Improved physical properties of ZnO nanostructures by In inclusion

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ARTICLE INFO

Article history:

Received 16 September 2008

Accepted 11 November 2008

Available online 21 November 2008

Keywords:

Nanomaterials

Chemical vapor deposition

Zinc oxide

Indium

Defects

ABSTRACT

An alternative route to improve the physical properties of ZnO nanostructures has been demonstrated. With In inclusion in the growth process, we show that the morphology of ZnO nanostructures can be changed from nanopins to nanowires. Besides, the major effects of In inclusion involve the reduction of crystallization velocity, improvement of crystalline quality, and suppression of defect density. Notably, the emission intensity can be enhanced by more than one order of magnitude. Our result therefore provides an excellent approach to obtain good crystalline quality of nanomaterials for the application of optoelectronic devices.

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1. Introduction

ZnO nanostructures have attracted great attention due to their unique optical, electrical and piezoelectric properties [1]. Especially, ZnO has a wide direct band gap of 3.37 eV and a large exciton binding energy of 60 meV, which are very useful for applications in UV optoelectronics with good stability [2]. There are various methods to synthesis ZnO nanostructures, such as vapor phase methods [3] and hydrothermal process [4]. Through these methods, a variety of one-dimensional (1D) ZnO nanostructures have been fabricated, including nanorods [5], nanobelts [1], nanotubes [6], and nanowires [7]. It has been well established that for the growth of 1D ZnO nanostructures, addition of impurities often induces dramatic changes in their electrical and optical properties [8–11], which are very crucial for their applications. In addition, the luminescence of ZnO films with impurities and defects typically consists of a near band edge emission and a deep level visible emission. Before achieving the fabrication of highly efficient optoelectronic devices, one needs to improve the crystallinity and reduce defects for the grown nanostructured materials.

In this paper, an alternative method for the fabrication of ZnO nanowires with excellent crystallinity is presented. With the inclusion of In in the growth process, we show that the morphology of the end products can be changed from nanopins to nanowires. In addition, we point out that the effects of In inclusion can improve crystalline quality of ZnO, and suppress defect density. Our results shown here pave a new route for the creation of high quality optoelectronic devices based on ZnO nanostructures.

2. Experimental procedures

The 1D ZnO nanostructures were fabricated by thermal evaporation method. First, a high purity ZnS (0.5 g) powder (99.99%) was mixed with In_2S_3 powder (10–30 mg, 99.98%), then placed in an alumina boat at the center of a tube furnace. The silicon (100) substrate, used to collect the synthesized products, was placed upside-down about 1 cm above the mixed powder. The reaction chamber was sealed, pumped, and kept at a pressure of 300 Torr throughout the experiment. Ar (purity: 99.9%) was introduced into the reaction chamber at a flow rate of 50 sccm as the carrier gas. Subsequently, the temperature of the furnace was raised to 1100 °C and maintained at this temperature for 2.5 h.

After the reaction, the synthesized sample was taken out and characterized by field emission scanning electron microscopy (FE-SEM, JSM-6500F) equipped with an energy-dispersive X-ray (EDX) spectrometer. X-ray diffraction analysis was carried out using a diffractometer (Panalytical X'pert PRO) with copper K_α line as incident radiation. Raman scattering spectra were recorded using a Jobin-Yvon T64000 Raman-scattering spectrometer at room temperature in the back-scattering geometry. The 514.5 nm line of a 100 mW Ar^+ laser was used for the excitation source. To study the emission properties of ZnO nanostructures, the cathodoluminescence (CL) spectra were carried out at room temperature using a temperature-controllable cathodoluminescence detector (Mono CL, Gatan) installed in the FE-SEM, which was performed at an accelerating voltage of 10 kV.

3. Results and discussion

Fig. 1(a) shows the SEM image of the sample grown without the inclusion of In. Quite interesting, it demonstrates that the morphology is similar to pin-like hexagonal nanostructure, with the base diameter in the range of 1–2 μm and the peak diameter in 10–20 nm. With the addition of In in the growth process, the morphology of ZnO

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Fig. 1. Scanning electron microscope (SEM) images of four ZnO nanostructured materials grown on Si(100) substrates without (a) and with different percentages of In inclusion in the growth process, (b) 10 mg In_2S_3 , (c) 20 mg In_2S_3 , (d) 30 mg In_2S_3 .

Fig. 2. (a) X-ray diffraction spectra of ZnO nanomaterials as shown in Fig. 1. (b) Raman scattering spectra of ZnO nanomaterials grown with and without In inclusion in the growth process.

Fig. 3. (a) Cathodoluminescence spectra of ZnO nanomaterials as show in Fig. 1. (b) The magnified figure of the green emission of Fig. 3(a).

Fig. 4. The variation of the composition of zinc and oxygen in ZnO nanowires with respect to the quantity of In inclusion in the mixed powder.

nanostructures changes to a wire-like shape as shown in Fig. 1(b)–(d), which is very different from that shown in Fig. 1(a). The diameters and lengths of the nanorods are in the range of 100–300 nm and 1–10 μm . This result indicates that the inclusion of In can drastically alter the growth mechanism and change the morphology of the products. When the weight ratio of the mixed In_2S_3 and ZnS powder exceeds 0.2, the 1-D nanostructures of ZnO disappear, and are replaced by disordered bulk.

Fig. 2(a) shows the XRD results. For the sample without In inclusion, it has two additional peaks not associated with ZnO, but with ZnO_2 or Zn. When the percentage of In incorporated in the mixed powders increases, the intensity of the peak of ZnO (002) is enhanced, while the intensity of ZnO (101) peak is diminished. Moreover, other peaks which do not belong to ZnO disappear. This result clearly shows that the crystalline purity of zinc oxide can be improved with the inclusion of In. From those reported previously [12], we now attempt to understand the above result. When the velocity of crystallization of ZnO is too fast, the morphology of the crystal will be a hexagonal awl. However, when the velocity of crystallization is steady, the crystal of ZnO will be hexagonal rods or wires. Under this circumstance, (101) faces would not appear and most crystal faces are (002) or (100). Our SEM results shown above are indeed in good agreement with this description. Because there is no any additional peaks appearing in the XRD data, the fraction of the inclusion of In in the growth process is therefore negligibly small, and its role is mainly to serve as a surfactant located on the newly grown surface, which will decrease the growth rate of zinc oxide. Besides, it can prevent the incorporation of impurities into the grown crystal and improve the crystalline purity. To further confirm our conjecture here, Raman scattering experiments were performed as shown in Fig. 2(b). We can clearly see that the half-width of the E_2 mode of ZnO decreases with increasing percentage of In inclusion and the peak intensity also increases. The result illustrates that the crystalline quality can be greatly improved with the inclusion of In in the growth process.

We next examine the optical properties of the grown ZnO nanostructures as shown in Fig. 3. The UV emission at 381 nm is the near band edge (NBE) emission, and the green luminescence belongs to the defect emission of zinc oxide [13]. For the sample grown without inclusion of In, the intensity of NBE emission is stronger than that of defect emission, and the ratio of the intensity is about 9:1. After the incorporation of In in the growth process, the NBE emission is enhanced, while the defect emission is suppressed, and the ratio of the intensity of the peaks changes to 200:1. Generally speaking, it is unusual that doping can enhance NBE emission and suppress the defect emission [11]. Since it is expected that doping adds impurities to the crystal, the defect luminescence will be enhanced. Besides, with excess acceptor or donor levels, they will trap photoexcited electron-hole pairs, and reduce the NBE emission. In addition to the XRD data, our result presented here indicates that the inclusion of In in the growth process does not lead to a significant amount of the incorporation of In inside the ZnO crystals. Furthermore, the fact that the CL peak remains the same for both kinds of samples also provides another supporting evidence. The major effect of In inclusion in

the growth process is therefore not to incorporate In elements inside the ZnO crystal lattice, but only to decrease the growth rate, improve the crystalline quality, and reduce defect concentration.

To learn more about the defect formation in the growth process, we have performed the EDX measurement for the samples grown under different percentages of In inclusion. Fig. 4 shows the variation of the composition of Zn and O contained in ZnO nanostructures with the percentage of In inclusion. Initially, the composition of zinc is less than that of oxygen. After indium inclusion, the zinc composition increases. The result is similar to the previous work for the inclusion of Se in the growth of GaN, in which the composition of gallium is reduced [14]. Since the composition of zinc is less than oxygen in the sample grown without In inclusion, the origin of defect emission may be attributed to Zn vacancies or O antisites. However, the energy level of Zn vacancy is too large (3.06 eV), so O antisite may be the most probable candidate. Many previous reports have also shown that O antisites may be responsible for the origin of defect emission in high oxygen content surroundings for ZnO materials [15]. With In inclusion, the composition ratio between oxygen and zinc decreases, and the number of O antisites will be reduced. The defect emission is therefore suppressed. This behavior may be understood as follows. Due to the weaker In–O bond than Zn–O bond, the migration velocity of indium is faster than zinc and oxygen atoms on the surface of ZnO crystal. Indium atoms can have more chance to reach Zn lattice site earlier than oxygen atoms during the growth, and O antisites would be reduced and the crystalline quality of zinc oxide would become more perfect. It thus leads to the changes in the morphology, crystallinity, defect density, as well as optical properties of the grown ZnO nanostructures.

4. Conclusion

In summary, we have reported an alternative method for synthesizing ZnO nanostructures with excellent crystallinity. With In inclusion in the growth process, the morphology of products can be changed from nanopins to nanowires. In addition, we demonstrate that the main effects of In inclusion are to decrease the velocity of crystallization, improve crystalline quality, and reduce defect concentration. The luminescence intensity can be enhanced by more than one order of magnitude. Our result therefore provides an excellent route to obtain high quality nanomaterials of ZnO for optoelectronic applications.

Acknowledgement

This work was supported by the Ministry of Education and National Science Council of the Republic of China.

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