at a low threshold voltage. Consequently, ZnO is considered as a promising photonic material for the UV/blue devices such as short wavelength light emitting diodes and laser diodes. Recently, much attention has been paid on ZnO low dimensional structures such as nanowires and nanotubes [2–4]. It also has been reported that ZnO two-dimensional (2D) and one-dimensional (1D) semiconducting

nanostructures have potential applications in manufacturing short-wave length nanolasers. An UV nanolaser working at room temperature has been fabricated using highly-oriented ZnO nanowire arrays [5]. In the same way, interfacing semiconducting nanostructures with substrates to attain a three-dimensional (3D) integrated platform is highly demanded for advanced nanoscale electronics and optoelectronics applications [6]. The nanowalls and high surface-to-volume ratio nanostructures with multiple dimensionalities may be useful also in energy storage and conversion, as well as memory devices. In this regard, the assembly and synthesis of these nanostructures manifesting multiple dimensionalities via a bottom-up method would be of use and importance. Ng et al. have successfully grown vertically well-aligned 2D and 1D ZnO semiconducting nanostructures by using Au as catalyst and highly-oriented pyrolytic graphite (HOPG) and insulating (1120) sapphire as substrates [7]. However, many issues including the capability of selective and aligned growth, physical properties should be further investigated before the unique

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properties of low dimensional ZnO can be fully applied in various fields. In this letter, we present high purity of ZnO nanowires at the junctions of nanowalls via a novel and simple vapor phase route at relative low temperature in the absence of catalyst. The structural and optical properties of as-prepared samples have also been investigated by using SEM, HRTEM, XRD and Raman scattering and photoluminescence (PL).

2. Experimental

Zinc acetate dihydrate (99.999%, Aldrich) and zinc (99.998%, 100 mesh, Aldrich) with appropriate weight ratio were mixed homogeneously in a mortar and ground using the pestle around 15 min. The mixture was placed in the middle of a quartz tube. The oxidated Si substrates by preheating to 1050 °C in air were cleaned and placed the downstream of the tube. The quartz tube was then placed in a horizontal furnace and heated up to 680 °C at the rate 10 °C/min with a pure argon flow of 120 sccm and subsequently kept at 680 °C for 45 min. The base vacuum was around 200 mTorr and the process pressure in the furnace was kept around 0.09 Mpa. During maintaining temperature, the air was introduced to reaction chamber to provide oxygen for Zn. After the system was cooled down to ambient temperature, a white layer was observed to cover on the SiO₂/Si wafer. The morphology of the products on the wafer was examined using scanning electron microscope (SEM) and JEOL-2010 high-resolution transmission electron microscopy (TEM) equipped with an energy dispersive spectrometry (EDS) system and Japanese Rigaku D/max γ A X-ray powder diffraction (XRD). Raman spectra were recorded at room temperature with an optical microscope using the 488 nm line of an Ar⁺ laser as excitation source. Photoluminescence (PL) measurements were carried out at room temperature at an excitation wavelength of 325 nm with a Hitachi F-4500 spectrofluorimeter.

3. Results and discussion

The highly intricate quasi-3D nanostructures were obtained; they consisted of an array of vertical 1D nanowires on top of the 2D network of intricate nanowalls. Fig. 1(A) showed a low magnification scanning electron microscope (SEM) image (top view). The distribution of the nanowalls and nanowires is nearly uniform over an entire substrate surface area. Fig. 1(B) and (C) (titled and perspective view, respectively) further showed a honeycomb pattern of nanowalls and the nanowires grown at the junctions of nanowalls. The average height of nanowalls is 80 nm and the average diameter of the nanowires and the thickness of the nanowalls are in the order of 10 nm. The nanowires were observed to grow at the junctions of nanowalls. As indicated in Fig. 1(C) by the arrow, the

surface of the substrate is rough. The shape of the patterning is nearly similar to that of honey-comb like nanowalls. The patterning seemed to have been formed before the nanowalls began to grow. In the higher temperature zone of the substrate (the length of the substrate 80 mm), we could occasionally see large nanowalls and nanowires (Fig. 1(D)). The thickness of nanowalls and the diameter of nanowires are in the same order of 50 nm and the length of the nanowires is up to 600 nm, and the aspect ratio about 10:1. This indicated that large ZnO nanostructures could be fabricated by adjusting process parameters such as temperature. It is noteworthy that there exist conical or stage tips on the top of nanowires, manifesting that ZnO nanostructures were grown by a non-vapor–liquid–solid method.

The crystallinity of an as-prepared sample was characterized using XRD (Fig. 2). The diffraction pattern indicated that the sample exhibits hexagonal ZnO crystal structure with lattice constants of $a=3.248$ Å and $c=5.199$ Å, being in agreement with the standard values of ZnO bulk crystal (JCPDS 36-1451). It is noteworthy that the diffraction pattern of nanowires shows noticeably strong peak (002) plane, whereas a standard bulk crystal exhibits the maximum intensity of (101) planes. It confirms that a great amount of our ZnO nanowires and nanowalls has aligned on the SiO₂/Si substrate and has grown with preferred orientation along the c -axis. No diffraction peaks from metallic Zn or a secondary phase have been observed.

Fig. 3(A) is the energy dispersive X-ray spectroscopy (EDX) analyses. It shows that an as-grown sample completely consists of Zn and O. The atomic ratio of Zn to O is 49:51, that is, nearly 1:1. Fig. 3(B) is a typical bright-field TEM image of a nanowire with a diameter of 40 nm. The nanowire is smooth and clean on the surface; interestingly there exists a small step on the tip (as indicated by the arrow). The inset is the selected area electron diffraction (SAED) pattern, which is parallel to the axis direction of the nanowire. It demonstrates that the nanowires is single crystal, being consistent with the above XRD results. A high-resolution TEM image for a single nanowire is shown in Fig. 3(C), the interplanar spacing is 0.258 nm, corresponding to (002) plane, depicting that the nanowires grew along [001] direction.

The vertically aligned growth of ZnO nanostructures was obviously observed. ZnO epitaxial growth began along the grain boundaries since these are the most thermodynamically active sites for saturation and precipitation of the ZnO [7]. As the ZnO nanowalls grow further, at a critical saturation point, 1D nanowires begin to grow from the junctions of nanowalls. Nonetheless, the growth mechanism of the nanowalls is most likely to be different from that of both ZnO nanowalls on HOPG and insulating sapphire [7] using Au as catalyst and carbon nanowalls pre-patterned by electrical field [8]. Experimentally, the nanowalls were also found when the SiO₂/Si substrate was replaced by SiO₂ substrate. The nanowalls were not observed in the absence

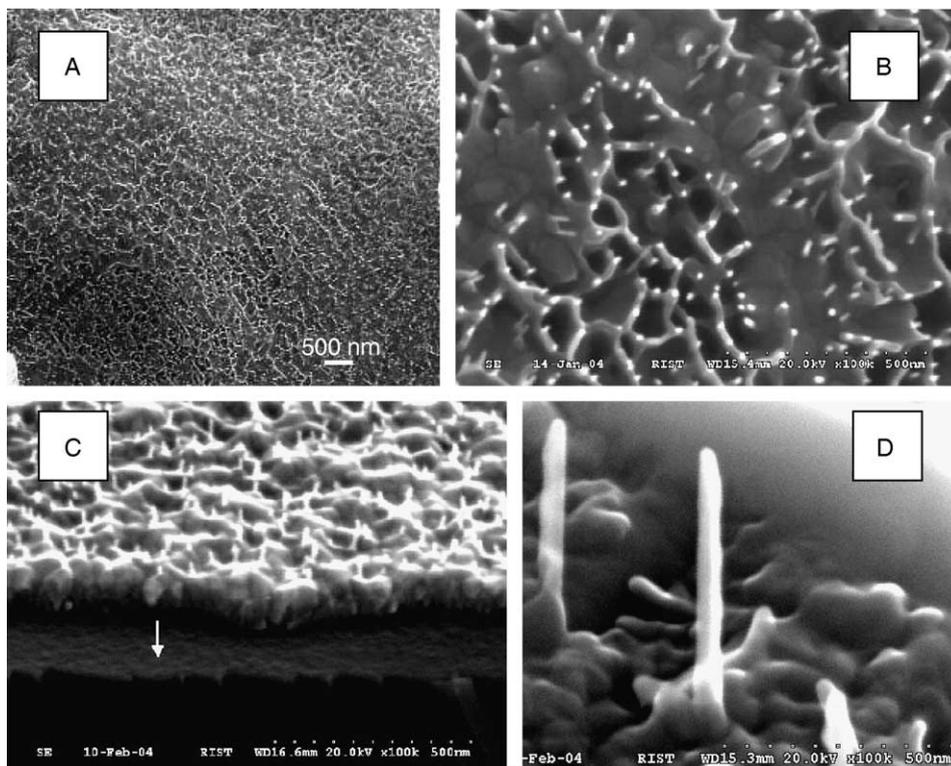


Fig. 1. Zinc oxide nanowalls and nanowires. (A) SEM image of top view quasi-3D ZnO nanostructures grown on SiO₂/Si substrate. (B) Magnified SEM image of titled view ZnO nanowalls and nanowires, showing that ZnO nanowires were grown at the junctions. (C) Perspective SEM image of nanowalls and nanowires. (D) A special array of free-standing 1D ZnO nanowires with conical tips.

of zinc acetate. When the Si substrate was substituted for SiO₂/Si substrate, no nanowalls were observed. We found that the ZnO nanowalls fail to form in the absence of either zinc acetate or SiO₂ substrates. ZnO nanowalls can only be formed in the presence of both suitable zinc acetate and SiO₂/Si or SiO₂ substrate. The grain boundaries are thermodynamically most active sites, which are favorable

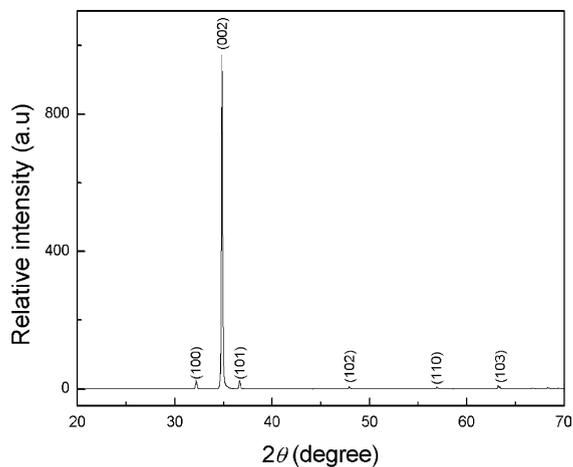


Fig. 2. XRD of as-prepared samples.

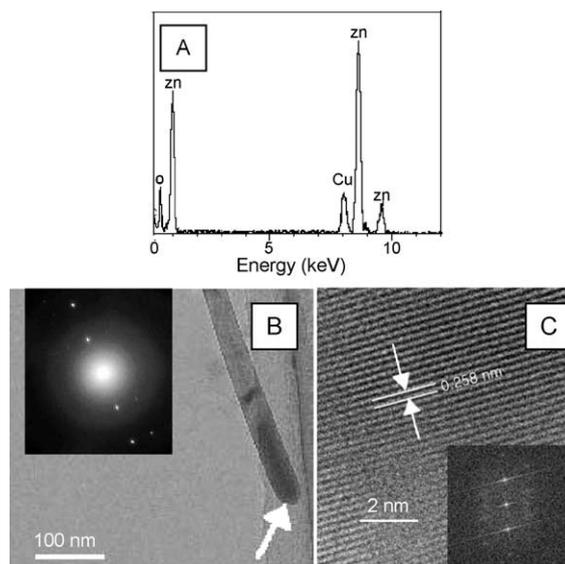


Fig. 3. EDX, TEM and HRTEM micrograph of as-prepared samples. The inset is FFT. (A) EDX of as-prepared sample. (B) TEM and SAED of as-prepared. (C) HRTEM micrograph of as-prepared sample, the inset is FFT.

for saturation and precipitation so that the Zn or ZnO nanoparticles easily deposit on the junctions. At a critical saturation point, the epitaxial growth of being self-assembled nanowires occurs at the junctions of nanowalls.

Raman scattering is very sensitive to the microstructure of nanosized materials. It is also used here to clarify the structure of ZnO nanowires. Fig. 4(a) shows the typical Raman spectrum of ZnO nanowires under excitation of a 515 nm laser line. The peaks at 310, 328, 375, 416, 437, 539 and 587 cm^{-1} are assigned to $3E_{2L}$, $E_{2H}-E_{2L}$, A_{1T} , E_{1T} , E_{2H} , $2LA$, E_{1L} of the bulk ZnO [9,10], respectively. The peak at 517 cm^{-1} can be assigned to Si, whereas the peaks at 493 and 549 cm^{-1} may result from the impurities or defects in the nanowires [9]. However, in comparison with the peaks of bulk ZnO as shown in Fig. 4(b), the peaks of ZnO nanowires shifted from higher frequency to lower frequency, the average shift being about 3 cm^{-1} .

The PL spectra of the samples were measured at room temperature and are shown in Fig. 5. A He–Cd laser (325 nm) was employed as the excitation source using a 350 nm filter. The PL spectrum exhibits narrow and weaker UV emission at 376 nm and a broad stronger green emission band peak around 492 nm. UV emission peak is closely related to the radiative annihilation of excitons [11], whereas the green emission may be assigned to oxygen vacancy [12]. It has been reported that the intensity of the green emission relative to the UV emission increases dramatically with decreasing diameter of nanowires and higher concentration of oxygen vacancies can be formed in the thinner nanowires [5]. In this regard, thinner nanowalls and smaller nanowires with higher surface to volume ratio are considered to contain more surface oxygen vacancies, causing higher intensity of the green emission relative to the UV emission.

4. Conclusions

In summary, we have successfully fabricated highly pure ZnO nanowires at the junctions of nanowalls via a novel and

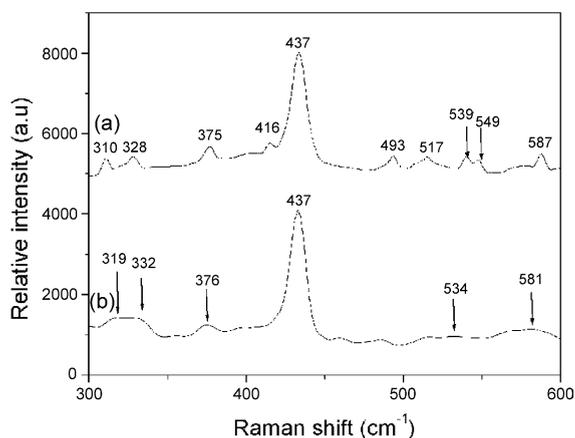


Fig. 4. Raman scattering of as-prepared sample.

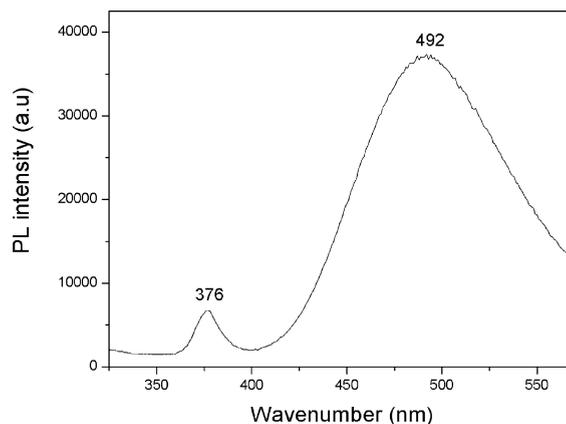


Fig. 5. Photoluminescence (PL) of as-prepared sample.

simple vapor phase route at relative low temperature in the absence of catalyst. The nanowires have average diameter of 10 nm with [001] growth direction. Raman scattering shifted from higher frequency to lower frequency. The higher ratio of PL intensity of the green emission to the UV results from smaller nanowires and thinner nanowalls. This type of nanostructure may have application in batteries, light-emitting and energy conversion devices and other field demanding high surface area materials.

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