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Growth of Highly Oriented ZnO Nanorods by Chemical Vapor Deposition

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ABSTRACT

Highly-oriented ZnO nanorods were grown on the fused silica substrates by a thermal CVD technique using Zinc acetylacetonate ($Zn(C_5H_7O_2)_2$). The substrate was heated to 500°C and the vaporization temperature of $Zn(C_5H_7O_2)_2$ was keep at around 135°C. X-ray diffraction and TEM analyses reveal that the nanorods are preferentially oriented toward the c-axis direction. Photoluminescence (PL) and absorption measurements show a strong emission at around 380nm which corresponds to the near band-edge emission of the bulk ZnO. Moreover, the negligible green emission band in PL spectrum and the absence of E_1(LO) mode of the ZnO crystal in Raman spectrum indicate a low concentration of oxygen vacancy in the highly-oriented ZnO nanorods.

INTRODUCTION

One-dimensional nanometer-sized semiconductor materials, i.e. nanowires and nanorods, have attracted considerable attention due to their unique properties and suitability for fundamental studies of the roles of dimensionality and size in their physical properties as well as for the application to optoelectronic nanodevices [1]. ZnO exhibits a direct band gap of 3.37 eV at room temperature with a large exciton binding energy of 60 meV. The strong exciton binding energy which is much larger than that of GaN(25 meV) as well as the thermal energy at room temperature(25 meV) can ensure an efficient exciton emission at room temperature under low excitation energy [2,3]. In consequence, ZnO is recognized as a promising photonic material in the blue-UV region. Room temperature UV lasing properties have been indeed demonstrated with ZnO epitaxial films, microcrystalline thin films and nanoclusters recently [4,5]. Moreover, room temperature UV lasing in ZnO nanowires has been demonstrated very recently [6]. The synthesis of one-dimensional single crystal ZnO nanostructures has been of growing interest owing to their promising application in nanoscale optoelectronic devices. Single crystalline ZnO nanowires have been synthesized successfully using VLS growth methods [6,7,8] at rather high temperatures for the VLS mechanism proceeding. Besides, single crystalline ZnO nanobelts have also been reported by simply evaporating the ZnO powders at a high temperature of 1400°C [9]. However, high density and well-ordered nanostructures will be needed from practical application point of view. Here, we present a simple catalyst-free CVD approach for the growth of the highly-oriented ZnO nanorods at a low temperature of around 500°C.

EXPERIMENTAL DETAILS

ZnO nanorods were grown in a two-temperature-zone furnace (see figure 1). Silicon wafers and fused silica plates were employed as substrates. They were cleaned in an ultrasonic bath of acetone for 20 min. Zinc acetylacetonate hydrate ($Zn(C_5H_7O_2)_2 \cdot xH2O$, Lancaster, 98%) placed in a glass cell was loaded into the low temperature zone of the furnace which was controlled to be at 130-140°C to vaporize the solid reactant. The vapor was carried by a 500-sccm N_2/O_2 flow into the higher temperature zone of the furnace in which substrates were located at 200 Torr. ZnO nanorods were grown directly on bare fused silica or silicon substrates at 500°C. It should be noted that there were no metal films, which are employed as catalyst in VLS method, pre-coated on the substrates.

The morphology and size distribution as well as elemental analyses of the nanorods were examined using SEM equipped with an EDS. The crystal structure of the nanorods was analyzed using XRD and HRTEM. Optical properties were characterized by absorption spectrometry as well as by photoluminescence spectrometry using a Xe lamp with an excitation wavelength of 325nm at room temperature.

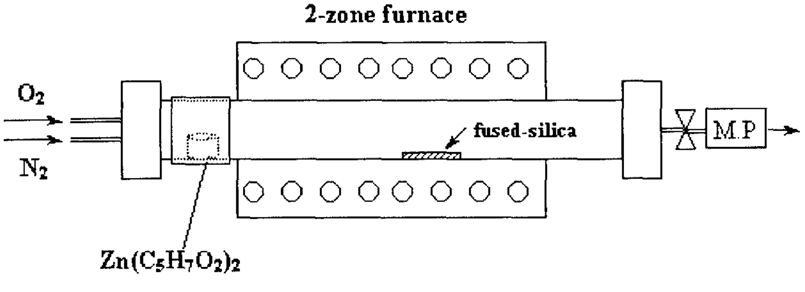

Figure 1. Schematic diagram of the experimental setup.

RESULTS AND DISCUSSION

As shown in figure 2, ZnO nanorods were grown directly on bare fused silica or silicon substrates at 500°C. A high density of highly-oriented nanorods with a diameter in the range of 60-80 nm uniformly formed over the entire substrate at a vaporizing temperature of 135°C and N_2/O_2 flow rates of 250/250 sccm. The energy dispersive spectrometry (EDS) taken from the nanorods shows that the atomic composition ratio of Zn:O is about 1:1. Size control of the highly-oriented ZnO nanorods diameters was achieved by adjusting the growth condition. Figure 3 shows that the ZnO nanorods with smaller diameters (~ 45nm) are obtained by increasing N_2 flow rate to 500 sccm.

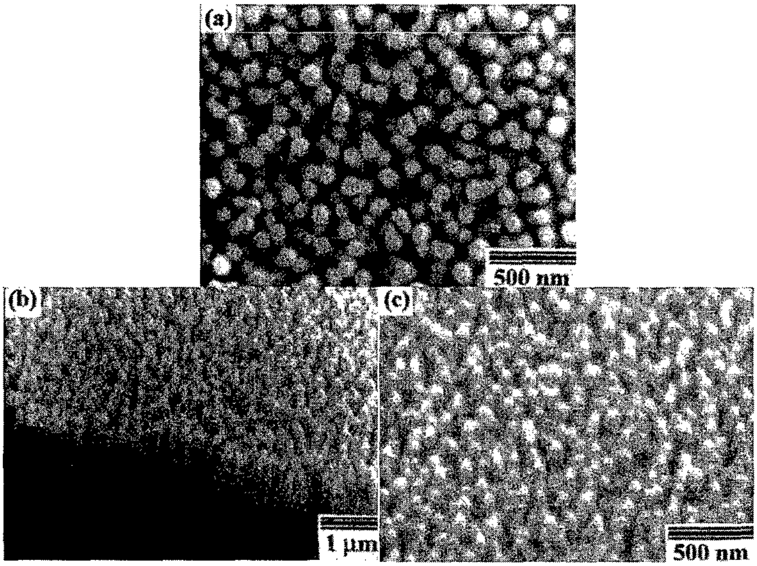

Figure 2. SEM images of ZnO nanorods grown on the fused silica substrates at N_2/O_2 flow rates of 250/250 sccm. (a) Top view, (b) and (c) 45° tilted view.

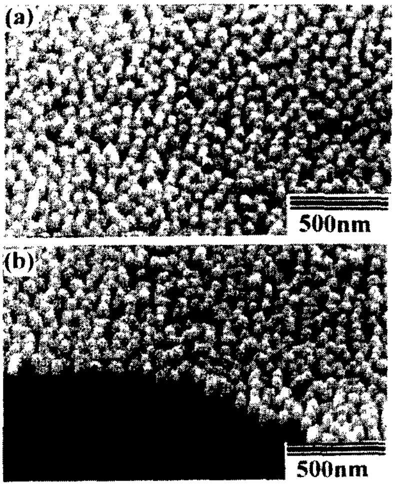

Figure 3. SEM images of ZnO nanorods grown on the fused silica substrates at N_2/O_2 flow rates of 500/250 sccm. (a) and (b) 45° tilted view.

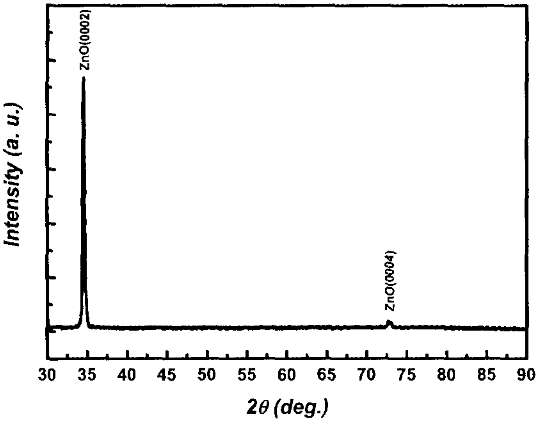

Figure 4. XRD pattern of ZnO nanorods on a fused silica substrate.

The crystal structure of the nanorods was examined by X-ray diffraction (XRD). Figure 4 shows a typical XRD pattern of the highly-oriented ZnO nanorods grown on a fused silica substrate. The two peaks are indexed as (0002) and (0004) of the wurtzite structure of ZnO, indicating that the nanorods are preferentially oriented toward the c-axis direction.

Further structural characterization of the ZnO nanorods was performed using transmission electron microscopy (TEM). Figure 5(a) shows a cross-sectional image of the ZnO nanorods, on a fused silica substrate, with a diameter in the range of 80-100 nm. It reveals that all nanorods were grown with a direction perpendicular to the substrate. Moreover, there is no additional metal particle appeared on the top or the bottom of the rods, implying a catalyst-free approach for the growth of the highly-oriented ZnO nanorods at a low temperature is achieved. Typical bright-field and dark-field images of the ZnO nanorods are illustrated in figure 5(b) and figure 5(c), respectively. The dark-field image indicates that the nanorod possesses the single crystalline structure. Figure 5(d) shows a high-resolution TEM image of a nanorod. The lattice spacing of 0.257 nm is corresponding to the d-spacing of (0002) crystal planes, confirming the XRD analysis that the ZnO nanorods are preferentially oriented toward the c-axis direction, as shown in figure 4.

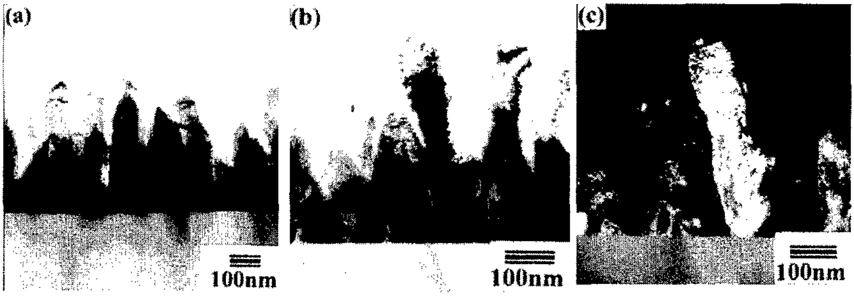

Figure 5(a)(b)(c). TEM cross-sectional images of ZnO nanorods grown on fused silica substrates at a vaporizing temperature of 138°C. (a) Low magnification image shows nanorods grown with a direction perpendicular to the substrate. (b) and (c) Typical bright-field and dark-field images of the ZnO nanorods, respectively.

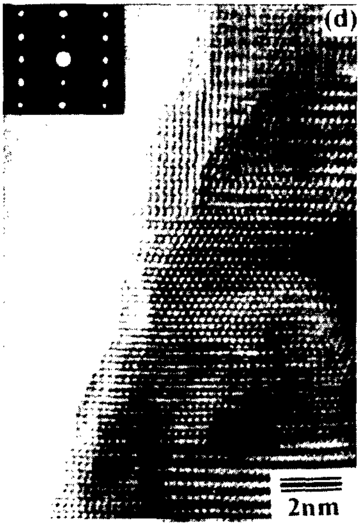

Figure 5(d). High-resolution TEM image of a single crystalline ZnO nanorods and the corresponding electron diffraction pattern (inset).

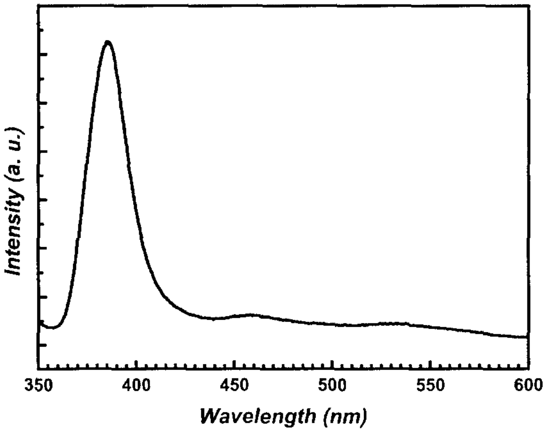

Figure 6. Typical photoluminescence spectrum of ZnO nanorods.

Figure 6 shows the PL spectrum of the ZnO nanorods with a diameter in the range of 60-80 nm. Three emitting bands, including a strong ultraviolet emission at around 380 nm, a very week blue band (440-480 nm) as well as an almost negligible green band (510-580 nm), were observed. Among them the UV emission must be contributed to the near band edge emission of the wide band gap ZnO. It has been suggested that the green band emission is corresponding to the singly ionized oxygen vacancy in ZnO and results from the recombination of a photogenerated hole with the single ionized charge state of this defect [10]. Thus the almost negligible green band in figure 6 shows that there is very low concentration of oxygen vacancy in the highly-oriented ZnO nanorods. The observation of blue band emission (440-480 nm) of ZnO film has been also reported using cathodoluminescence [11]. However, the mechanism of this emission is not clear yet.

In addition to photoluminescence measurement, we also used absorption spectrometry to further examine the optical property of the highly-oriented ZnO nanorods. As illustrated in figure 7, the absorption spectrum at room temperature shows that there is an absorption peak at around 380nm, which is consistent with the result of PL measurement. The Raman spectrum of the highly-oriented ZnO nanorods grown on fused silica substrate is shown in figure 8. Only the ZnO E_2 mode at 437cm^{-1} is appeared in this spectrum. The absence of the E_1(LO) mode at 583cm^{-1} of the ZnO associated with oxygen deficiency [12] indicates the high quality of the ZnO nanorods as the negligible green band in the PL spectrum.

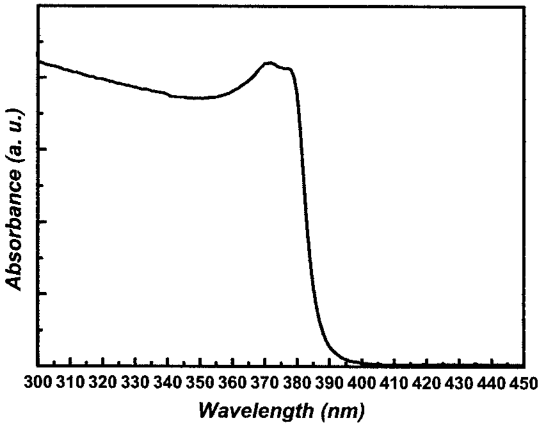

Figure 7. Absorption spectrum of the ZnO nanorods at room temperature.

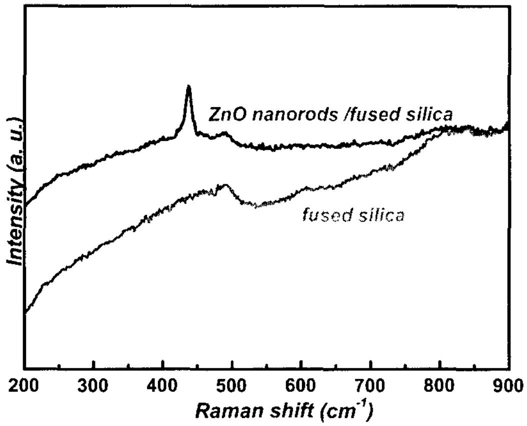

Figure 8. Raman spectra of the bare fused silica substrate and the ZnO nanorods grown on it.

CONCLUSIONS

A simple catalyst-free CVD method for the growth of the highly-oriented ZnO nanorods at low temperature has been demonstrated in this report. The nanorods grown on fused silica are preferentially oriented toward the c-axis direction. Photoluminescence (PL) and absorption characteristics of the ZnO nanorods shows a strong UV light emission peaked around 380 nm at room temperature. PL and Raman measurements also show a concentration of oxygen vacancy in the highly-oriented ZnO nanorods. We believe the presented approach is a simple one for practical application to nanoscale optoelectronic devices.

ACKNOWLEDGEMENTS

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