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Growth and Formation Mechanism of Sea Urchin-Like ZnO Nanostructures on Si

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Abstract−Sea urchin-like nanostructures of ZnO consisting of ZnO nanowires with blunt faceted ends were grown on Si (100) substrates by oxidation of metallic Zn at 600 °C. ZnO nanowires having a diameter of 30-60 nm and length of 2-4 μm were in similar shape with uniform diameter along its entire length with well faceted blunt ends. X-ray diffraction and transmission electron microscope analysis showed that the as-grown nanostructures were highly crystalline with wurtzite hexagonal structure having lattice constants of a=b=3.25 Å and c=5.21 Å. Room temperature photoluminescence (PL) measurements showed a weak near band-edge emission at 380 nm, but a strong green emission at 500-530 nm. A model for vapor-solid (VS) growth mechanism of ZnO nanowires was presented, in which nucleation of ZnO is crucial for the growth of the nanostructures.

Key words: ZnO, Nanowires, Growth Mechanism, Structural and Optical Properties

INTRODCUTION

Zinc oxide (ZnO) is probably the richest family of nanostructures among all one-dimensional nanostructures including carbon nanotubes. It is a wide direct band gap (3.37 eV) semiconductor with large exciton binding energy (60 meV), has received much attention due to the potential applications for optoelectronics field [Huang et al., 2001; Kind et al., 2002; Lee et al., 2005]. Different fabrication methods such as anodic aluminum oxide (AAO) template method [Li et al., 2000], vapor transfer process [Huang et al., 2001; Yao et al., 2001; Lao et al., 2002; Gao et al., 2003; Yan et al., 2003], thermal evaporation with catalyst [Kim et al., 2004], metal organic chemical vapour deposition (MOCVD), and hydrothermal synthesis [Lyu et al., 2003; Yan et al., 2003; Pan et al., 2001; Park et al., 2002, 2003; Wu et al., 2003; Vayssieres, 2003] have been widely reported for the preparation of one dimensional ZnO nanostructures such as nanowires, nanorods, and nanobelts. Especially, Park et al. first reported a metal-catalyst-free growth method of ZnO on sapphire by metalorganic vapor-phase epitaxy, but they used expensive diethyl zinc as the Zn source. Although the nanostructures of ZnO have been widely investigated using different techniques, similar to our nanostructures (i.e., sea urchin-like structure), little work has been reported except by Banerjee et al. [2003, 2004] They synthesized ZnO nanowires by thermal evaporation of a mixed source of ZnO and graphite powders at 1,000-1,200 °C.

In most of the reports on ZnO nanostructure growth, the vapor-liquid-solid (VLS) mechanism has been proposed. In the VLS mechanism [Wagner and Ellis, 1964], catalysts play an essential role in forming liquid alloy, which provides a preferred site for deposition from the vapor. However, this technique needs very high growth temperatures, so that Zn vapor can be dissolved into a metal catalyst to form an alloy droplet. After saturation, Zn precipitates out from the droplet and is oxidized as ZnO nanostructures. Another drawback of the VLS method is that, at the tips of the ZnO nanorods or nanowires there are always impurity metal particles, that will lead to contamination and so these nanostructures are not directly utilized for device fabrication.

In this work, commercially available Zn powders were used as the source and oxidized in the presence of oxygen to grow ZnO nanowires on Si substrates at a lower temperature (600 °C). The growth process was carried out in a rapid thermal reactor, in which the required temperatures are attainable in a short time. The main objective of this work is to grow quality ZnO nanostructures at a low temperature and to propose a growth mechanism. More importantly, the method employed in this work is quite simple and easily produces ZnO nanowires having uniform diameter and length distributions, which are useful for many device applications.

EXPERIMENTAL

Zinc oxide nanowires were grown in a horizontal rapid thermal reactor, which consists of 50 cm long horizontal quartz tube, sample holder that is also made of quartz, and halogen lamp heating system. One side of the quartz tube is connected with gas inlet and other side is connected with rotary vacuum pump. ZnO nanowires were grown on Si substrates at a heating rate of 10 °C/s. A commercially available high purity Zn metal powder and high purity (99.99%) oxygen gas were used as source materials for Zn and oxygen, respectively. Before loading into the reaction chamber, the Si(100) substrate was first scratched with fine quality sand paper and then ultrasonic cleaned in acetone for 10 minutes and in iso-proponal alcohol for 5 minutes and dried by blowing nitrogen gas on the substrate. After cleaning and drying of the substrate, a thin layer of fine quality and high purity metallic zinc powder is sprayed on the substrate and annealed for 10 minutes to get bonded with the substrate. After the annealing, the Zn-coated substrate is loaded into the quartz tube by using a sample holder. After loading of the sample, the chamber was down to 2 Torr pressure using rotary vacuum pump before introducing N_2 gas into the chamber.

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After the evacuation process, a pretreatment step proceeded by increasing the temperature of the chamber rapidly up to 500 °C. High purity H_2 and N_2 gases were introduced into the chamber with the flow rates of 20 sccm each for 15 min. After the pretreatment step, the temperature of the substrate was increased up to 600 °C and high purity O_2 and N_2 gases were introduced at the flow rates of 20 and 10 sccm, respectively, for a period of 90 minutes. After the growth period, the furnace was suddenly switched off and cooled down to room temperature.

The crystal structure and chemical nature of as-grown ZnO nanowires were analyzed by X-ray diffractometry (XRD) and energy dispersive X-ray spectroscopy (EDX), respectively. The morphology and microstructure of the sample were analyzed by using field emission scanning electron microscope (FE-SEM) and Transmission Electron Microscope (TEM), respectively. The optical properties of the ZnO structures were characterized by photoluminescence (PL) measurements using a continuous-wave He-Cd laser (λ=325 nm) as the excitation source at room temperature.

RESULTS AND DISCUSSION

Fig. 1 presents typical FE-SEM images of the sea urchin-like ZnO nanostructures with different magnifications. In Fig. 1(a), high density sea urchin-like assemblies grown on Si substrate are observed. Furthermore, one can see ZnO nanoneedles arising from the sea urchin-like nanostructures, having a length of several micrometers, as clearly shown in Fig. 1(b). Fig. 1(c) and (d) are the magnified images of the nanowires composing the sea urchin-like ZnO structures and the nanoneedle arising from the sea-urchin assemblies, respectively. The sea-urchin like nanostructures with the blunt faceted ends with sudden reduction in diameter projecting out are observed from the most of the regions, having a diameter of 30-60 nm and length of 2-4 μm (Fig. 1(c)). This observation suggests that the ZnO nanowires are grown by a non-catalysis growth mechanism and assembled into a sea urchin-like structure. In particular, no branching is observed, which implies that the ZnO nanorods were grown from spontaneous nucleation with high crystal perfection.

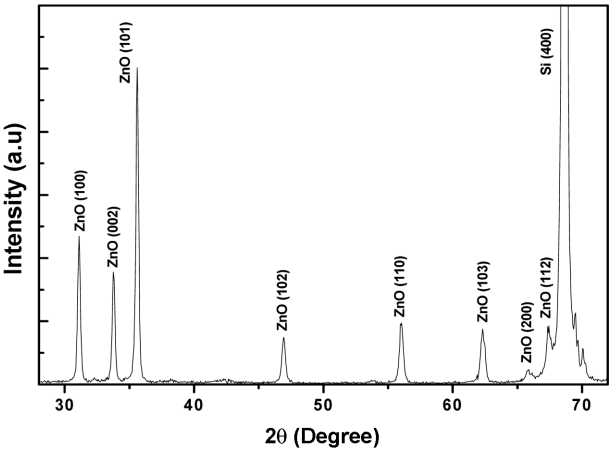

Fig. 2. XRD patterns of the sea urchin-like ZnO nanostructure grown on Si(100).

The phase of the as-grown ZnO nanowires and their crystallo-

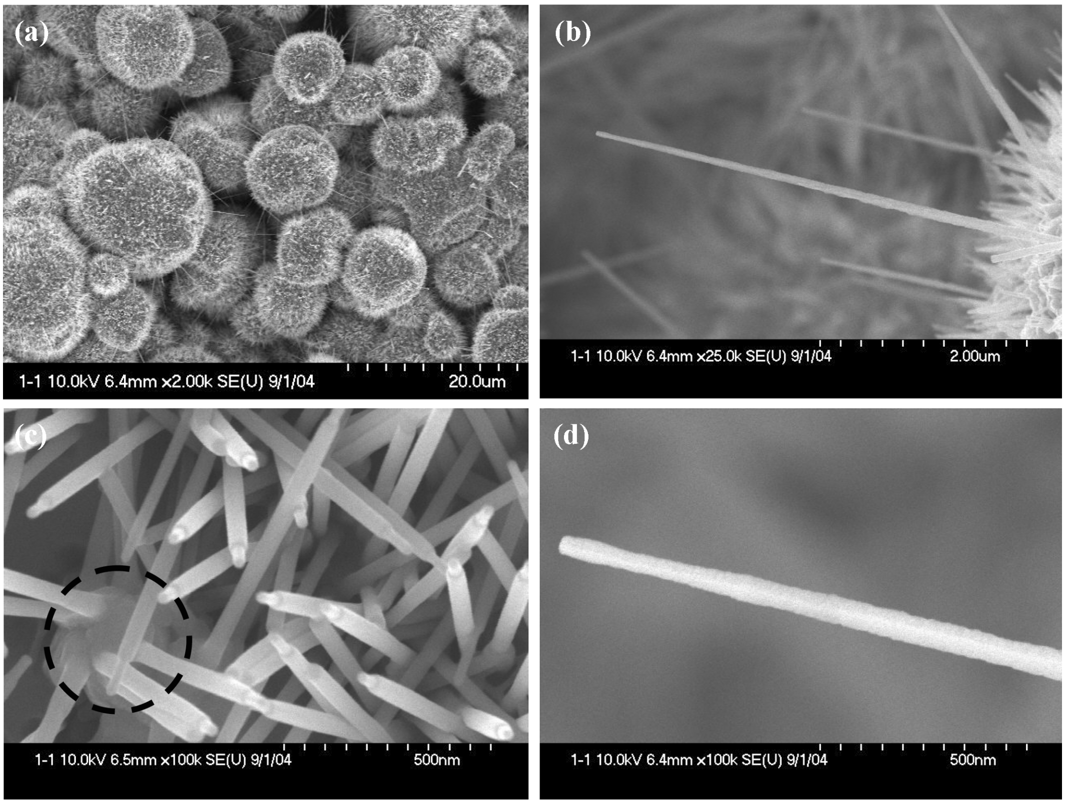

Fig. 1. FE-SEM images of sea urchin-like ZnO nanostructures grown at 600 °C: (a) low and (b) medium magnification images, (c) magnified images of the nanowires from the sea-urchin like nanostructure, and (d) high magnification image of the nanoneedle.

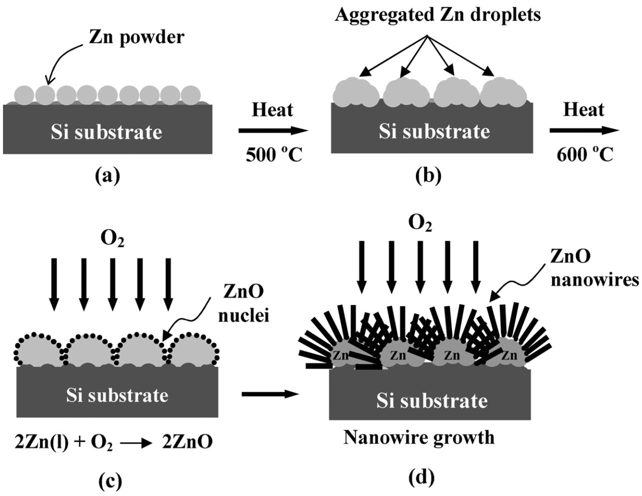

Fig. 3. Schematic illustration of the growth mechanism of the sea-urchin like ZnO nanostructures: (a) Zn powders dispersed on Si substrate, (b) formation of aggregated Zn droplets, (c) formation of ZnO nuclei on the surface of Zn droplets, and (d) growth of nanowires out of the droplets.

graphic orientation were identified by XRD analysis as shown in Fig. 2. On the basis of the XRD patterns taken from the sea urchin-like structures, the crystallographic phase of the zinc oxide nanowires belongs to the wurtzite type, and the measured lattice constants of the hexagonal phase are $a=b=3.25$ Å and $c=5.21$ Å. The strong intensity and narrow width of the ZnO diffraction peaks indicate that the as-grown nanowires are of high crystallinity. Although not illustrated, EDX analysis showed that the ZnO nanowires contained only Zn and O.

To explain the growth process of the sea-urchin like ZnO nanostructures, a growth mechanism was proposed. Since no metal catalyst was used in this research, the ZnO nanostructures were probably formed by a vapor-solid (VS) mechanism. This mechanism consists of two stages: nucleation and growth. The schematic diagram for the proposed growth mechanism is illustrated in Fig. 3. When the metallic zinc powders dispersed on the Si(100) substrate are heated at 500 °C, the metal Zn powders (m.p.=419.53 °C) are first melted and aggregated to form micro-sized Zn droplets on the surface of the Si substrate (b). After the introduction of oxygen into the reaction chamber at 600 °C, the oxygen may react with the outer surface of the previously formed Zn droplets and form nanosized ZnO nuclei on the surface of these Zn droplets (c). Since a metal catalyst is not used, a liquid alloy is not formed. Instead, as the aggregated Zn droplets become supersaturated, the liquid Zn reacts with oxygen and forms ZnO nuclei on the surface. These ZnO nuclei individually further grow in the upper direction in the form of nanowires (d), which is supported by the FE-SEM observation (see the dotted circle area in Fig. 1(c)). The nuclei thus play a crucial role in the growth of ZnO nanowires, which grow till the Zn source is almost used up. So from each zinc droplet there is an origination of several ZnO nanowires which lead to the formation of sea urchin-like structure. These structures are grown on the substrate surface with a high density and cover the substrate fully. This fact was confirmed by the FE-SEM images of the grown structures. Almost all the nanowires observed in sea urchin-like structures are grown in similar shape with uniform diameter.

The morphology and crystal orientation of the ZnO nanowires were further investigated by using transmission electron microscope (TEM). Although the majority of the ZnO nanowires were assembled into sea urchin-like aggregates, individual nanowires were readily separated by ultra-sonication. Fig. 4 shows the typical TEM images of ZnO nanostructures. Fig. 4(a) shows a ZnO nanowire having a straight shape and a uniform diameter, which was further characterized by selected area electron diffraction (SAED) and high-resolution transmission electron microscope (HRTEM), as illustrated in Fig. 4(b) and (c), respectively. The SAED pattern clearly shows that the ZnO nanowire is single crystalline with hexagonal structure. The HRTEM employed to observe the fine structure of the nanowires shows that the as-grown nanowires are highly crystalline nature with preferred orientation in [0001] direction, and shows that the lattice fringes are spaced 0.52 nm apart, which is equal to the lattice constant of ZnO.

Fig. 5 shows the room temperature photoluminescence spectrum of the as-grown (a) and the annealed (b) ZnO nanowires. From the PL spectra, two luminescence bands are seen: a UV near band-edge emission (NBE) around 380 nm and a green emission at 500-530 nm. The UV peak is attributed to band-edge emission of the wide bandgap ZnO, while the broad green band is generally attributed to

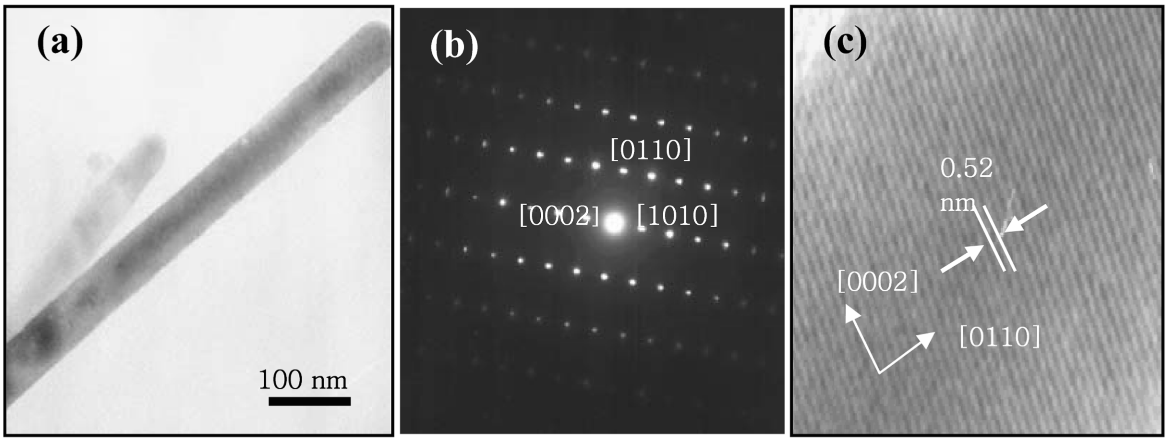

Fig. 4. TEM image (a), SAED pattern (b), and HRTEM image (c) of the ZnO nanowire.

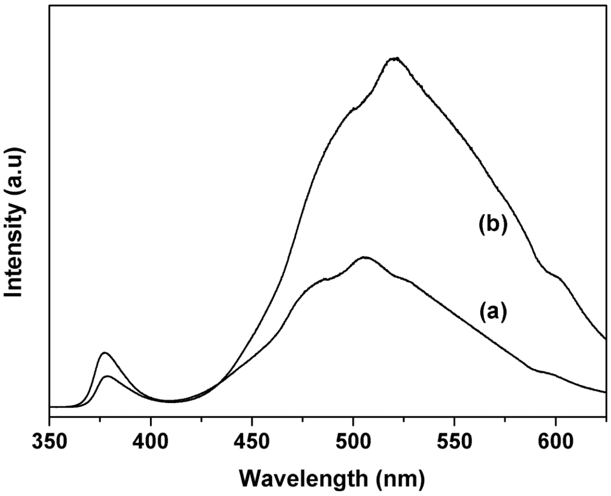

Fig. 5. Room temperature PL spectra of ZnO nanowires grown on Si(100): (a) as-grown and (b) annealed in atmospheric oxygen at 400 °C.

deep level defects in ZnO crystals, such as vacancies and interstitials of zinc and oxygen. A broad green emission from the nanorod structure is stronger than the UV emission. Vanheusdan et al. attributed such a green emission to the single ionized oxygen vacancy and suggested that the visible emission comes from the recombination of a photon-generated hole with the single ionized charged state of the defect in ZnO [Vanheusdan et al., 1996; Xing et al., 2003] Hence, a stronger intensity of the green emission is presumably related to the high quantity of the surface oxygen vacancies and defects of the ZnO nanowires.

CONCLUSIONS

Large amounts of ZnO nanowires were grown on Si(100) substrates by oxidation of metallic Zn powder at 600 °C. Sea urchin-like nanostructures consisting of straight nanowires of ZnO with the blunt faceted ends with sudden reduction in diameter projecting out was observed, having a diameter of 30-60 nm and length of 2-4 µm. X-ray diffraction and transmission electron microscope analysis showed that the as-grown nanostructures were highly crystalline with preferred orientation in the [0001] direction, a wurtzite hexagonal structure having lattice constants of a=b=3.25 Å and c=5.21 Å. The growth mechanism of the sea-urchin like ZnO nanostructures and nanowires is explained by a vapor-solid mechanism because no metal catalyst is used. The growth mechanism consists of two stages: one nucleation and another growth, in which the ZnO nuclei play a crucial role in the growth of ZnO nanowires. A room temperature photoluminescence study showed a reduced band-edge ultraviolet emission and a strong green emission due to oxygen vacancies and defects of the ZnO nanowires. Most importantly, these ZnO nanowires have been produced by a simple, easy, and low cost method without the use of any catalyst.

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Retraction: "Growth and formation mechanism of sea-urchin like ZnO nanostructures on Si" [Korean J. Chem. Eng., 22(3), 489 (2005)]

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Although the scientific content of the paper mentioned above is fully approved by all authors, we hereby retract this article because it was published in almost identical form in Journal of Crystal Growth, **277**, pp471-478, 2005. The corresponding author apologizes to the journal publisher, editors, and the scientific community for this serious breach of the accepted protocol for scientific publications.

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