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Abstract
Large-scale zinc oxide (ZnO) nanowires were grown via a simple chemical reaction involving water vapour. Electron microscopy observations reveal that the ZnO nanowires are single crystalline and grow along the *c*-axis ([001]) direction. Room temperature photoluminescence measurements show a striking blue emission at 466 nm along with two other emissions in the ultraviolet and yellow regions. Annealing treatment of the as-grown ZnO nanowires results in an apparent reduction of the intensity of the blue emission, which indicates that the blue emission might be originating from the oxygen or zinc defects generated in the process of growth of the ZnO nanowires.

1. Introduction

In the past decade, due to the strong commercial desire for ultraviolet (UV) and blue optical devices, great interest has been focused on the synthesis and optical properties of wide-band-gap semiconductors [1]. The materials researched cover the range from III–V nitrides to II–VI compounds. $In_xGa_{1-x}N$- and ZnSe-based semiconductors have been successfully used for the fabrication of room temperature green–blue light-emitting diodes (LEDs) and laser diodes (LDs) [2, 3]. Many studies have been carried out in exploring new semiconductor systems with more distinctive properties, such as high efficiency of exciton emission and high thermal stability. One new system attracting increasing attention is zinc oxide (ZnO). ZnO, a II–VI compound semiconductor with a wide and direct band gap of 3.37 eV at room temperature, has been recognized as a good candidate for use in blue and UV light emission and room temperature optical UV lasing because of its large exciton binding energy (60 meV), which is much greater than that of GaN (25 eV) and the thermal energy at room temperature (26 meV). The strong exciton binding energy can provide an efficient exciton emission at room temperature under low excitation energy. Already, the progress on the low-dimensional

nanosized materials [4] has prompted more and more researchers to pay increasing attention to the synthesis of semiconductor nanostructures. Some low-dimensional nanostructures of wide-band-gap semiconductors, including GaN [5], SiC [6] and Ga_2O_3 [7], have been synthesized and their optical and electrical properties have been extensively investigated. Recently, polycrystalline ZnO nanowires have been synthesized by space confinement within a porous alumina template [8]. Some nanostructures such as nanorods, whiskers and nanobelts synthesized by the vapour-phase transport process, catalyst-assisted growth and chemical vapour deposition [9–11] have also been reported. Very recently, room temperature UV lasing in ZnO nanowires and nanoclusters has been demonstrated [12, 13]. Due to the promising applications of ZnO in nanoscale optoelectronic devices, it is important to synthesize single-crystalline ZnO nanostructures and investigate their optical features. Here, we present a simple vapour deposition approach for the growth of large-scale very thin single-crystalline ZnO nanowires. Their photoluminescence spectrum exhibits three emissions at 379, 466 and 612 nm.

2. Experimental details

The method employed to synthesize the ZnO nanowires is based on the following chemical reaction under an argon atmosphere: $Zn + H_2O \rightarrow ZnO + H_2$. The reaction was carried out in a horizontal quartz tube. In a typical run, the pure zinc metal powder and the polished silicon substrate, separated by 10 cm in a quartz boat, were loaded into the centre of the horizontal quartz tube. An alumina crucible filled with 10 mm distilled water was placed near the gas inlet of the tube. The quartz tube was inserted in a conventional tube furnace. In our experiments, the reaction system was heated to 1000 °C at the rate of 5 °C min^{-1} and kept at the upper temperature for 30 min. Meanwhile, a carrier gas of high-purity argon was kept flowing through the quartz tube at the rate of 50 sccm (standard cubic centimetres per minute). The gas pressure in the tube was kept at close to 1 atm. After the synthesis was over and cooling to room temperature had occurred, white wool-like products were observed on the silicon substrate.

The deposited products were characterized and analysed by x-ray diffractometry (XRD; using a Rigaku D/max-2400 diffractometer with Cu Kα radiation), transmission electron microscopy (TEM; using a Philips CM12) and high-resolution transmission electron microscopy (HRTEM; using a Philips CM200 FEG at 200 keV). The photoluminescence spectra were measured at room temperature in a Hitachi F-4500 fluorescence spectrophotometer with a Xe lamp upon excitation at 330 nm (3.76 eV).

3. Results and discussion

The as-grown product was collected from the Si substrate to perform the morphology observation by TEM. As shown in figure 1, under the relatively low magnification, the TEM image of the deposition shows that the large-scale wire-like nanostructures spread well on the surface of the substrate. The nanowires are uniform in structure; their typical diameters vary from 5 to 15 nm and their lengths range up to several hundreds of nanometres. In energy-dispersive x-ray (EDX) spectroscopy, only oxygen and zinc are detected. The ratio of O and Zn contents is approximately stoichiometric (see the inset of figure 1). The XRD measurement was carried out to identify the crystal structure of the nanowires. Figure 2 shows the XRD pattern; it can be well indexed to the crystalline hexagonal ZnO phase with cell parameters $a = 3.250$ Å and $c = 5.07$ Å, which is in good agreement with the known data [14].
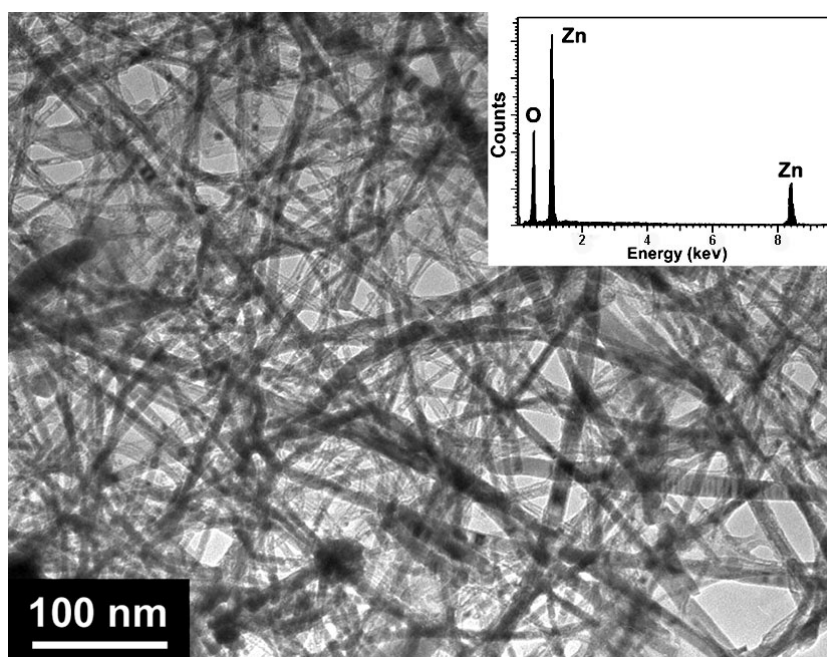
Figure 1. The morphology of the large-scale ZnO nanowires observed by TEM, showing diameters ranging from 5 to 15 nm; the EDX analysis shown in the inset indicates that only O and Zn are detectable.
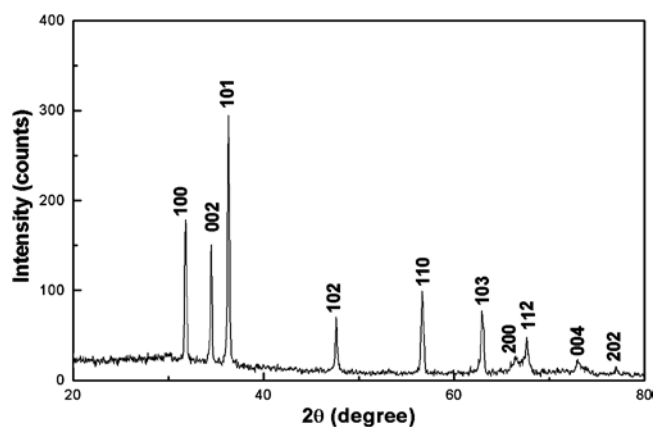

Figure 2. The XRD pattern of the ZnO nanowires.

Detailed structural characterization of the ZnO nanowires was performed using HRTEM. Figure 3 shows a typical lattice-resolved HRTEM image of an individual ZnO nanowire with a diameter of 15 nm. It reveals that the ZnO nanowire is single crystalline in nature and free of dislocations and structural defects. The selected-area electron diffraction (SAED) pattern indicates that the nanowires are parallel to the [001] direction. The lattice spacing of 0.521 nm corresponds to the d-spacing of the (001) crystal facets, which is further confirmation that the nanowires have been preferentially grown along the c-axis direction. The same structural features are found in other nanowires by careful HRTEM observations.
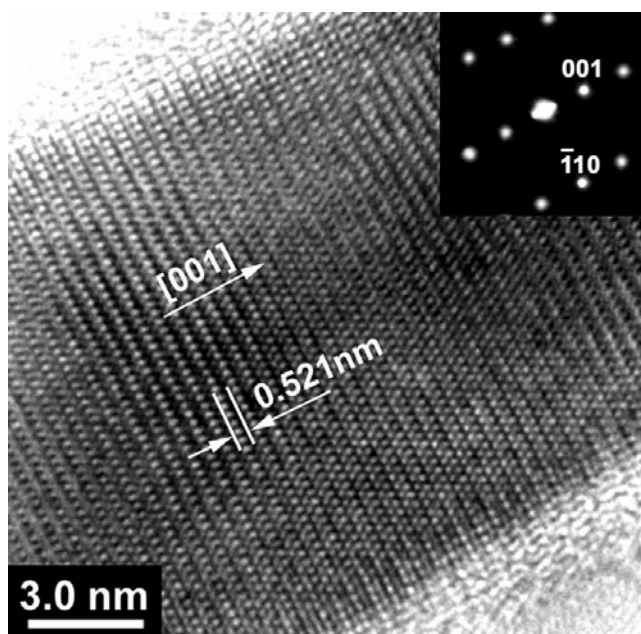
Figure 3. The HRTEM observation and SAED pattern (inlet) for an individual ZnO nanowire, revealing the single-crystalline state of the ZnO nanowire and the [001] growth direction.
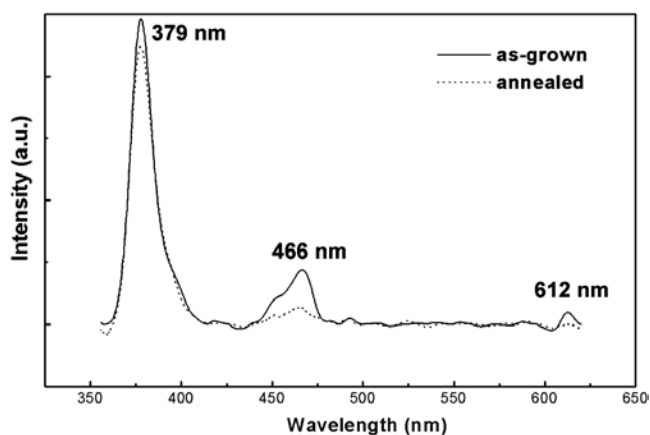

Figure 4. Room temperature PL spectra of as-grown and annealed ZnO nanowires.

One question that needs addressing is how the ZnO nanowire system grows. Traditionally, VS (vapour–solid) [15] and VLS (vapour–liquid–solid) mechanisms [16] were used to explain the growth pattern of the nanowires. In our system, the ZnO nanowires cannot be produced by a VS process because the heating temperature is far lower than the melting point of ZnO (over 2000 K). The most likely explanation for the growth of the ZnO nanowires is as follows: when water vapour reacts with evaporated zinc vapour it forms ZnO and the excess zinc present in the ZnO precipitate formed (eutectic), by acting as the catalyst; this controls the further growth in the substrate through the VLS mechanism. To confirm our assumption regarding the growth pattern of ZnO nanowires, a more detailed investigation is to be carried out.

The room temperature photoluminescence of ZnO nanowires was measured and this is displayed in figure 4. Three luminescence bands, including a strong near-band-edge (NBE) UV emission at ∼379 nm, a blue emission at 466 nm with a shoulder at 452 nm, as well as a weak yellow band at 612 nm, were observed. Generally, there are three PL bands in the UV, green and yellow regions observed in ZnO. The UV emissions are commonly attributed to the direct recombination of excitons through an exciton–exciton collision process, where one of the excitons radiatively recombines to generate a photon (the exciton emission process). The green and yellow emissions are identified as being from the radiative recombination of the electrons from shallow donors with the trapped holes from singly ionized oxygen vacancies and interstitial oxygen [17]. In our results, the green emission is not observed; however, a broad blue band appears. Some researchers have reported this blue emission for ZnO films and whiskers [10, 18]. Yet the mechanism behind this luminescence is still not clear. The blue emission (2.36 eV) cannot come from the impurities introduced since no impurities were detected in the samples by EDX measurement. We think that this blue emission might be related to the intrinsic defects (O and Zn vacancies or interstitials and their complexes) in ZnO nanowires. To verify our assumption, we annealed the as-grown sample and measured its photoluminescence at room temperature again. The as-grown sample was annealed at 500 °C for 3 h under oxygen gas. The PL spectrum of the annealed sample (shown in figure 4 by a dotted curve) exhibits an obvious weakening in the emission intensity of the blue luminescence. This phenomenon might be resulting from the following process. After annealing in the oxygen atmosphere, the density of oxygen vacancies in the as-grown sample decreases because of the entry of oxygen and combination with the oxygen vacancies in the ZnO nanowires. At the same time, the O and Zn interstitials diffuse towards the vacancies during the heat treatment. As a result, the density of defects decreases. Therefore the reduction of the number of radiative recombination centres results in the lessening of the blue PL emission intensity. A similar reduction of the intensity of the yellow emission (612 nm) from the annealed sample can be seen. That can be attributed to the decrease in number of oxygen interstitials with improvement of the structural order in ZnO nanowires upon annealing.

Due to the complexity of the microscopic detail, there is still much speculation as regards the explanation of the luminescence emission of ZnO nanowires. For example, in nanostructures, an effect on the PL features due to the surface state cannot be ruled out. Further work is ongoing.

4. Conclusions

In summary, we have fabricated large-scale ZnO nanowires with diameters of 5–15 nm. These nanowires are single crystalline and were grown along the *c*-axis direction. The room temperature photoluminescence measurements show three emissions in the UV, blue and yellow regions. Annealing treatment of as-grown ZnO nanowires results in a great reduction in intensity of the blue and yellow emissions, which gives some evidence that the blue emission might be originating from the oxygen or zinc defects generated in the process of growth of the ZnO nanowires.

Acknowledgments

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