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Photoluminescence properties of catalyst-free growth of needle-like ZnO nanowires

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Abstract

Catalyst-free needle-like ZnO nanowires have been grown on Si(111) substrate at 430 °C via a simple solid–vapour process. The obtained nanowires are found to have a uniform size distribution with sharp tips. The lengths of the nanowires range from 2.8 to 3.2 μm with diameters of about 100 nm for the root and 30 nm for the tip parts. The x-ray diffraction (XRD) result shows the nanowires are *c*-axis preferentially oriented. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) analysis reveal that every single nanowire is a well developed single crystal. The room temperature photoluminescence (PL) spectrum shows a dominant near-band-edge emission peak. The near-band-edge emission is further identified to originate from the radiative free exciton recombination by the temperature-dependent PL.

1. Introduction

Since the first discovery of carbon nanotubes [1], one-dimensional nanomaterials have attracted great interest because of their unique and fascinating optical, electrical, mechanical and thermoelectrical properties together with their wide uses in fundamental scientific research and potential technical applications. By being tailored in size and shape, they can display various properties. For example, nanostructures have size-dependent optical properties: with the size changed, the emission peaks of the photoluminescence (PL) will be red-shifted or blue-shifted.

Among them ZnO has drawn great attention, due to its wide bandgap (3.37 eV), large exciton binding energy (60 meV), low lasing threshold, friendliness to the environment and cheapness. ZnO nanostructures can serve for ultraviolet light emitters or laser diodes [2, 3], and one-dimensional ZnO nanostructures have been proved to be valuable candidates for field emission devices [4].

Up to now, various methods have been used to prepare ZnO nanostructures, such as metal catalyst assisted vapour–liquid–solid (VLS) deposition [5], metallorganic vapour deposition [6], thermal evaporation [7], the wet chemical process [8], template-based growth [9], and the solid–vapour process [10]. Although the most popular method to synthesize ZnO nanowires is catalyst assisted growth through the VLS process, the as-synthesized products have metal nanoparticles on their tips, which would affect their properties. Catalyst-free synthesis can successfully avoid the metal nanoparticles on their tips and enable the growth of sharp-tipped needle-like ZnO nanowires [11]. Because of their sharp curvature on the tips, it has been demonstrated that electrons are more easily emitted from ZnO nanoneedles with sharp tips than from nanowires with uniform diameters [12, 13]. Needle-like ZnO nanowires can also offer potential applications as probing tips with high spatial resolution in both vertical and horizontal dimensions or field-emission tips due to the increased field enhanced factor [14].

In this paper, we present a catalyst-free growth of needle-like ZnO nanowires using a simple solid–vapour process on

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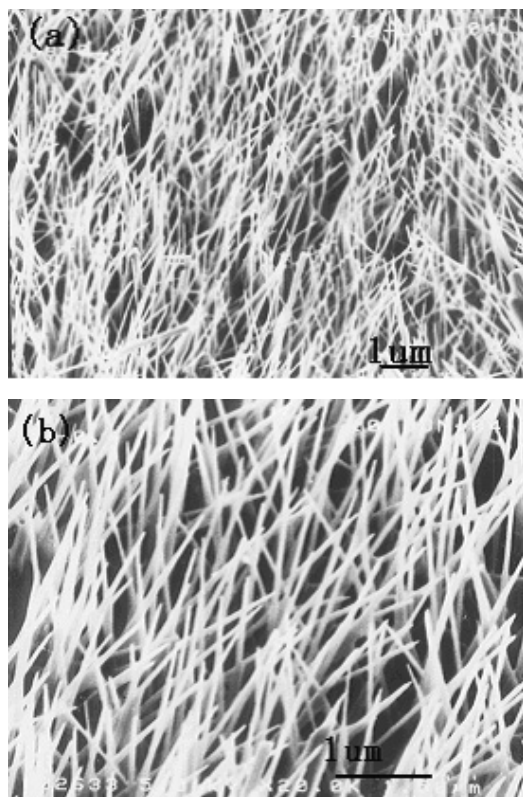


Figure 1. FESEM images of high-density needle-like ZnO nanowires grown on Si(111) substrate at 430 °C with different magnifications. The measurement is tilted for 45°.

Si(111) substrate at 430 °C. Commonly, low-temperature catalyst-free growth is accomplished in an MOCVD [15, 16] or PLD [17] system; compared with their products, we used a simpler solid–vapour process and obtained higher-aspect-ratio needle-like ZnO nanowires. The needle-like ZnO nanowires with *c*-axis preferred orientation are almost vertically aligned to the substrate surface with small angle distribution. Strong UV emission was observed at room temperature, which is identified to originate from the exciton related emission.

2. Experimental details

The material growth was carried out in a horizontal tube furnace by the solid–vapour process. Zinc powder (99.99%) loaded into a quartz boat, which was put in the centre of the furnace, served as the source material. Si(111) substrate was laid above the source material with a vertical distance of 4 mm. Before loading, the Si substrate was cleaned by organic solvent, etched by HF acid and washed with deionized water followed by drying in the nitrogen gas. The furnace was heated up to 430 °C at a rate of 16 °C min⁻¹ under a constant flow (150 sccm) of pure Ar. When the desired temperature was reached, pure Ar gas was substituted by normal nitrogen gas at the same flow rate to start the ZnO growth. The oxygen is unintentionally introduced by the residual O₂ in the nitrogen gas. The pressure during the growth process was kept to be about 1 Torr. After deposition, the substrate surface was covered with a white–grey layer. The as-grown sample was then investigated by the field-emission scanning

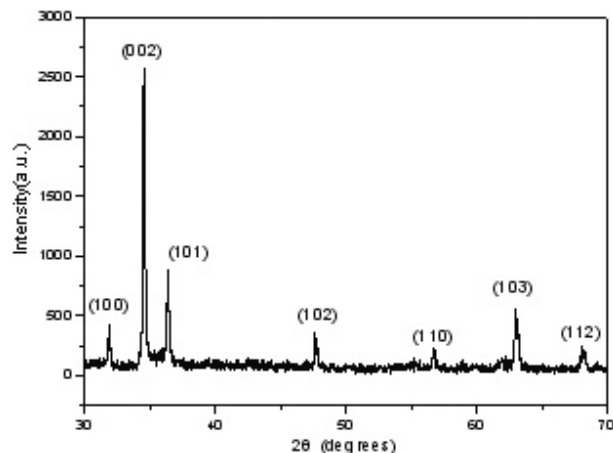


Figure 2. XRD θ – 2θ scan of the ZnO nanowires on Si(111).

electron microscopy (FESEM), the energy-dispersive x-ray spectroscopy (EDX) attached to the SEM, the x-ray diffraction (XRD) and the transmission electron microscopy (TEM). PL measurement was performed using a He–Cd laser line of 325 nm as the excitation source.

3. Results and discussion

Figure 1 shows the FESEM images with different magnification of the ZnO nanowires grown on Si(111) substrate at 430 °C for 30 min, verifying the high-density ZnO nanowires. The nanowires have a uniform length of 2.8–3.2 μm with an average diameter of 100 nm. The size and morphology of the tips grown by this method are different from those obtained by MOCVD [15, 16] and PLD [17] methods; in our results, we obtained a larger size of the nanowires, indicating a faster growth rate of the solid–vapour method. EDX analysis (the graph is not given) shows that the nanowires consist of only zinc and oxygen. Though there is a large orientation divergence for the nanowires compared with the nanorods gained from the above MOCVD and PLD methods, we observed that most of the nanowires are vertically pointing to the substrate surface preferentially and their sizes are almost uniform.

The x-ray diffraction spectrum of the ZnO nanowires is shown in figure 2. All the diffraction peaks are originated from wurtzite ZnO, with lattice parameters of $a = 0.325$ nm and $c = 0.521$ nm. The (002) diffraction peak is dominant in the spectrum, which means the products are with *c*-axis preferred orientation [18]. This is also in agreement with the observation in the SEM.

Figure 3 shows the TEM image of a single ZnO nanowire. The needle-like nanowire has a smooth surface and a sharp tip. The diameters of the nanowires are found to decrease from the root (~ 100 nm) to the tip (~ 30 nm). The selected area electron diffraction (SAED) characteristic (shown in the top inset of figure 3) indicates that an individual ZnO nanowire is single crystalline with the growth direction along the *c* axis.

To study the optical properties, PL spectrum was measured using a He–Cd laser line of 325 nm as the excitation source. Figure 4 shows the PL spectrum measured at room temperature. The emission of the nanowires consists of two main parts: a

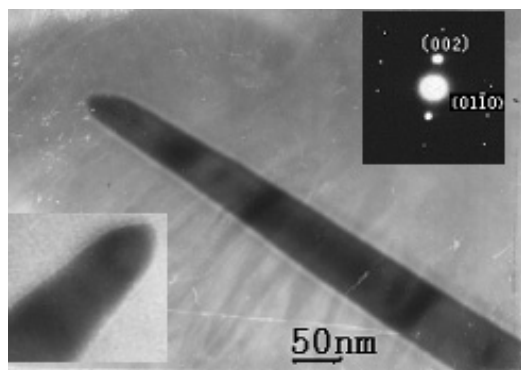


Figure 3. TEM image of a single nanowire, with the top inset its SAED analysis. The bottom inset is the magnified view of a nanowire tip.

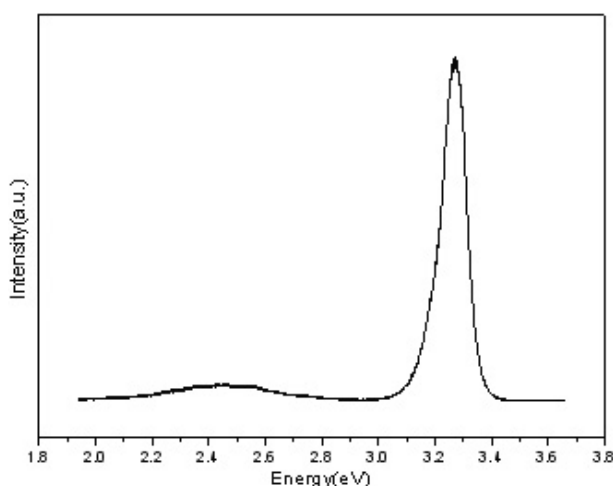


Figure 4. PL spectrum of ZnO nanowires measured at room temperature.

strong UV emission located at 3.27 eV and a much weaker deep-level related emission located at 2.47 eV. The deep-level emission is commonly believed to come from the singly ionized oxygen vacancy [19] or surface states [20]. The UV emission is attributed to the near-band-edge exciton emission, which will be identified later by the temperature-dependent PL spectra.

The inset in figure 5 is a typical PL spectrum at 83 K. The dominant peak at 3.358 eV is a shallow donor related bound exciton (BE) emission. At the higher energy shoulder of the BE, we observed a free exciton (FE) peak located at 3.369 eV. Also at a lower-energy position of BE, two emission peaks emerge, which we assign as X1 and X2, and they are often disputable ones. The energy separation of FE-X1 is 60 meV as Zhao *et al* [21] reported, but they considered the two emission peaks as a free-to-bound (FB) transition and an FB-1LO replica. Here we think it is more reasonable to attribute them to FE-1LO for X1 and FE-2LO for X2, since the energy and temperature relation in our case is not in accordance with the equation of $\hbar\omega = E_g - E_B + K_B T/2$ [22] as that of normal FB. Nor are they donor-acceptor pairs (DAPs), as they do not show an energy shift at different exciting power at 83 K (figures not given), which is one of the proofs to characterize DAPs [23]. Here, the energy separation of FE-1LO is smaller

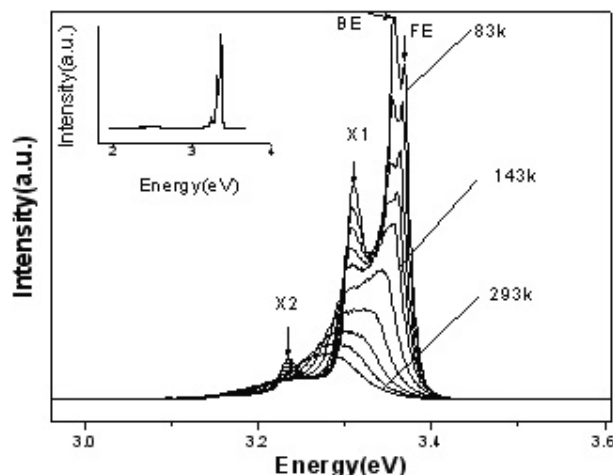


Figure 5. PL spectrum of the ZnO nanowires measured at different temperatures (from 83 to 293 K). The inset is a typical PL spectrum measured at 83 K.

than the LO phonon energy (72 meV) due to the energy softening of FE-1LO. The origin of the energy softening can be explained by the strong exciton-phonon coupling in ZnO. As ZnO is a polarized semiconductor with wurtzite structure, exciton-phonon coupling is favoured in it, where the lattice can be readily polarized [24]. The exciton-phonon coupling formed an exciton polaron; Liang *et al* [24] call it an exciton-phonon complex (EPC). As in ZnO crystal the free exciton binding energy is 60 meV, which is almost resonant with the LO phonon energy, free excitons are easy to couple with LO phonons [25]. The observed peaks should not be regarded as phonon emission stimulated by excitons in ZnO, but as transitions into exciton-phonon complexes, and the energy of the complexes cannot be thought of as a simple sum of the exciton and phonon energies as a result of coupling of excitons and phonons.

The main part of figure 5 illustrates the temperature dependence of the UV peak in the PL spectra. With the increase of temperature, the emission peaks move toward the lower-energy side and gradually get broadened due to the LO-phonon scattering and increased exciton thermal ionization [26]. The bound exciton emission peak intensity decreases quickly with the increase of temperature and finally disappears above the temperature of 140 K, which is due to the thermal ionization of bound excitons into free excitons at higher temperature due to its smaller binding energy [27]. In contrast, the FE related peak gets relatively stronger with the increase of temperature and finally dominates the emission spectrum up to room temperature. The FE phonon replicas have different temperature dependence than excitons, as they show slower intensity decrease by the increase of temperature. Gradually they get weaker and broadened at higher temperatures and finally merge into the low-energy tail of the FE peak.

From the above structural and optical analysis, we found that the fabricated ZnO nanowires are of high crystal and optical quality. Since the growth temperature is as low as 430 °C, it can effectively avoid the unexpected impurity incorporation and defect formation. Moreover, low-temperature growth can also reduce the stress between the film and the substrate caused by lattice mismatch, thus can

be applied to various device applications. Moreover, we can freely select the substrates, such as ITO, to adapt to different requirement of ZnO-based nanoscale devices.

4. Conclusions

We have synthesized catalyst-free needle-like ZnO nanowires at low temperature with a simple solid–vapour process. The nanowires have almost uniform size with sharp tips. XRD results show the nanowires have *c*-axis preferred orientation. TEM images indicate that the single nanowires have smooth surfaces and are each single crystalline. The room-temperature PL result shows the nanowires have strong UV emission, which mainly originates from free exciton emission.

Acknowledgments

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