Ga-Assisted Synthesis and Optical Properties of ZnO Submicron- and Nanotowers

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Tower-like ZnO submicron- and nanostructures were synthesized by simply evaporating a mixture of Zn and Ga. Scanning electron microscopy and transmission electron microscopy observations showed that the regular hexagonal tower-like structure is likely to be made up in a layer-by-layer fashion and consist of sheets. According to our experiments, the amount of Ga has a large effect on their morphologies. The growth of such tower-like structures is ascribed to the vapor−solid mechanism. The introduction of Ga hinders the growth of ZnO along the [0001] direction, resulting in the formation of the novel tower-like structures. In addition, the photoluminescence of such structures shows a strong green-light emission.

Introduction

Recently, one-dimensional (1-D) nanostructures, such as nanowires,[1] nanoneedles,[2] nanorods,[3] nanotubes,[4] nanobelts[5] or nanoribbons, nanorings,[6] and nanosprings, have been attracting great attention due to their specific physical and chemical properties and potential applications in nanoscale field emission,[7] optoelectronic devices,[8] sensors,[9] nanolasers,[10] ultraviolet photodetectors, and optical switches.[11] Among them, 1-D zinc oxide (ZnO) nanostructures have become a research focus in the nanotechnology field. So far, many kinds of 1-D ZnO nanostructures with different morphologies have been synthesized successfully by the vapor−solid process,[12] aqueous method,[13] chemical vapor deposition,[14] metal−organic chemical vapor deposition,[15] and so on. As is well-known, different morphologies can have a large effect on the properties of nanostructures themselves.[7,16,17] For ZnO, the polar crystalline structure and unique growth habit in different conditions lead to the formation of a variety of morphologies. Thus, many researchers are interested in the controlled synthesis of novel 1-D ZnO nanostructures with different morphologies. In this paper, we synthesized ZnO submicron- and nanotowers by coevaporating a mixture of Zn and Ga and could control their morphology by tuning the amount of Ga in the source. Furthermore, we investigated their growth mechanism and optical properties.

Experimental Procedures

Owing to the lower cost of experimental setup, chemical vapor deposition (CVD) is a common method used to prepare ZnO nanostructures. In our experiment, the tower-like ZnO structures were also fabricated by the simple CVD method. A mixture of Zn (0.98 g) powder and Ga (0.10 g) droplet as precursor was placed in a quartz boat at the center of a tube furnace. The silicon (100) substrates, used to collect the synthesized products, were placed downstream and over the source (the polished Si side facing source). The reaction chamber was sealed and pumped to and kept at a pressure of 23 Torr throughout the experiment. N_2 (purity: 99.5%) was introduced into the reaction chamber at the flow rate of 560 sccm as a carrier gas. Subsequently, the temperature of the furnace was raised to 1150 °C and maintained at this temperature for 1 h. After the reaction, the synthesized samples were taken out and characterized by X-ray diffraction (XRD, Rigaku RU-300) with Cu Kα radiation, field-emission scanning electron microscopy (FE-SEM, Hitachi 4800), equipped with an energy-dispersive X-ray spectrometer, and transmission electron microscopy (TEM, Philips CM120) with an energy-dispersive X-ray (EDX, Oxford Link II) spectrometer. Photoluminescence (PL) spectra of the synthesized samples were taken at room temperature using the 325 nm line of a He−Cd laser as the excitation source.

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Results and Discussion

Figure 1a shows a SEM image of the product synthesized on the substrate over the source. It can be clearly seen that there are a large number of submicron towers with sharp tips or flat tops over the entire surface of the substrate. And there are also some flower-like assemblies, consisting of hundreds of submicron towers, as shown in the inset of Figure 1a. The magnified SEM image reveals the morphological details of the submicron towers (Figure 1b). It is of a layer-by-layer tower-like structure and different from the reported nanorods with a smooth surface. Such a submicron structure is of the length of 40−50 μm and a diameter of about 1.5 μm in the middle. The diameters gradually become smaller along the growth direction, leading to the formation of the tapered structures with sharp tips or flat tops. The thickness of each layer is about 80 nm. Note that the submicron towers have a regular hexagonal cross-section, consistent with the symmetry characteristic of ZnO along the [0001] direction, indicating that it is likely to grow along the [0001] direction. The crystalline phase of the as-synthesized products was identified by the X-ray diffraction pattern shown in Figure 1c. All diffraction peaks can be indexed to the wurtzite ZnO phase structure, and no other phases are found. Figure 1d is an EDX spectrum showing that the products only include elements Zn (57%) and O (43%), while Ga is not detected.

In addition, we also observed tower-like submicron structures on the substrates placed downstream, as shown in Figure 2a.

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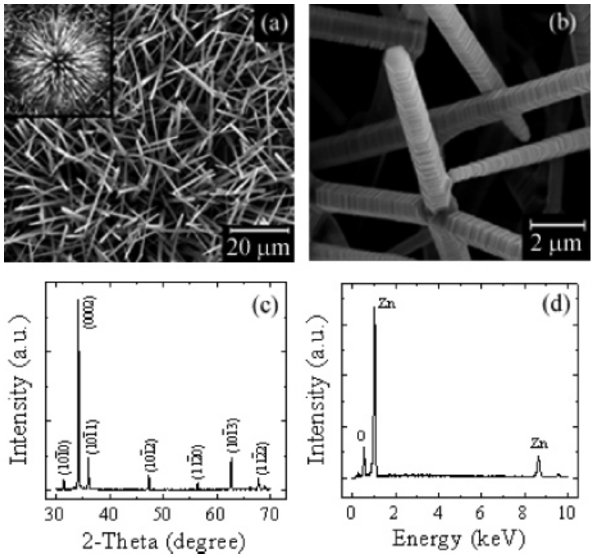

Figure 1. (a) SEM image of the product synthesized substrates over the source, clearly revealing a tower-like structure, and the inset is a flower-like assembly of submicron towers, (b) a magnified SEM image of a selected area in panel a, (c) XRD pattern of the sample, and (d) EDX spectrum of the sample.

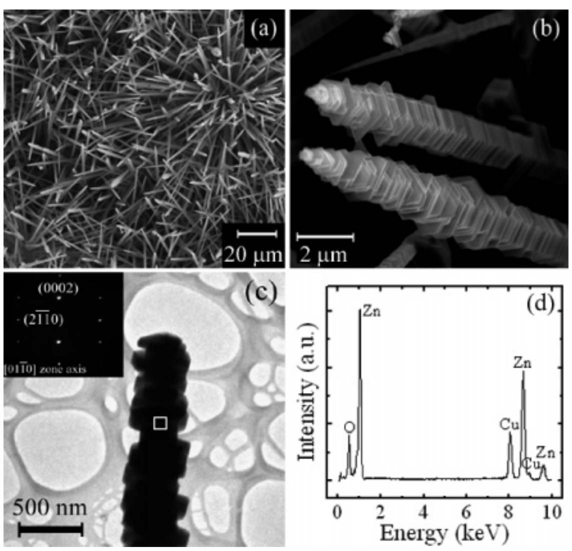

Figure 2. (a) SEM image of the synthesized sample downstream, clearly revealing the irregular array on the top of the submicron tower, (b) the magnified SEM image of a selected area in panel a, (c) TEM image of a typical submicron tower, inset is a SAED pattern of the submicron tower taken from the square region, and (d) EDX spectrum of this submicron tower.

Figure 2b is an enlarged SEM image of a selected area in Figure 2a. Note that the cross-section of the submicron towers here is not a regular hexagon near their tops. Figure 2c shows a TEM image of the typical submicron tower top, revealing that this structure is likely to be made up in a layer-by-layer fashion and consists of sheets with a lateral dimension of 80−100 nm. However, these sheets are not well-aligned, resulting in the formation of an irregular hexagonal, tower-like morphology. To further study their crystalline structure, selected area electron diffraction (SAED) measurements were conducted. The inset of Figure 2c shows an SAED pattern recorded from the square region, showing that the submicron tower is of a single-crystalline structure and grows along the [0001] direction. In addition, the EDX spectrum (Figure 2d) also shows that their composition consists of 56% Zn and 44% O. The extra Cu signals originate from the TEM grid. Although Ga existed in the precursor, it was not detected by EDX measurements, indicating that it could act as a catalyst to promote the formation of this structure.

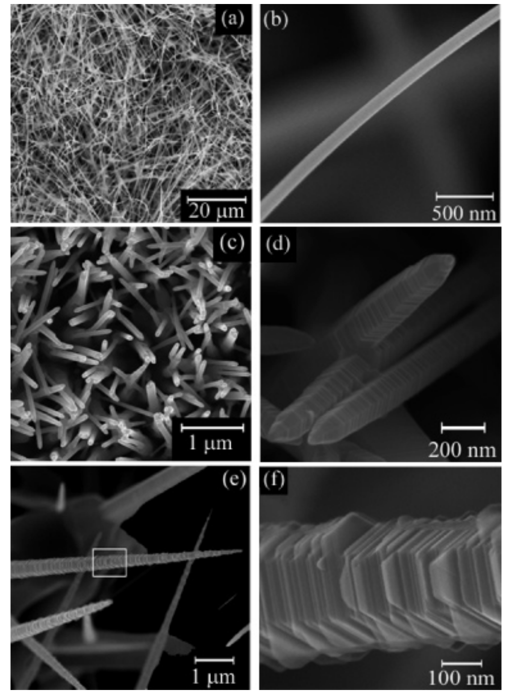

Figure 3. SEM images of the samples synthesized under Zn (0.49 g) fixed and Ga as a precursor: (a and b) none, (c and d) 0.05 g, and (e and f) 0.10 g.

To study the effect of Ga as a catalyst on the formation of a tower-like structure, we synthesized three different samples under the same temperature, pressure, and flow rate, but with precursors Zn: 0.49 g and Ga: 0, 0.05, and 0.10 g, which are called sample 1, sample 2, and sample 3, respectively. Si substrates were all placed downstream. Figure 3a,b shows the SEM images for sample 1. Note that the synthesized ZnO nanowires have a uniform diameter of about 110 nm and a smooth surface and that their length is up to tens of micrometers. Figure 3c,d shows the SEM images of sample 2. It can be seen that the diameter of the nanotowers is about 180 nm and that the single-layer thickness is about 15 nm. Figure 3e,f shows the SEM images of sample 3. The tower-like nanostructures cover the entire substrate. The diameter of the nanotowers quickly decreases from 600 to 150 nm along its axis, and the thickness of the single layer is about 10 nm. All nanotowers are of hexagonal cross-sections. Therefore, we infer that the amount of Ga has an important effect on the formation of the nanotowers.

Similar nanostructures have been prepared by a solution-based approach under citrate anion assistance.[18] They chose citrate as a catalyst because it can adsorb strongly on the ZnO (0001) surface and hinder ZnO in growing along the [0001] direction, resulting in the formation of ZnO plate-like structures. In our study, it is possible that Ga has a similar effect to slow growth along the [0001] direction. We believe that the growth of the ZnO nanotowers is possibly ascribed to the vapor−solid (VS) mechanism, ruling out the traditional vapor−liquid−solid mechanism because no alloy drops are observed on the top of nanostructures in the TEM images. The real-growth mechanism is not clear. On the basis of the previous information we gathered, we infer that the zinc powder was evaporated to generate zinc vapor at the high-temperature region. The zinc

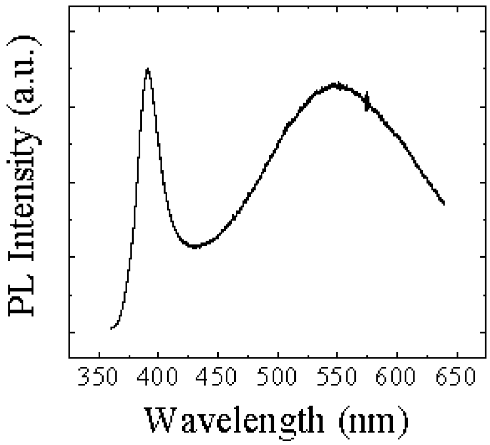

Figure 4. PL spectrum taken from the sample shown in Figure 2.

vapor reacted with oxygen (from the nitrogen gas (purity: 99.5%)) to form the ZnO vapor during the transport process, which was then transported downstream by carrier gas to deposit on the Si substrate and nucleate and grow. In our experiments, when the amount of Ga was increased by 0.1 g (sample 3) from 0.05 g (sample 2), the thickness of the single layer became thinner (~10 nm), as shown in Figure 3e, indicating that the catalytic effect of Ga was enhanced, strongly restricting the growth of ZnO along the [0001] direction while forming a thinner submicron sheet. The formed sheet probably acted as a template. Under stable conditions, the central position of a hexagonal ZnO sheet may be a favored nucleation site to form the next sheet. Such a process is repeated again and again, leading to a regular, hexagonal, tower-like morphology. In addition, zinc powder is gradually decreased during growth, and the towers have a slightly tapered structure along the axis.[19,20] However, there are some irregular, hexagonal, tower-like structures shown in Figure 2b due to the influence of a change in growth kinetics—a slight fluctuation of reaction conditions, such as growth temperature and partial pressure of the reactants, etc. Such small fluctuations of these factors would cause the nucleation sites of the ZnO sheets to slightly deviate from the center of the formed sheets, but nearby the center, the centers of the nanosheets are not along the same axial line, forming irregular hexagonal tower-like morphologies.

Photoluminescence (PL) spectra of all the samples were taken at room temperature. Figure 4 is a PL spectrum of the sample shown in Figure 2. The PL spectra of other samples are similar to that shown in Figure 4, revealing a sharp UV emission peak and a broad visible emission peak centered at 550 nm. As is well-known, the strong UV emission originates from the radiation combination of the excitons. The green-light emission is usually attributed to the oxygen vacancies, surface states, and some structural defects.[17,21] For submicron- and nanotowers, there is a large surface/volume ratio, which will result in the enhancement of the green-light emission.[22]

Conclusion

In summary, the tower-like structures with different sizes and morphologies were prepared by a simple chemical vapor deposition method under the assistance of Ga. Here, when the mass of Zn was fixed, we could control the morphology of the nanotowers by tuning the amount of Ga in the precursor. The PL spectra of all samples show a strong green-light emission. Usually, such a novel structure is believed to have potential in optical and environmental applications.[18,22] Herein, the size and morphology of tower-like structures have been well-controlled, which will improve their application region in functional devices.

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