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An alternative approach to *in situ* synthesize single crystalline ZnO nanowires by oxidizing granular zinc film

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Abstract ZnO nanowires were synthesized by a relatively simple process—oxidizing granular Zn films at a relatively low temperature (450–600 °C) without catalyst. The zinc film was initially fabricated by sputter deposition in an argon atmosphere at ambient temperature using Zn metal as the sputter target. After subsequent annealing in an air or oxygen atmosphere, ZnO nanowires were found to grow from individual Zn nanograins. The investigation has also showed that the nanowires preferably grow from relatively porous Zn film and a small amount of oxygen flow is beneficial to the growth of nanowires. The resultant single crystal ZnO nanowires obtained from annealing at 600 °C in an oxygen atmosphere had a mean diameter less than 50 nm and had a very good structural quality. This process provides an alternative method to produce ultra-fine ZnO nanowires standing on the substrate.

Introduction

As a wide band-gap semiconductor, ZnO is currently generating substantial interest. Recently, various types of ZnO nanostructures such as film, balls [1], nanowires [2], nanoring [3] and nanorods [4–6] have been synthesized by different methods. Among these various nanostructures, one-dimensional (1D) ZnO nanocrystals, i.e., nanowires or nanorods, have been extensively investigated because they have not only wide applications in electrooptic nanodevices but also have great potential for fundamental studies of the effects of morphology, dimensionality, and size on the material properties. To synthesize 1D ZnO nanowires and nanorods, numerous techniques have been accomplished, such as chemical or physical vapor deposition [7, 8], plused-laser deposition [6], anodized aluminum oxide (AAO) template-assisted routes [9], template-free aqueous route [10]. Of these preparation methods, the vapor phase transport process assisted with the noble metal or template are major approaches and relatively successful to fabricate 1D ZnO nanowires with controllable diameter. However, they generally require expensive equipments, high temperatures and complex process control. On the other hand, the solution synthesis is perhaps the simplest way to prepare sufficiently crystallized materials [11], but obtained materials are difficult to collect, and are in the form of powders, not standing on the substrate, which may restrict their application.

Recently, In_2O_3 nanowires were *in situ* synthesized from indium film at a temperature of 400 °C using a thin layer of Au as the catalyst, which provided an attractive approach to obtain oxide nanowires [12]. In this paper, we report an alternative *in situ* synthesis method to produce ultra-fine ZnO nanowires by a simple combination of sputtering and thermal oxidation with no catalyst being used. It has been demonstrated that single crystalline ZnO nanowires standing on various substrates can be synthesized at a relatively low temperature and single nanowire is actually growing from individual Zn grain, which is different from those reported previously on growing nanowires from Zn resources, such as Zn nanowires [13], Zn particle [14, 15] and Zn vapor [16].

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Experimental details

Zn film was deposited on various substrates, including glass, quartz, silicon and sapphire, in Ar atmosphere at ambient temperature by RF Magnetron Sputtering. Pure Zn (99.99%) and argon gas were used as the sputtering target and the work gas, respectively. The base pressure of the chamber was ~3×10^{-7} torr. During the deposition, a gas flow rate of 10–20 sccm and a gas pressure P_{Ar} of 3×10^{-3} torr were employed. To synthesize ZnO nanowires, Zn film was thermally oxidized in a conventional tube furnace at a temperature of 450–600 °C in an ambient environment or in oxygen atmosphere by introducing a small amount of oxygen flow. The crystallographic property of the samples were described by X-ray diffraction (XRD) using a Philip 1710 diffractometer with Cu-Kα resource. The morphology of the nanorod array was investigated by field emission scan electron microscopy (FESEM) using a JEOL JSM-6700F system. The high resolution transmission electron microscopy (HRTEM) was employed to analyze the fine structure of the nanowires using a JEOL JEM 3010 system. The photoluminescence (PL) spectrum at room temperature was obtained by a Renishaw spectrophometer with the Hd–Cd laser as the excitation light source.

Results and discussion

Dark-colored pure Zn films were fabricated by a sputtering process described above. The thicknesses of the films were in the range of 0.5–1.0 μm, depending on the depositing parameters. After being oxidized at 450–600 °C for more than 30 min, as-deposited films turn to white color, indicating a complete transition from Zn to ZnO. The XRD spectra of as-deposited and oxidized films deposited on the glass substrate are shown in Fig. 1, indicating well-crystallized structures. All diffraction peaks for as-deposited film and oxidized film can be well indexed to the hexagonal phase Zn and the hexagonal phase ZnO, respectively. It was also found that there is no significant difference in XRD pattern for the white-colored films oxidized at various temperatures, implying that the ZnO morphology has no significant effect on the crystal structure.

We initially investigated the films deposited on the glass substrate. In our experiments, Zn films with both dense and porous structures were produced by employing various sputtering parameters, mainly argon gas flow, which affects the depositing rate. The microstructures for the Zn films produced at high and low depositing rates are shown in Fig. 2. Both films comprise of Zn grains, but the film deposited at low depositing rate has dense grain structure, whereas that produced at high depositing rate has porous grain structure, with a mean grain size less than ~200 nm.

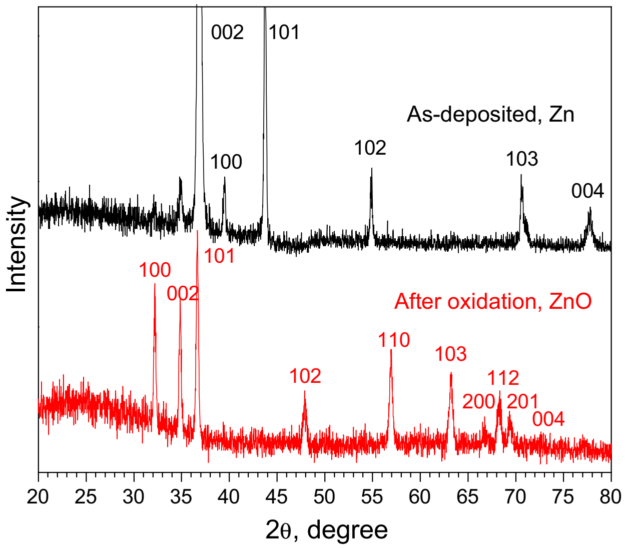


Fig. 1 XRD spectra for the Zn films deposited on the glass substrate before and after oxidation

At first, we oxidized the Zn film at ambient atmosphere. Figure 3 show the microstructures of dense and porous Zn films after exposure at a temperature of 600 °C for 1 h in the air. It was found that a small amount of nanowires were obtained by oxidizing dense film (Fig. 3a). These nanowires have needle-like shape and are less than 1 or 2 microns long. On the other hand, relatively large amount of ZnO nanowires with large length (up to a few microns) can be obtained by oxidizing porous film (Fig. 3b), though the nanowires have relatively large diameter size distribution. The results indicate that the ZnO nanowires favorably grow from porous Zn film. In order to further increase the quantity of the ZnO nanowires, we tried to adjust the annealing process, but our investigation have showed that it is difficult to obtain a large number of ZnO nanowires by simply changing annealing temperature and time. That is to say, only a small part of Zn film grows into nanowires in the ambient atmosphere.

Next, we introduced a small amount of oxygen flow in the tube furnace during thermal oxidation and we found that the growth of ZnO nanowires can be improved. By employing oxygen during annealing, we are able to obtain ZnO nanowires by annealing Zn film for 0.5–3 h in a temperature range of 450–600 °C. Figure 4 show the nanowires synthesized at 550 °C (a, c) and 600 °C (b, d, e) from dense (a, b) and porous (c, d, e) films after 1 h exposure. Compared to that obtained at ambient atmosphere (Fig. 3), the nanowires obtained at oxygen atmosphere have larger quantity, smaller diameter and larger length, especially for the porous Zn films. For example, the nanowires produced at 600 °C in oxygen atmosphere have a very uniform and fine diameter (less than 50 nm) with

Fig. 2 As-sputtered porous (**a**) and dense (**b**) Zn films on glass substrate produced by various deposition processes

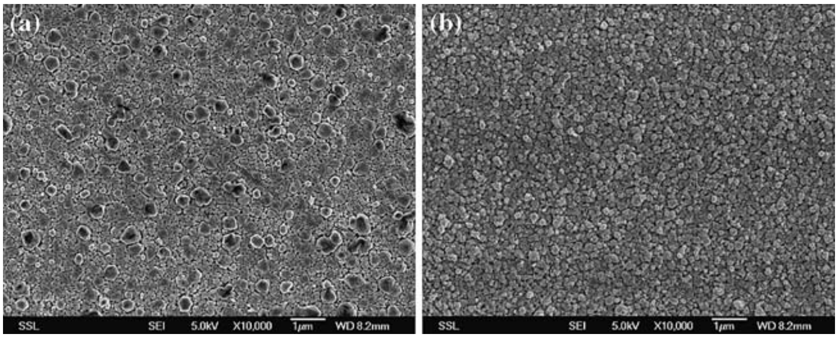


Fig. 3 Microstructures of oxidized dense (**a**) and porous (**b**) Zn films. ZnO nanowire obtained by oxidizing porous films for 1 h in the air

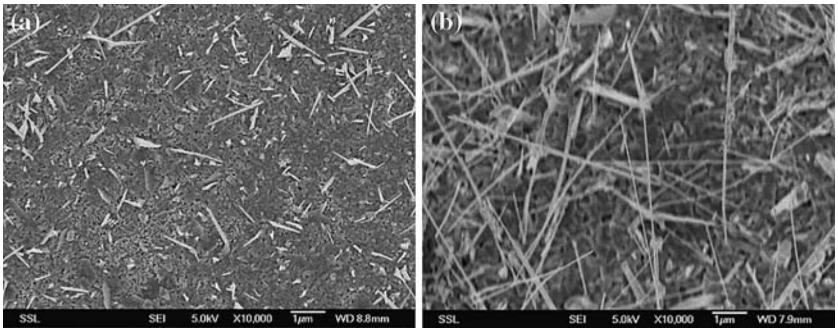
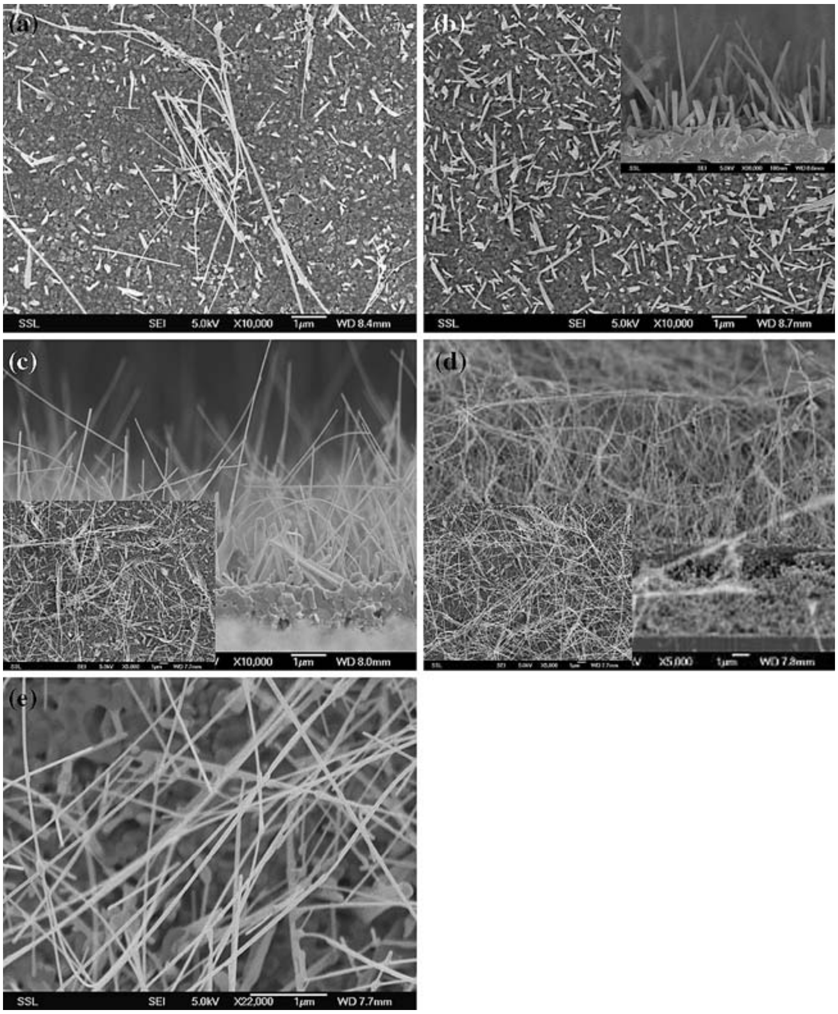


Fig. 4 SEM images for the dense (**a**, **b**) and porous (**c**, **d**, **e**) films after annealed at 550 °C (**a**, **c**) and 600 °C (**b**, **d**, **e**) for 1 h at an oxygen atmosphere (insets in **b**, **c** and **d** show side-view of the nanowires growing on the films)



very narrow size distribution (Fig. 4d, e). The lengths of the nanowires are up to >10 μm. Comparing Fig. 4 a, b with Fig. 4 c, d, and e, we also found that, for the dense film, it is more difficult to grow small and long nanowires with a large quantity.

Further structure characterization of the ZnO nanowires was performed by TEM. Figure 5 show the TEM and HRTEM images and corresponding selected SAED pattern of a single ZnO nanowire obtained at 600 °C in oxygen atmosphere. The diameter of the nanowire is ~23 nm. The SAED pattern (Fig. 5a, inset) and the HRTEM images (Fig. 5b) confirm that the nanowires are single crystals and are growing along [0001] direction. The lattice spacing of 0.28 nm in Fig. 5b corresponds to the d-spacing of the $(\bar{2}110)$ crystal facets, which is perpendicular to the [0001] direction. The results also show that the ZnO nanowires are free from defects and dislocations and have very uniform diameter size distribution along length direction.

In our case, the growth of ZnO nanowires was done without catalyst. Therefore, the growth mechanism of the nanowires was thought to be controlled by the traditional vapor–solid (VS) mechanism. This mechanism consists of two stages: nucleation and growth [17]. In the growth, Zn has an important role. When the Zn film is heated at above the melting point of Zn (419.53 °C), the granular Zn becomes Zn droplets on the film surface. Since a metal catalyst is not used, a liquid alloy is not formed. Instead, as Zn droplets become supersaturated, the liquid Zn reacts with oxygen and forms nanosized ZnO nuclei on the surface of the droplets. These ZnO nuclei individually further grow in the upper direction in the forms of nanowires. In the SEM observation, we have found that the individual nanowire is indeed growing from individual Zn grains, as shown in Fig. 6, where the nanowires were obtained after the film was exposed at 550 °C for a short time (20 min). This growth mechanism ensures that the nanowire is single crystallite without defects. The diameter of the nanowire depends on the size of the initial ZnO nuclei and the length of the nanowire is determined by the volume of one single Zn grain. For the porous Zn film with small grains, supersaturated nano-sized droplets are easy to form and subsequent growth leads to the formation of nanowires, whereas for the dense film with large grains size, since the grains are contacted each other, it is more difficult to form the nano-droplets and a continuous liquid layer was formed instead. Thus ZnO nanowires are easier to grow form porous Zn films. It is also understandable that enhancing the contact of Zn droplet and oxygen by introducing a small oxygen flow provides a better environment for nanowire growth. In addition, it is worthy noting that our nanowires are growing in the ambient pressure, while most previous processes require a relatively low pressure for ZnO growth.

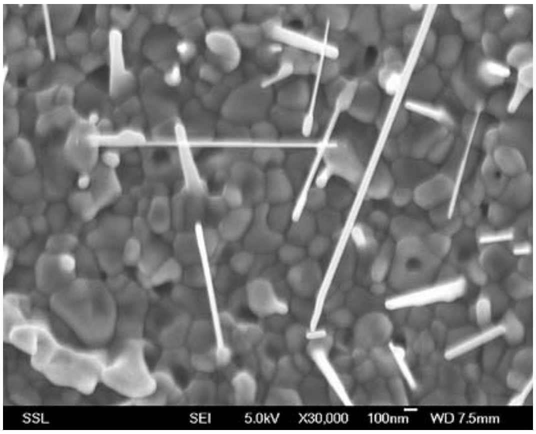


Fig. 6 SEM micrograph for showing nanowires growing from individual Zn grains (the film was annealed at 550 °C for 20 min)

We have also grown ZnO nanowires on other substrates, including silicon, quartz and sapphire. It was found that the substrate has no significant effect on the growth of the nanowires. This is easy to understand since the nanowires are grown from Zn film. Once the Zn film is produced, the growing procedure of the nanowires has nothing to do with the substrate. However, in order to obtain whole nanowires

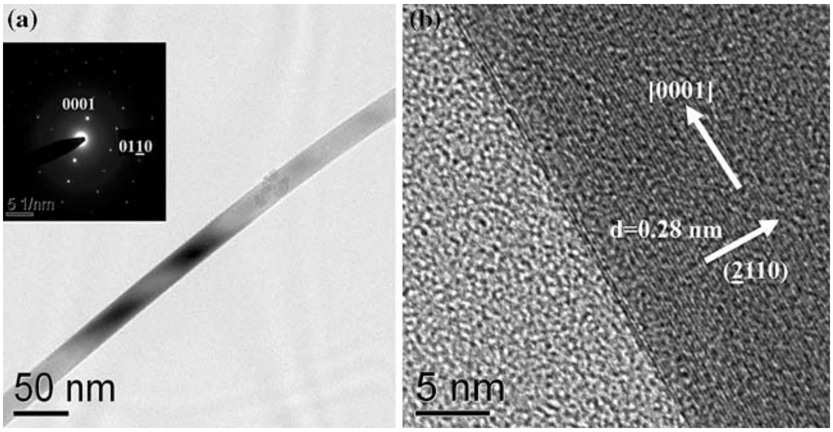


Fig. 5 TEM (**a**) and HRTEM (**b**) images and SAED pattern (**a**, inset) for ZnO nanowires

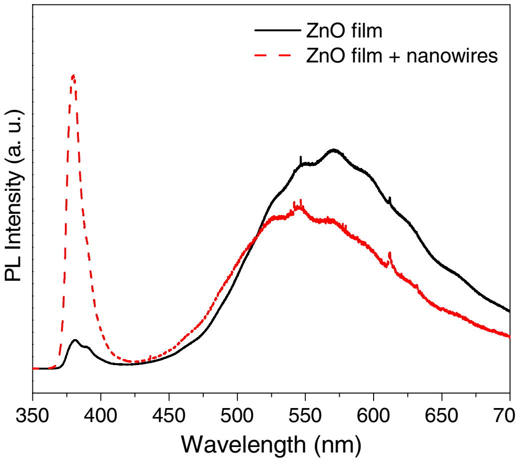


Fig. 7 PL spectra for ZnO film and ZnO nanowires standing on the ZnO film

standing on the substrate without using ZnO as a buffer layer, we suggest that the substrate, the film thickness and the rate of increasing or decreasing annealing temperature should be carefully selected to ensure that the film will not separate from the substrate due to the stress during annealing.

Room temperature PL spectra of the samples were measured and shown in Fig. 7. For comparison, both the ZnO film without nanowires and ZnO nanowires standing on the ZnO film were investigated. Two luminescence bands have been observed. One is an UV emission peak at ~380 nm, which corresponds to the near-band-edge emission. The other luminescence band, a green light emission peak, was observed at 550–570 nm. The green transition has been attributed to the singly ionized oxygen vacancy in ZnO and the emission resulted from the radioactive recombination of a photogenerated hole with an electron occupying the oxygen vacancy [6, 18]. The strong intensity of the green emission band indicates a large fraction of oxygen vacancies exists in ZnO film. In contrast, the PL spectrum of nanowires + film shows an enhanced emission at ~380 nm and a reduced emission at ~550 nm. The results, thus, indicate that the ZnO nanowires have better structure quality with fewer defects than the film.

Conclusion

ZnO nanowires were synthesized on the substrate by oxidizing granular Zn film. The zinc film was initially fabricated by RF sputter deposition. It was found that the nanowires are more easily grown from relatively porous film than from dense film. A small amount of oxygen flow during annealing greatly improved the growth of nanowires. The growing process of ZnO nanowires is thought to follow VS mechanism. The resultant single crystal ZnO nanowires have a mean diameter less than 50 nm. PL analysis indicated a good structural quality. This process is believed to provide an alternative method to produce ultrafine ZnO nanowires with high structure quality.

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