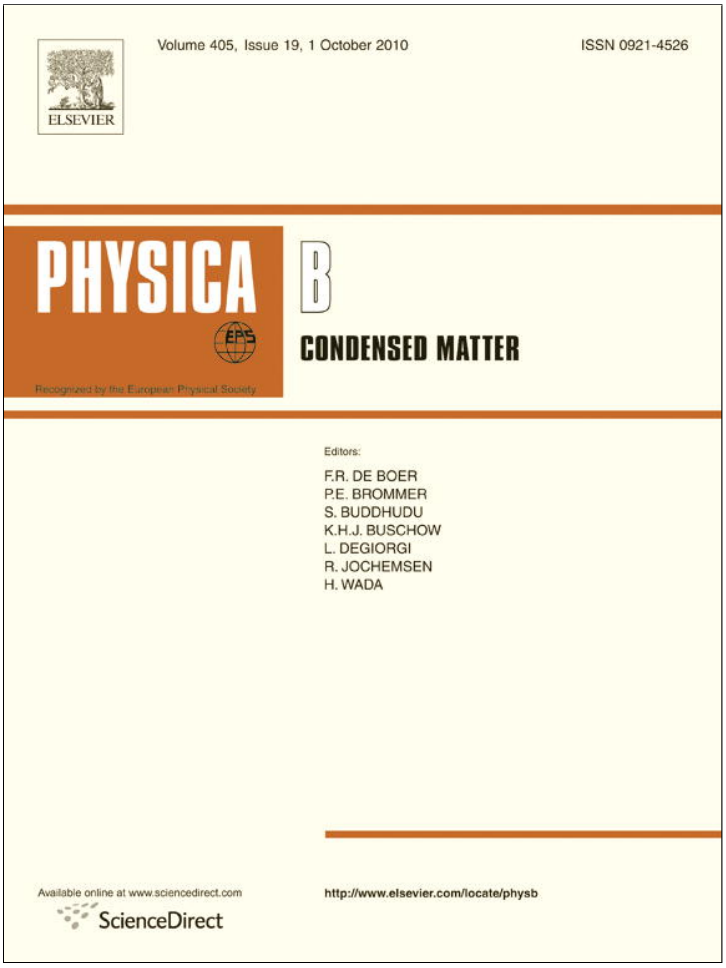

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Growth of high-quality ZnO nanowires without a catalyst

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In this study, an efficient method to achieve a wide range of high-quality zinc oxide (ZnO) nanostructures through zinc powder evaporation at lower temperatures is developed. ZnO nanowires could be synthesized on n-type silicon substrates by a simple thermal-evaporation technique without a catalyst at 550, 600, and 650 °C. Samples are annealed in wet oxygen and ambient argon gases. Surface morphology, crystallinity, and optical properties of the ZnO nanowires are examined by scanning electron microscopy, X-ray diffraction, and photoluminescence measurement. The optimum temperature for synthesizing high-density, long ZnO nanowires was determined as 650 °C. The possible growth mechanism of ZnO nanowires is also proposed.

1. Introduction

Zinc oxide (ZnO) has been intensively studied because of its unique properties and versatile applications in transparent electronics, ultraviolet (UV) light emitters, piezoelectric devices, chemical sensors, and spin electronics. Recently, one-dimensional (1D) ZnO nanostructures, such as nanowires, nanobelts, and nanoneedles, have attracted increasing research interest. These structures are emerging as a better candidate for the said applications, paving the way for a new generation of nanoscale devices [1,2].

ZnO is an important II–VI semiconductor with a direct wide bandgap of 3.4 eV and a large exciton binding energy of 60 meV [3]. It has a stable wurtzite structure with lattice parameters of $a=0.325$ nm and $c=0.521$ nm. One-dimensional ZnO nanostructures could be synthesized using various methods. Many techniques have been successfully used to synthesize ZnO nanowires, including vapor–liquid–solid (VLS), thermal-evaporation and condensation by vapor–solid (VS), and solution-based growth techniques [4–6].

1D metal oxide semiconductors are applied in many devices. Applications include UV sensors [7], gas and biosensors sensors [8], memory switching devices [9], and different electronics blocks [10]. Most nanowire properties are derived from their high surface-to-volume ratio, which increased their surface activities. Although many experiments have been conducted on nanowires, wires with unique axial and radial are still required.

The most common method to synthesize ZnO nanowires is the vapor transport process based on the VS mechanism of crystal growth. In this study, we fabricated ZnO nanowires through thermal evaporation of Zn powder without a catalyst.

2. Experiment

The synthesis process was carried out in a controllable tube furnace with a quartz tube (inner diameter, 25 mm). N-type silicon (Si) wafers cut into 1 × 1 cm^2 pieces with a single polished side were used as substrates. The substrates were ultrasonically cleaned with acetone and isopropyl alcohol (IPA), and then rinsed with distilled water. The wafers were then dried by a nitrogen gas blow system.

A pure metallic Zn powder (99.9%) as source material was placed into a ceramic boat. The Si substrates (with the polished side facing the source material) were inserted into a quartz tube within the furnace at a temperature of 400 °C. Together with the ceramic boat, the tube was positioned at the center of the tube furnace. Temperature was increased to 550, 600, and 650 °C under a continuous flow of highly pure argon (Ar) and wet oxygen (O_2) gases with flow rates of 350 sccm (Ar to O_2 ratio was 1:1) for 1 h to examine the effect of heating temperature on the growth of ZnO nanostructure. After evaporation, the quartz tube was removed from the furnace and cooled to room temperature. A white layer of ZnO was observed on the Si substrate surface. The surface morphology and structure of the ZnO nanostructures were examined by scanning electron microscopy (SEM, JEOL) attached with an energy dispersive X-ray spectroscopy (EDS). The high-resolution PANalytical X-ray diffractometer (HR-XRD) was used for phase identifications. The photoluminescence (PL) spectra

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were obtained at room temperature using the Jobin Yvon Horiba HR800UV system with a 325 nm line of the He–Cd laser at a power of 20 mW.

3. Results and discussion

The typical morphologies of the synthesized ZnO nanostructure grown at different temperatures of 550, 600, and 650 °C are shown in Fig. 1. The images of the three temperatures show that ZnO grew as nanowires. The diameters of ZnO nanowires grown at 550 °C normally range from 40 to 50 nm, with 3–5 μm length, as seen in Fig. 1(a). At a growth temperature of 600 °C, the diameter of the nanowires measured more than 50–70 nm, and 6–9 μm long wires formed in high yield (Fig. 1(b)). After increasing growth temperature to 650 °C, ZnO nanowires formed high-density nanowires, as shown in Fig. 1(c), with measured diameter of approximately 100 nm, and the length of approximately 9 μm. Most nanowires were entangled with each other, making it difficult to measure the length accurately. Hence, we find increase in density of synthesized ZnO nanowires with increase in temperatures.

EDX analysis indicates that the composition of the ZnO nanowires grown at different temperatures consists of Zn and O; no other elements were observed.

The high-density ZnO nanowires obtained at a heating temperature of 650 °C show that the conversion of the Zn metal to ZnO is higher than that at lower temperatures. Therefore, longer ZnO nanowires could be obtained at 650 °C with the same amount of heating time. Only a few nuclei sites were formed at 550 °C. Therefore, the length and density of the nanowires were dramatically reduced.

The produced samples were examined by HR-XRD to investigate the crystal structure. The XRD pattern of the prepared ZnO nanowires synthesized at 550, 600, and 650 °C is shown in Fig. 2. The diffraction peaks can be indexed to the hexagonal structure of the ZnO according to JCPDS Card No. 01-089-7102.

XRD pattern shows the enhancement of the peak height as the growing temperature increased from 550 to 650 °C, which proves that the conversion of Zn metal to ZnO peaks at 650 °C, compared with the other temperatures. The crystallite sizes of the prepared ZnO nanowires were calculated using the full width at half maximum (FWHM) of the (0 0 2) peak using Scherrer's formula [11]

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{1}$$

where λ, θ, and β are the X-ray wavelength (0.154 nm), Bragg diffraction angle, and FWHM, respectively. The results show insignificant effect of the growth temperature on the crystallite sizes, and the average value of the size is 30 nm. The PL spectrum of ZnO nanowires grown at 550, 600, and 650 °C was recorded at room temperature. Fig. 3 shows the characteristic narrow band at

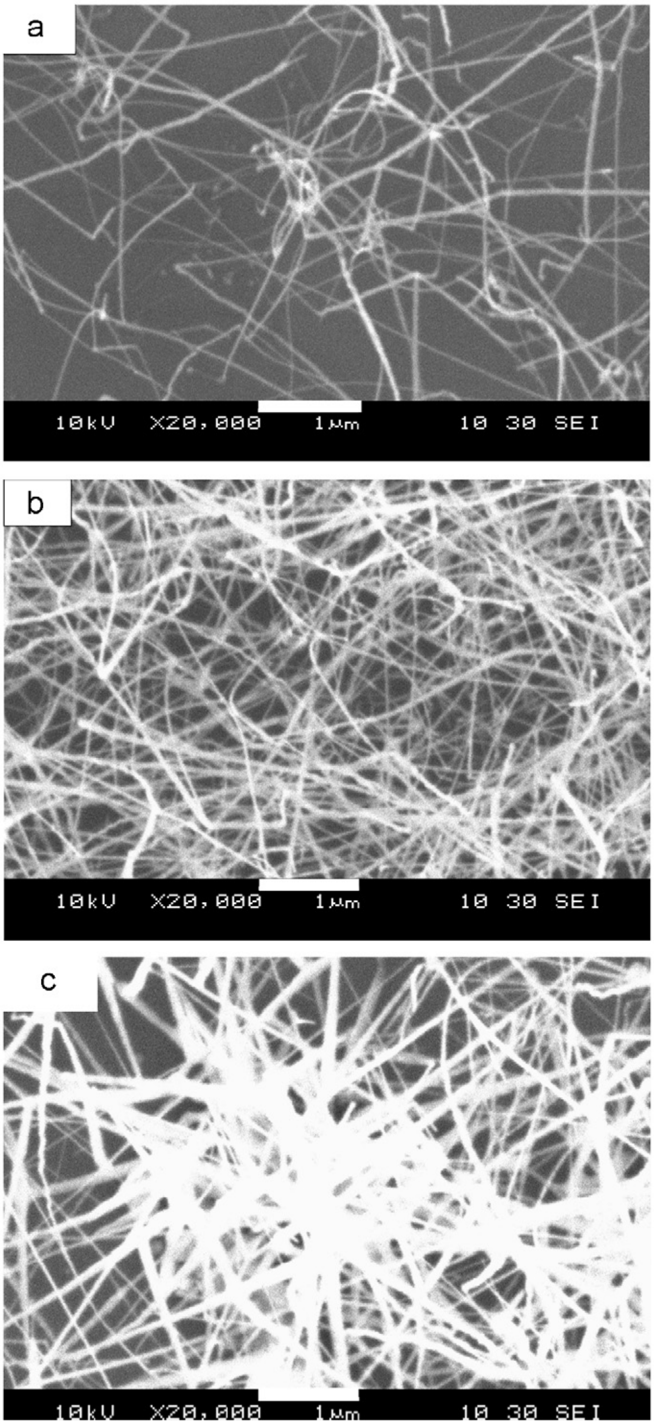

Fig. 1. SEM images of ZnO nanowires grown on a Si substrate at (a) 550, (b) 600, and (c) 650 °C.

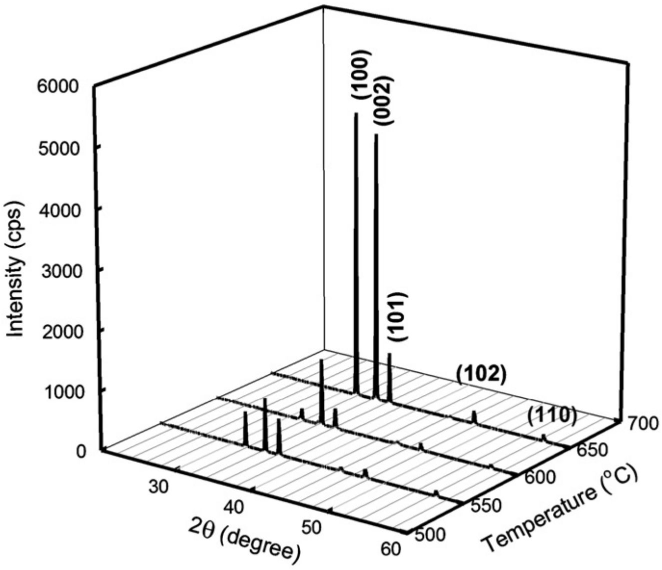

Fig. 2. The XRD pattern of the prepared ZnO nanowires at different growing temperatures.

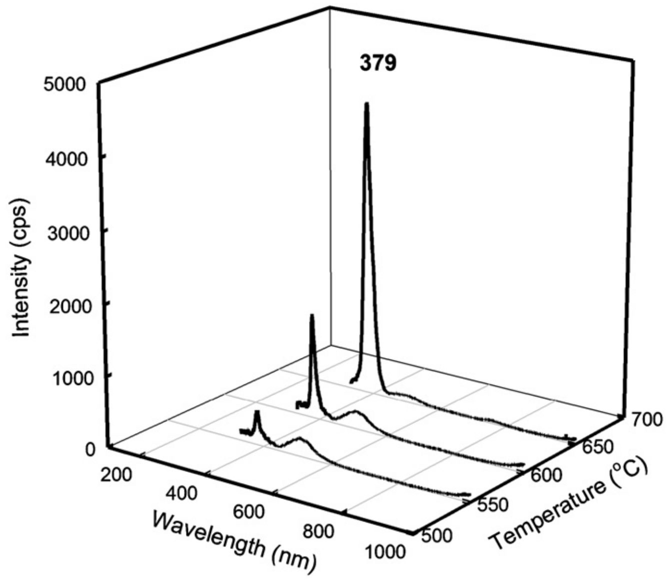

Fig. 3. PL spectrum at room temperature of ZnO nanowires grown at different temperatures.

approximately 379 nm and a weaker band at approximately 500 nm. The 379 nm emission corresponds to the recombination of free excitons between the conduction and the valence bands; this is called the near band-edge emission [12].

The band at the longer wavelength could be attributed to the radial recombination of photo-generated holes with electrons belonging to the singly ionized oxygen vacancy in ZnO [13]. The strong UV emission in the PL spectra indicates that ZnO nanowires have good crystalline quality with the disappearance of green emission. The absence of deep-level emission indicates low impurity concentration and high crystallinity in ZnO nanowires [14]. The large area of growth and high quality of prepared ZnO nanowires make it a potentially good material for applications in optoelectronic devices.

4. Conclusion

An efficient method of achieving a wide range of high-quality ZnO nanowires by a simple thermal-evaporation technique without a catalyst has been developed. ZnO nanowires could be grown at different heating temperatures from 550 to 650 °C. Long, thin ZnO nanowires could be synthesized with high density at 650 °C. The morphology of the as-grown nanostructures is readily adjustable by controlling the growth temperature. This technique is important in developing advanced optical and electrical nanowire devices.

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