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Aligned ZnO nanorods synthesized by a simple hydrothermal reaction

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Abstract

Zinc oxide (ZnO) nanorods were fabricated by a hydrothermal reaction in ammonia and zinc chloride solution without any surfactant at 95°C in a sealed bottle. In the area near the solution surface, the product presented urchin-like arrays composed of needle-tipped nanorods with about 40 nm diameter. In the middle and the bottom of the solution, the ZnO nanorods grew vertically on the substrate and showed tapered and flat ends and bigger diameters of about 300–400 nm. The microstructure characterization of x-ray diffraction and high resolution transmission electron microscopy images demonstrated that all ZnO nanorods grew along the [0001] direction. The influence of the chemical reactions and the depth-dependent growth along various facets of ZnO are discussed.

1. Introduction

With a direct wide bandgap and a strong excitonic binding energy [1], zinc oxide (ZnO) has attracted much attention recently. Meanwhile, aesthetic ZnO nanostructures have also been employed to fabricate multifunctional nanodevices, such as nanolasers [2], nanosensors [3, 4], field-effect transistors [5,6], and field emitters [7,8]. The basic and important work for building nanodevices is fabricating suitable nanostructures. So far, the vapour-phase transport (VPT) method has become the most widely used technology to fabricate various ZnO nanostructures [1–11]. At the same time, the hydrothermal decomposition method [12–16] has also attracted considerable attention because of its unique advantages. Compared with VPT, the hydrothermal technique involves a simpler, lower temperature, higher yield and more controllable process. Moreover, the structure fabricated is more uniform. Besides essential reactants of zinc salt and alkali or ammonia, some surfactants or molecular templates, such as ethylenediamine [14, 15] and cetyltrimethylammonium bromide [16], were often introduced into the reaction solution in order to favour nucleation and nanostructure growth in a general hydrothermal reaction. In this paper, we shall report a simple solution approach designed to fabricate aligned ZnO nanorod arrays. This

method only involves two chemical agents, which effectively avoids contamination in other complicated chemical reactions. Meanwhile, the product can be grown on a conductive substrate for utilization directly as field emitters and chemical/biological sensors. It would probably provide an economic way to produce low-cost nanomaterials for industrial applications.

2. Experimental

The hydrothermal reaction took place in a bottle with autoclavable screw cap. First, a proper quantity of ammonia (25%) was added to 0.1 M zinc chloride solution to adjust the pH value to 10. Then, a clean Cu strip collector was vertically inserted into the reaction solution as shown in figure 1(a). Finally, a white layer of product was deposited on the Cu substrate after the sealed bottle was heated at 95° for 1 h in an oven. The sample was thoroughly washed with DI water and dried in air for further characterization.

A JEOL scanning electron microscope (SEM) was employed to examine the morphology of the product. The crystal structure of the sample was characterized by x-ray diffraction (XRD) using the copper K α line under an accelerating voltage of 40 kV. A JEOL 2010 transmission electron microscope (TEM) operated at 200 kV was employed to detect high resolution images and the selected area electron diffraction (SAED) pattern. The photoluminescence (PL) was measured under the excitation of an He–Cd laser (325 nm) at room temperature.

3. Results and discussion

Figures 1(b), (c) and (d) show the SEM images taken from different depths corresponding to the circled areas illustrated in figure 1(a). It is noted that the product presents different morphologies in different parts of the substrate. In area 1, a very shallow region near the solution surface, ZnO nanorods are aligned vertically on many microscopic spheres to form urchin-like arrays (figure 1(b)). In the middle and the bottom of the solution (area 2 and area 3), ZnO nanostructures present nanorod morphologies, which grow vertically on the substrate, as shown in figures 1(c) and (d), respectively.

Figures 2(a), (b) and (c) present the enlarged SEM images corresponding to figures 1(b)–(d). The nanorods in the urchin arrays have very small and uniform sizes with sharp tips about 40 nm in diameter, as shown in figure 2(a). It is clearly seen, from figures 2(b) and (c), that the nanorods fabricated in both the middle and bottom areas (area 2 and area 3 in figure 1(a), respectively) stand vertically on the substrate surface. The diameter of the nanorods obtained from area 2 is a bit smaller than that from area 3. The diameter of the nanorods in area 2 is about 300nm and that in area 3 is about 300–400nm. Moreover, the nanorods in the middle area present tapered ends; however, the nanorods in the bottom area present flat hexagonal ends.

The XRD measurement showed a similar diffraction pattern for all areas across the sample. A representative XRD spectrum is shown in figure 3. As indexed in the pattern, all diffraction peaks match the wurtzite ZnO structure with the lattice constants of $a = 3.250 \text{ \AA}$ and $c = 5.207 \text{ \AA}$. The high resolution TEM images were

further employed to characterize the microstructures of the ZnO nanorod crystals. All the ZnO nanorods presented the same high resolution TEM images and SAED patterns, although the morphologies were not the same. In figure 4, the lattice fringes with a d -spacing of 0.52 nm match the interspacing of (0001) planes of the wurtzite ZnO, which was further confirmed by the corresponding SAED. These results demonstrate that the ZnO nanorods grew along the [0001] direction. Consistent with the XRD pattern, the clear lattice image and SAED indicated good crystal quality of the ZnO nanostructures.

The formation process of the ZnO nanostructures can be divided into two stages of initial nucleation followed by crystal growth. Figure 5 shows the SEM images taken from area 1 and area 3 in the initial growth stage. It can be seen that there are sphere shape powders with rough surfaces in area 1 close to the solution surface and that spare rods stand vertically on the substrate surface in area 3 close to the bottom. The ZnO formation involved the following dissolution and chemical reactions:

It is noted that the NH_3 gas as a by-product of reaction (4) will fill the sealed bottle and gradually become supersaturated. In this case, reaction 4 will be suppressed in the solution near the liquid surface due to higher concentration of NH_3 [17]. This is an important reason for the diameter of the ZnO nanorods in area 1 to be much smaller than that in the deeper regions of area 2 and area 3.

With increase in depth, it is noted, from the SEM images in figures 1 and 2, that the thinner ZnO nanoneedles with sharp tips gradually transformed into hexagonal rods with flat ends. Besides the influence of NH_3 discussed above, the pressure also plays an important role. In general, ZnO grows preferentially along the [0001] direction because of the faster growth velocity in this direction than in other directions [18–20]. Hence, it is reasonable to observe the tips at the end of ZnO nanorods. This growth process is confirmed by the high resolution TEM image and the corresponding SAED in figure 4. However, the investigation by the VPT method has demonstrated that the growth velocity along [0001] could be suppressed in higher vapour pressure, which could drive the incoming atom to migrate and form flat (0002) surfaces, thus further preventing them from accumulation [21–24]. In our solution case, the growth velocity in the [0001] direction should be slightly slower with the increase in the liquid pressure in the deeper regions due to gravity. Relatively, the growth velocity along other directions, such as $\langle 10\bar{1}0 \rangle$ and $\langle 10\bar{1}1 \rangle$, became a bit faster. Therefore, the nanorods became thicker and flattened with the gradual increase in depth.

It is well known that the PL of nanostructural ZnO generally presents two typical emission bands peaked at ultraviolet and visible regions, originating from the excitonic recombination corresponding to the band-edge emission of ZnO and the defect-related (such as oxygen vacancies) recombination [25]. Consistent with the good crystal

quality shown in the XRD pattern and high resolution TEM image, in the present case, the PL illustrates a strong UV emission band and a very weak green band, as shown in figure 6. This might be related to the simple ingredients in the solution where the contamination is avoided effectively and good crystallized ZnO nanorods are formed.

4. Conclusion

In summary, vertically aligned ZnO nanorod arrays were fabricated by a simple surfactant-free hydrothermal reaction between aqueous solutions of ZnCl_2 and ammonia. Due to the influence of NH_3 concentration and the corresponding basicity, ZnO nanoneedles aggregated on sphere-shaped nuclei and extended epitaxially to form urchin-like arrays in the area near the solution surface. In the middle and bottom of the solution, the ZnO nanorods grew along the [0001] direction and vertically aligned on the substrate. The diameter was gradually increased and gradually flattened with an increase in depth, possibly due to the increase in pressure. XRD, high resolution TEM and PL spectrum measurements demonstrated good crystal quality of the ZnO nanorods.

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List of Figures

- Figure 1 Schematic of the reaction setup (*a*) and the SEM images taken from area 1 (*b*), area 2 (*c*) and area 3 (*d*).
- Figure 2 Enlarged SEM images of ZnO nanostructures in area 1(*a*), area 2 (*b*) and area 3 (*c*) corresponding to figures 1(*b*), (*c*) and (*d*), respectively.
- Figure 3 XRD pattern of the ZnO nanorods in area 2 (figure 1(*c*)).
- Figure 4 High resolution TEM image of a ZnO nanorod in area 2 (figure 1(*c*)) and the corresponding SAED pattern.
- Figure 5 SEM images taken, respectively, from area 1 (*a*) and area 3 (*b*) in the initial growth stage.
- Figure 6 PL spectrum of the ZnO nanorods detected from area 2 (figure 1(*c*)).

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6