Complex nanostructures of ZnO: growth and properties

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Abstract: Variety of complex ZnO nanostructures such as flower-shaped structures, hierarchical and star-shaped nanostructures have been grown by the novel cyclic feeding chemical vapour deposition (CFCVD) process on various substrates at low-temperatures of 475°C to 550°C. Metal organic source, diethyl zinc (DEZn) and oxygen gas was used as source materials for zinc and oxygen, respectively for the growth of ZnO nanostructures synthesised by CFCVD process. The selected area electron diffraction (SAED) pattern of the flower-shaped structures confirmed that the grown products are single-crystalline ZnO. In addition to the ZnO nanostructures grown CFCVD process, comb-like ZnO structures were also synthesised, in a high density, via simple thermal evaporation process by using metallic zinc powder and oxygen as source materials for zinc and oxygen, respectively. The X-ray diffraction pattern of the synthesised comb-like structures exhibited that these structures are possessing single-crystallinity and wurtzite hexagonal phase of ZnO.

Keywords: zinc oxide; ZnO; complex nanostructures; II-VI semiconductor; cyclic feeding chemical vapour deposition; CFCVD; thermal evaporation.

Reference to this paper should be made as follows: Umar, A., Park, Y.K., Hahn, Y.B. and Al-Hajry, A. (xxxx) 'Complex nanostructures of ZnO: growth and properties', *Int. J. Nanomanufacturing*, Vol. X, No. Y, pp.000–000.

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1 Introduction

Semiconductor nanostructures have been particularly attractive because of interest in investigating their fundamental physical properties and their potential applications in various electronic and optoelectronic devices. Among various semiconductor nanostructures, the II-VI compound semiconductors have attracted much attention because of their exotic properties and many potential applications. Among different II-VI semiconductor nanostructures, the nanostructures of ZnO have a special place due to their versatility on nanostructures morphologies and interesting properties. Due to versatility in the morphologies, it is considered that the ZnO has the richest family of nanostructures including carbon nanotubes (Umar et al., 2008a–d; Umar and Hahn, 2008, 2006a, 2006b; Sekar et al., 2005; Kong and Wang, 2003; Umar et al., 2005a–e; Umar et al., 2007a, 2007b). Zinc oxide (ZnO) nanostructures are one of the most promising photonic materials due to their wide band gap (3.37 eV) and larger exciton binding energy (60 meV) larger than other semiconductor materials such as ZnSe (22 meV) and GaN (25 meV). The exotic nature of ZnO makes it a valuable material for various applications, for instance, sensors, room temperature UV lasers, solar cells, photocatalysts, field effect transistors, nano-resonators and nano-cantilevers, and so on (Umar et al., 2008a–d; Umar and Hahn, 2006a, 2006b; Sekar et al., 2005; Kong and Wang, 2003; Umar et al., 2005c, 2005d; Umar et al., 2007c). It is generally believed that the properties of nanostructured materials are strongly dependent on their shapes and sizes. In this endeavour, recently scientists are inclined to pay much attention on the fabrication of materials with specific morphologies because of the expectation of novel properties. For the use of specific applications, so far variety of ZnO nanostructures are already fabricated and reported in the literature (Umar et al., 2008a–d; Umar and Hahn, 2006a, 2006b; Sekar et al., 2005; Kong and Wang, 2003; Umar et al., 2005a–d; Umar et al., 2007c, 2007d). Fabricating complex nanostructures consisting 1D ZnO moieties in a controllable manner is required to improve the performance and to broaden the application, but one still faces remarkable challenges.

In this paper, we present the growth of some complex ZnO nanostructures such as flower-shaped structures, hierarchical and star-shaped nanostructures and comb-like structures grown by two different fabrication techniques i.e., novel cyclic feeding chemical vapour deposition (CFCVD) and simple thermal evaporation process.

2 Experimental details

Variety of complex ZnO nanostructures such as flower-shaped nanostructures; hierarchical and star-shaped nanostructures were grown by novel CFCVD process. The CFCVD system was firstly introduced in literature by Umar et al. (2005c, 2005d). Before loading the substrates in the CFCVD reactor, they were ultrasonically cleaned by acetone and methanol, and finally dried with inert gas (N_2). Commercially available diethyl zinc (DEZn) and high purity oxygen (99.999%) gas was used as precursors of Zn and oxygen, respectively. The argon gas was used as a carrier and purge gas. The DEZn was transported into the reaction chamber by the argon gas. During the growth of complex ZnO nanostructures, the DEZn and O_2 were alternatively exposed to the substrate which was automatically controlled by a computer. The temperatures of the substrates were kept according to the fabrication of desired nanostructures. The substrate temperatures for all the reactions were in between 475°C to 550°C. After completing the desired number of cycles, the reactor was cooled to room temperature and products were deposited onto the substrates.

For the growth of comb-like ZnO structures, simple thermal evaporation process was employed in which metallic zinc powder and oxygen gas was used as source materials for zinc and oxygen, respectively. The Si(100) substrates were used to deposit the comb-like ZnO structures. In a typical reaction process, high purity metallic zinc (99.999%) powder was put in a quartz boat and placed at the centre of the quartz tube furnace. The substrate was kept 10 cm away from the source material where the temperature was 700°C. After this arrangement, the chamber was evacuated up to 180 Torr using rotary vacuum pump. The furnace temperature was ramped rapidly in 20 minutes. A high purity O_2 and N_2 were introduced inside the reactor when the furnace reached the desired temperature. The reaction lasted in 120 minutes. The grown products were examined by using field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM) equipped with the selected area electron diffraction (SAED) pattern and X-ray diffraction (XRD) patterns measured with Cu-*K*α radiation.

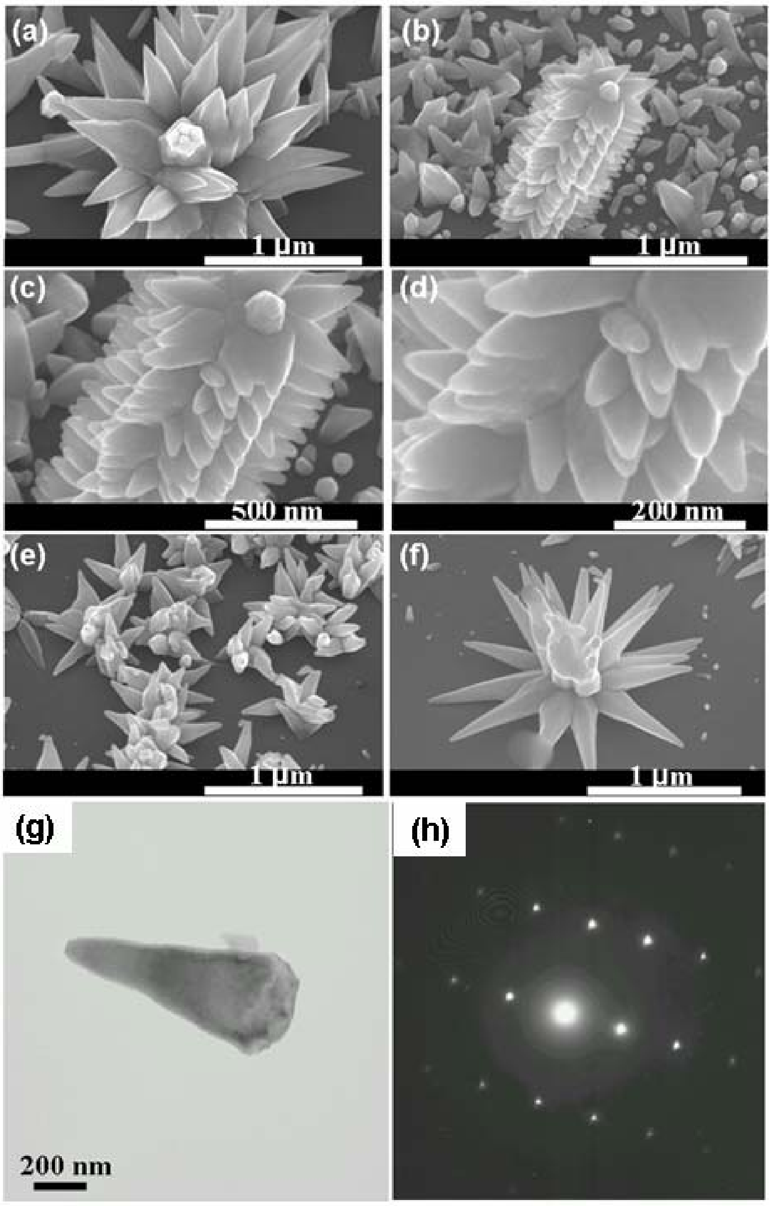
3 Results and discussions

Figure 1(a)–1(d) show some complex nanostructures of ZnO, i.e., flower-shaped and hierarchical nanostructures grown onto the Si(111) substrate at 550°C by using diethyl zinc and oxygen as source materials for zinc and oxygen, respectively. Figure 1(a) exhibits the typical flower-shaped structure. The corresponding image of flower-shaped structure reveals that these structures contain the triangular shaped petals which are rooted in one centre. All the petals have sharpened tips with the wider bases. The typical length of one petal in flower-shaped structure is about 800 nm^{-1} µm while the diameters at their bases and tips are in the range of 200 nm to 350 nm and 80 nm to 100 nm, respectively. The full width of flower-shaped ZnO structure is about 1 µm to 2 µm and the height is about 1.0 µm to 1.5 µm. It was interesting to note that on the same substrate, some hierarchical structures were also found. Figure 1(b), 1(c) and 1(d) show the low- and high-magnification images of hierarchical structures. It seems from the FESEM images that the hierarchical nanostructures are formed by the accumulation of many star-shaped nanostructures and deposited in a layer by layer manner on one to another and finally makes the hierarchical nanostructures. Each star-shaped structure consists of triangular shaped blades with the length of 150nm to 200 nm [Figure 1(c) and 1(d)]. Moreover, each blade of star-shaped structures contains a sharp tip and a wider base. The wider bases of each blade were joined to each other at one centre and form the star-shaped structure. Interestingly, it was observed from these hierarchical nanostructures that they are exhibiting ZnO characteristics hexagonal shape at their upper portions.

Figure 1(e) and 1(f) show the typical FESEM images of the star-shaped ZnO nanostructures grown by CFCVD process onto the Si(100) substrate at 475°C. It is seen from the FESEM images that the star-shaped nanostructures consist of triangular shaped blades with the length of 200nm to 500 nm. The diameters of the nanoblades varies, from tip to the bottom, between of 70nm to 90 nm at the tip and 100nm to 120 nm at the bases. These nanoblades were joined to each other through their wider bases in such a special fashion that they make beautiful star-shaped morphologies. The full arrays of most of the star-shaped nanostructures are in the range of 400nm to 800 nm. However, some bigger star-shaped nanostructures i.e., up to 1.2 μm were also found onto the substrate surface [Figure 1(f)]. For the detailed structural characterisations, the flower-shaped ZnO nanostructures [shown in Figure 1(a)] grown onto the Si(111) substrate at 550°C have been chosen. The detailed structural characterisation was performed using the TEM. For TEM analysis, the as-grown products were ultrasonically dispersed in acetone solution and a drop of the acetone solution which contains the dispersed nanostructures were placed to a copper grid and examined. During ultrasonication, the deposited products, flower-shaped nanostructures, break down into petals. Figure 1(g) shows the low-magnification TEM image of one petal of the as-grown flower-shaped structures which reveals that the petals have sharpened tips with the wider bases. The observed TEM result for the petal of flower-shaped structure is fully consistent with the FESEM observation in terms of morphologies and dimensions [Figure 1(a)]. The observed diameters of the petal of flower-shaped structures at their bases and tips are in the range of 200 nm to 350 nm and 80 nm to 100 nm, respectively. Figure 1(h) exhibits the typical SAED pattern of the corresponding petal shown in Figure 1(g). The corresponding SAED pattern of the single petal projected to the [2110] zone axis shows that the formed nanostructures are single crystalline with the wurtzite hexagonal phase and grown along the [0001] direction.

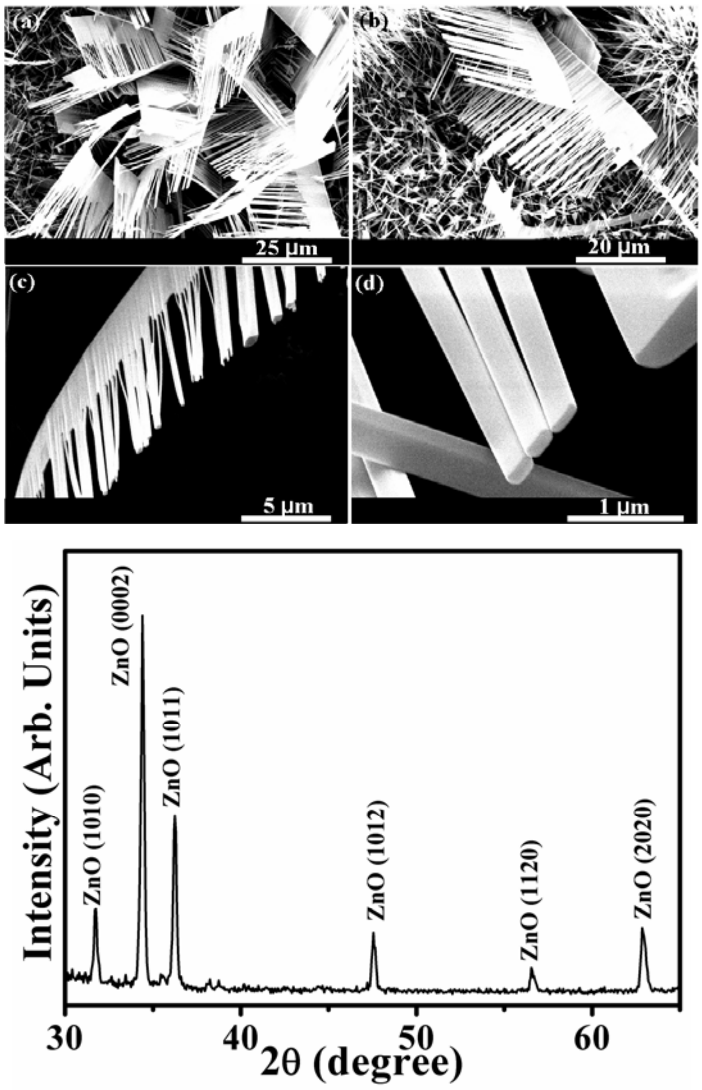
Figure 2 shows the typical FESEM images of the comb-like ZnO structures grown via simple thermal evaporation process by using metallic zinc powder and oxygen gas as source materials for zinc and oxygen, respectively. The comb-like structures were grown on Si(100) substrate at substrate temperature of ~700 °C. The low-magnification FESEM images of comb-like structures exhibited that these structures were grown in a high-density over the most of the substrate [Figure 2(a) and 2(b)]. By clear examination of the comb-like structures using high magnification FESEM, it is apparent that these structures are made by two structures, i.e., nanowire branches (teeth) and ribbon-like stems. The branches (teeth) of the combs are made by uniform ZnO nanowires which are nicely attached along one side of the ribbon-like ZnO stem. The widths and lengths of the stems are about 4 μm to 6 μm and 25 μm to 30 μm, respectively. However, the diameter and length of each tooth is about 150 nm to 250 nm and 10 μm to 15 μm, respectively [Figure 2(c) and 2(d)].

Figure 1 Complex ZnO nanostructures grown by novel CFCVD process



Notes: Typical FESEM images of (a) flower-shaped, (b) low- and (c, d) high-magnification hierarchical ZnO nanostructures grown onto the Si(111) substrate at 550°C. (e) and (f) star-shaped ZnO nanostructure grown onto the Si(100) substrate at 475°C. Typical (g) TEM image and (h) SAED pattern of a single petal of flower-shaped ZnO nanostructures grown onto the Si(111) substrate at 550°C.

Figure 2 (a, b) low and (c, d) high-magnification typical FESEM images and (e) typical XRD pattern of the comb-like ZnO structures grown via simple thermal evaporation process by using metallic zinc powder and oxygen gas as source materials for zinc and oxygen, respectively on Si(100) substrate at substrate temperature of ~700°C



To determine the crystal phase and crystallinity of the as-grown ZnO combs, the XRD pattern, measured with Cu-*K*α radiation, have been done and shown in Figure 2(e). The observed diffraction peaks are quite similar to those of a wurtzite single-crystalline hexagonal bulk ZnO. Except ZnO, no characteristic peaks for other impurities such as zinc and substrate were observed in the pattern which confirmed that the obtained products are single-crystalline wurtzite hexagonal phase ZnO.

4 Conclusions

Various kinds of complex ZnO nanostructures, such as flower-shaped structures, hierarchical and star-shaped nanostructures and comb-like structures were grown by two different fabrication techniques i.e., novel CFCVD and simple thermal evaporation process. The complex ZnO nanostructures synthesised by CFCVD process were grown at low-temperatures of ~475°C to 550°C on different orientations of silicon substrates. However, the comb-like structures were grown via simple thermal evaporation process at relatively higher substrate temperature of ~700°C on Si(100) substrate by using metallic zinc powder and oxygen as source materials for zinc and oxygen, respectively. The grown nanostructures may have application for the fabrication of various high-efficient nanodevices and nanosystems in near future.

Acknowledgements

This work was supported in part by the Brain Korea 21 project in 2008 and by the Korea Research Foundation grant (KRF-2005-005-J07502) funded by the Korean Government (MEST).

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