Effect of source temperature on the morphology and photoluminescence properties of ZnO nanostructures

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ABSTRACT

ZnO nanostructures have been synthesized by heating a mixture of ZnO/graphite powders using the thermal evaporation and vapor transport on Si(1 0 0) substrates without any catalyst and at atmospheric argon pressure. The influence of the source temperature on the morphology and luminescence properties of ZnO nanostructures has been investigated. ZnO nanowires, nanoflowers and nanotetrapods have been formed upon the Si(1 0 0) substrates at different source temperatures ranging from 1100 to 1200 °C. Room temperature photoluminescence (PL) spectra showed increase green emission intensity as the source temperature was decreased and ZnO nanowires had the strongest intensity of UV emission compared with other nanostructures. In addition, the growth mechanism of the ZnO nanostructures is discussed based on the reaction conditions.

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1. Introduction

Zinc oxide is a wide direct band gap (3.37 eV at room temperature) II–VI semiconductor with a large exciton binding energy (60 meV). It has attracted increasing interest due to its potential applications in electronics [1], photonics [2], sensors [3], transistors [4], field emission displays [5], etc. It is one of the most promising materials for the fabrication of short-wavelength optoelectronic devices including blue-UV light-emitting and room temperature UV lasing diodes [6]. In geometrical morphologies, various ZnO nanostructures, such as nanorods [7], nanowires [8], nanocombs [9] and nanotetrapods [10] have been synthesized by different methods [11–13]. The study of ZnO nanostructures has attracted many research groups because of their excellent optical, electrical, gas sensing and piezoelectric properties [14,15]. However, morphology and size control of ZnO nanostructures is still an issue and many groups have focused on this problem. Huang et al. [16] have suggested that the diameter of nanowires can be controlled by varying Au layer thickness and longer reaction times. Yao et al. [17] reported that the diameter of ZnO nanowires was temperature dependent and substrates placed in low-temperature zone resulted in small diameters of ZnO nanowires. Very recently, Manzoor and Kim [18] reported that the diameters of ZnO nanostructure were extremely influenced by the gas flow rate.

In addition, the luminescent property of ZnO nanostructures is principally related to electronic and crystalline structures and it is strongly influenced by the preparation methods [19]. Khan and Kordesch [20] studied the dependence of the substrate temperature on the optical properties of the ZnO nanostructures. Therefore, the understanding of dependence of different growth parameters on the morphology and optical properties of the ZnO nanostructures is important before employing these materials for various applications. Thus, this is the first, to the best of our knowledge, report about the effect of source temperature on the luminescent properties of ZnO nanostructures. In this study, we used a simple and low cost method to fabricate ZnO nanostructures with low impurities.

In this paper, ZnO nanostructures have been synthesized by heating a mixture of ZnO/graphite powders using thermal evaporation and vapor transport on Si(1 0 0) substrates without any catalyst at atmospheric argon pressure. The effects of the source temperature on the morphologies and luminescence properties of ZnO nanostructures were investigated systematically.

2. Experimental

ZnO nanostructures have been synthesized by thermal evaporation and vapor transport using a mixture of high-purity ZnO powder (Sigma–Aldrich 99.9%) and graphite powder (Sigma–Aldrich 99.95%) with 1:1 mass ratio as a source. The source material was kept in a porcelain boat (2 cm diameter, 8 cm long) and pushed to the centre of the tube furnace. One end of the tubes was connected to the supply and flow control system and the other end was opened to the air. High-purity Ar gas (99.9%) flow of 40 standard cubic centimeters per minute (s.c.c.m.) was used as a carrier gas inside the tube during thermal evaporation. The source material was heated at different temperatures that varied from 1100 to 1200 °C, while the
substrates distance was kept at 11 cm downstream from the source boat. Due to the temperature gradient downstream, the temperature of substrate region was less than the source temperature. After 30-min deposition time, the porcelain boat was drawn out from the furnace and cooled down at room temperature. At the end of deposition process, white and gray color products were formed on the surface of the silicon wafers.

The deposited products were characterized by field emission scanning electron microscopy [FESEM, Quanta 200F], energy dispersive X-ray spectroscopy [EDX, Quanta 200F] and X-ray diffraction diffractometer [XRD, Siemens D-5000] by using copper-monochromatized Cu Kα1 radiation (λ = 1.54 Å) under the accelerating voltage of 40 kV and the current of 40 mA. PL measurements were performed at room temperature by using a Jobin Yvon Horiba HR 800 UV system, where a He–Cd laser (325 nm) was used as an excitation source with power of 20 mW.

3. Results and discussion

Fig. 1 shows typical FESEM images of as-prepared samples grown at different source temperatures. Aligned ZnO nanowires with 50–200 nm diameters and 4–8 μm lengths were formed on the Si(1 0 0) substrate when the source temperature was 1200 °C as illustrated in Fig. 1a. As the source temperature decreased to 1150 °C, ZnO nanotetrapod structures were obtained on the surface of silicon substrate. As shown in Fig. 1b, the typical diameter and length of the tetrapods were about 50–100 nm and 0.5–1 μm, respectively. At 1100 °C, nanoflowers-like were synthesized on the substrate as shown in Fig. 1c. The typical length of one leaf was about 3 μm with a diameter ranging from 50 to 100 nm. A representative EDX spectrum of these nanostructures is shown in Fig. 2. Only peaks associated with Zn and O atoms are seen in EDX spectrum, while the Si-related peak in the spectrum comes from the Si substrate, leading to the fact that the nanomaterials are indeed ZnO material. Therefore, different ZnO nanostructures were formed on Si(1 0 0) substrates at different source temperatures. Rajendra Kumar et al. [21] have also reported different ZnO morphologies at different source temperatures.

Fig. 3 shows the XRD patterns of deposited ZnO products on silicon substrates at different source temperatures. The XRD diffraction peaks can be assigned to (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 0 3) and (1 1 2) hexagonal wurtzite structure of ZnO with cell parameter of \(a = b = 3.249 \text{ Å}, \) and \(c = 5.206 \text{ Å}[22]\). The diffraction peak at \(2θ = 34.4°\) is overwhelming revealing a preferred orientation of the nanowires grown on silicon substrates that was at 1200 °C. No diffraction peaks corresponding to Zinc or other impurities have been detected which confirms the high-purity of the obtained products.

Photoluminescence (PL) spectra of as-prepared samples at room temperature are measured and shown in Fig. 4. The excited wavelength we used in this experiment is 325 nm. It is very interesting to observe UV emission and broad green emission peaks from the three as-prepared samples. It can also be seen that ratio of UV emission and green emission is clearly dependent on the morphology of the nanostructures. All the structures grown at different source temperatures showed a UV emission peak located at 381 nm and a wide green emission band, which ranges from 450 to 600 nm dominated around 520 nm. While the UV emission corresponds to the near-band-edge emission, arises from the recombination of free excitons through an exciton–exciton collision process [23]. The green emission of ZnO is usually ascribed to structural defects, which included zinc vacancy, oxygen vacancy, interstitial zinc, interstitial oxygen and antisite oxygen [24]. As the ZnO nanostructures in our experiment are synthesized in a relatively low oxygen deficient ambient, it is reasonable to believe that the green emission band is related to oxygen vacancies and the same result was reported in the literatures [23,25]. According to our result, it can be seen that the green emission peak is decreased with increasing the source temperature. The progressive increase of the green light emission intensity relative to the UV emission as the source temperature decrease suggests that there is a greater fraction of

**Fig. 1.** FESEM micrographs of ZnO nanostructures grown on Si(1 0 0) at (a) 1200 °C, (b) 1150 °C and 1100 °C source temperatures. The bar scale is 2 μm.

**Fig. 2.** EDX spectrum of as-synthesized ZnO nanostructures.

**Fig. 3.** XRD patterns of ZnO nanostructures synthesized at different source temperatures.

**Fig. 4.** PL spectra of as-prepared samples at room temperature.
oxygen vacancies in the nanostructures that grow at 1150 and 1100 °C source temperatures. Comparing with green emission, the UV emission enhanced as the source temperature is increased as shown in Fig. 4. The stronger intensity of the UV emission relative to the green emission suggests that there is a stoichiometric composition of ZnO, and a lower fraction of oxygen vacancies exists in the ZnO nanostructures fabricated at 1200 °C source temperature. The intense UV emission of the aligned ZnO nanowires suggests that they may have excellent application potential in optoelectronic devices. As a result, the source temperature has a great influence on the optical properties of ZnO nanostructures.

Based on the above synthetic process and the experimental results, ZnO nanostructures’ growth does not follow the conventional metal-catalytic Vapor–Liquid–Solid (VLS) mechanism [26]. The growth mechanism can be described as self-catalytic VLS growth model [27], i.e., Zn liquid droplets function as catalysts during the growth process. As pointed out by other researchers [17, 28], Zn vapor can be generated by the reduction of ZnO powder by carbon at the high temperature region. Then, the Zn vapor can be transported or diffused to a low-temperature region (downstream of carrier gas flow), where the Zn vapor is partly oxidized to ZnO or ZnO$_x$ (x < 1) species again. So, a part of the Zn vapor will condense on the substrate to form liquid droplets, which are the preferred sites to absorb ZnO or ZnO$_x$ vapor species. It means that the Zn/ZnO or Zn/ZnO$_x$ liquid droplets will be formed and ZnO nanostructures will grow from the supersaturated liquid droplets.

The present results prove that the morphology of the ZnO products can be controlled by adjusting the furnace temperature during the synthesis of ZnO via a carbothermal reduction process. In other words, the growth morphology of ZnO nanostructures is strongly dependent on the furnace temperature because the density of vapor component that generated from the carbothermal reaction is different at different furnace temperatures [29]. Therefore, a high source temperature (1200 °C) increases the partial pressure of vapors’ component, thus yielding a high supersaturation of Zn vapor which favors the growth of ZnO nanowires. In contrast, when the source temperature is lower than 1150 °C, growth of the flower-like ZnO occurs due to the low supersaturation of Zn, ZnO$_x$ vapor. On the other hand, a medium supersaturation of Zn vapor leads to the formation of ZnO nanotetrapods.

In addition, we tried to speculate the possible growth mechanism of tetrapods and flower-like nanostructures. According to self-catalytic VLS growth model, the Zn (g) or ZnO$_x$ (g) were transported and condensed on the silicon substrate. Because the substrate temperature is lower than the source temperature, the deposited Zn or ZnO$_x$ will change to liquid phase Zn or ZnO$_x$ (x < 1) and be segregated into droplets as a result of surface migration [30]. In our opinion, the morphology differences between the tetrapod and the flower-like structures might be a consequence of the different sizes of the nucleus. At medium supersaturation, Zn or ZnO$_x$ droplets migrated and merged on the substrate surface and formed larger ZnO nuclei. According to the octa-twin nucleus model [31], ZnO nuclei formed in the atmosphere are octahedral nuclei [32]. The octahedral nucleus was considered to lead to the formation of the tetrapod structures [33]. At low supersaturation, more nuclei merged together to form a multiple facets probability. It finally led to the formation of the polyhedral ZnO nuclei. As a result, the formation of the flower-like ZnO nanostructures nuclei on the silicon substrate is owing to the merging and growth of the polyhedral ZnO nuclei.

4. Conclusion

The dependence of the source temperature on the morphology and the optical properties of ZnO nanostructures were investigated. ZnO nanowires, nanotetrapods and nanoflower-like have been synthesized on Si(1 0 0) substrates at different source temperatures. PL results show that the green emission peak was attributed to the defects in the ZnO nanostructures and can be lowered by increasing the source temperature. It has been found that the low level of defects in ZnO nanostructures was obtained in nanowires which were deposited at 1200 °C source temperature. The growth mechanism of ZnO nanostructures can be explained by a self-catalytic VLS growth model.

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References

[22] JCPDS-International center for diffraction data, Card No. 03-0888.


