

SYNTHESIS OF WELL-ALIGNED ZnO NANOWIRES WITHOUT CATALYSTS

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Abstract. Well-aligned ZnO nanowires were synthesized by thermal evaporation method using c-oriented ZnO thin films as substrate without any catalysts or additives. The synthesized nanowires have two typical average diameters: 60 nm in majority and 120 nm in minority. The ZnO nanowires are about 4 μm in length and well aligned along the normal direction of the substrate. Most of the ZnO nanowires are single crystalline with a hexagonal structure and grow along the [001] direction. Photoluminescence spectrum shows that the ZnO nanowires have a single strong ultraviolet emission at 380 nm, indicating that the ZnO nanowire arrays can be used in optoelectronic devices.

1. INTRODUCTION

ZnO is a wide-band-gap n-type semiconductor, which has direct band gap energy of 3.37 eV and an excitation banding energy of 60 meV. The near-band emission, transparent conductivity and piezoelectricity make 1D ZnO nanomaterials (especially aligned ZnO nanowires) one of the most important functional semiconductor oxide nanostructures, serving to field emitters, optoelectronic devices and sensors, etc. Since Huang *et al.* reported vapor-phase synthesis of ZnO nanowire arrays using Au catalyst via a vapor-liquid-solid (VLS) process, several methods [3,4,5] were reported to synthesize aligned 1D ZnO nanostructures, among which the vapor transport and deposition method is most commonly used. However, such method often uses catalysts such as Au [2], Cu [6], Sn [7] or other additives such as NiO [8], Ga [9] to assist and control the growth process. Hence, the remains of catalysts or additives will unavoidably influence the pu-

rity of the final products. In another respect, some catalyst-free methods have been reported to synthesize 1D ZnO nanostructures via a self-catalysis process of Zn or ZnO [10,11]. However, only disarrayed nanostructures can be acquired by these methods.

Here, we report a simple thermal evaporation approach to synthesize well-aligned ZnO nanowires on c-oriented ZnO thin films. Such thin films are used as substrates to control the growth direction of ZnO nanowires; in addition, no extra catalysts or additives appear in this approach.

2. EXPERIMENTAL

In our work, we used zinc powders ($\sim 74 \mu\text{m}$ in diameter and 99.99% in purity) as source material and the whole experiment was performed in a horizontal tube furnace. About 1.00 g zinc powders were spread in an alumina boat and the boat was placed at the center of the furnace tube. A layer of c-oriented ZnO

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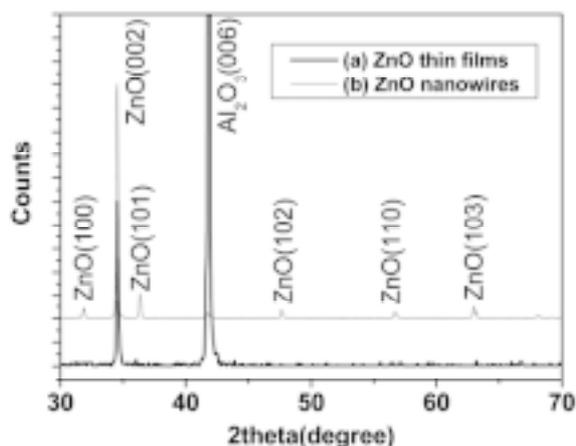


Fig. 1. XRD results of ZnO thin films and synthesized ZnO nanowire arrays.

thin films was put about 8 cm downstream of the tube center. Those ZnO thin films were prepared on a sapphire (Al_2O_3) substrate using pulsed laser deposition (PLD) method. The acquired thin films are about 400 nm thick and the X-ray diffraction (XRD) measurement shows that they are well c-oriented (see spectrum a in Fig. 1). A flow of Ar gas (200 sccm; standard cubic centimeter mass) was used as the carrier gas. The temperature at the tube center increased at a constant rate of 25 °C/min from room temperature to reaction temperature (~750 °C), and then preserved for 90 min. During that period, zinc powders were heated, vaporized, then transported along the Ar flow and finally deposited on the downstream substrate to form the final products.

The synthesized products were characterized using scanning electron microscopy (JSM-6301F), transmission electron microscopy (JEM-2010F) and X-ray diffraction (D/max-RB). The photoluminescence of the products was measured by the Hitachi 850 fluorescence spectrophotometer with a Xe lamp at room temperature.

3. RESULTS AND DISCUSSION

The morphology of the products on the ZnO thin films is shown in Fig. 2. Aligned ZnO nanowires are found to be synthesized on the c-oriented ZnO thin films (Fig. 2a). Higher magnification image (Fig. 2b) shows that the diameter of each ZnO nanowire has little variation from bottom to top and there are two typical diameters among those nanowires. The majority have similar diameters around 60 nm and the rest are about 120 nm in diameter which can be

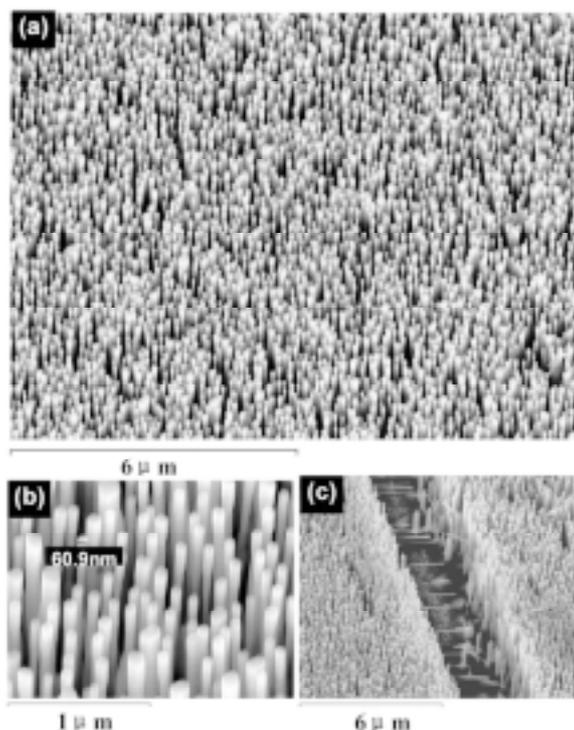


Fig. 2. Typical morphologies of ZnO nanowire arrays (a) Low magnification image; (b) High magnification image; (c) Side-on image.

regarded as the combination of two thinner nanowires. The lengths of the synthesized nanowires are approximately 4 μm . It is also observed that the cross section of the nanowire is hexagonal, indicating partially that the ZnO nanowires are hexagonal in crystal structure and are preferentially oriented in the c-axis direction. Side-on image (Fig. 2c) shows that those well-aligned nanowires grow vertically on the ZnO thin films. In addition, they are in high density and are uniformly distributed over most of the substrate. Hence, we suggest that the method in our experiment can be applied to large-scale manufacture of aligned ZnO nanowires.

Fig. 1 is the XRD results of the ZnO thin films and our synthesized ZnO nanowires on the films. As shown by Spectrum a, besides the substrate peak (Al_2O_3 (006)) only ZnO (002) peak appears, indicating that the ZnO thin films are well c-oriented. Although there are some extra peaks in Spectrum b compared to Spectrum a, the ZnO (002) peak is much higher than any other peak, including the substrate peak. Such result confirms that Spectrum b mainly reflect the structure property of the ZnO nanowires. It can be concluded that the synthesized ZnO nanowires which grow on the ZnO thin films

are well crystallized in hexagonal structure and grow along the *c*-axis direction by preference. In addition, the sharp (002) peak shows that those nanowires are well aligned along the normal direction of the ZnO substrate. High-resolution transmission electron microscopy (HRTEM) image of a single ZnO nanowire further clearly reveals the fringes of ZnO {001} planes with an interplanar spacing of about 0.52 nm, indicating the ZnO nanowire is single crystalline and grows along the [001] direction, which is in accordance with selected-area electron diffraction (SAED) pattern.

The introduction of ZnO substrates to synthesize ZnO nanostructures has been reported before. Tseng *et al.* [9] acquired needle-like zinc oxide nanowire arrays on Ga-doped ZnO films; however, they still used foreign atoms (Ga) as growth nuclei. Yu *et al.* [12] used ZnO nanocrystal substrates to synthesize ZnO nanostructures; however, the ZnO nanorods they acquired were only 1 μm in length and not well aligned. In our experiment, we demonstrate that the absence of catalysts or additives is feasible during the growth of ZnO nanowire arrays and our method using *c*-oriented ZnO thin films as substrates is proved effective to synthesize well-aligned ZnO nanowires.

Temperature influences the growth of the ZnO nanowires. It provides energy for zinc particles to vaporize, transport along the Ar flow and oxidize. If the heating temperature is too low (lower than 700 $^{\circ}\text{C}$ in our experiments), the energy for growing the ZnO nanowires is not sufficient, and there will be rarely nanowires.

The best region to grow ZnO nanowires (about 8 cm downstream of the source in our experiments) is exactly where most zinc particles begin to deposit. In its upstream region, only a few particles deposit, so the lengths and the density of the nanowires reduce dramatically. In its downstream region, the main products change to taper-like nanorods. The reason is that: on one hand, zinc particles drop and deposit heavily because of the decrease in temperature there, causing thick roots of the products; and on the other hand, zinc vapor there attenuates gradually during the growth, leading to the nanorods thinner and thinner.

To interpret the growth process of 1D nanomaterials, VLS mechanism [13] and vapor-solid (VS) [14,15] mechanism have been proposed respectively. In VLS mechanism, metal nanoparticles are always used as catalysts and there will be a metal droplet remaining at the tip of each nanowire. Since such droplets do not appear in our experiment, the

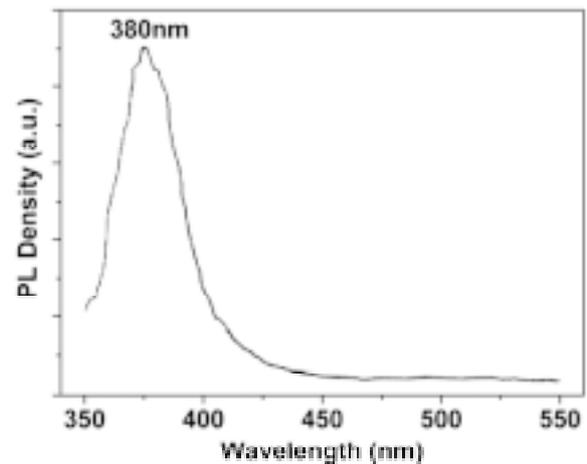


Fig. 3. PL spectrum of synthesized ZnO nanowire arrays.

growth process of our ZnO nanowires does not follow the VLS mechanism but VS mechanism. After vaporized and transported to the downstream substrate, zinc particles self-catalyze during the deposition and formation of ZnO nanowires. Hence, catalysts are not necessary during the growth process of ZnO nanowires. It has been demonstrated [16] that after an initial period of nucleation and incubation, ZnO tend to form 1D structures because they can maximize the areas of the {210} and {010} facets, which have lower energy. The control of growth direction depends on the substrate of ZnO thin films. Since the thin films are oriented along the [001] direction, which is also the preferential growth direction of ZnO nanowires, and the lattice constant of the substrate and the nanowires are exactly the same, the ZnO nanowires continue to grow along the [001] direction easily after zinc particles deposit on the substrate. As a result, the main products are ZnO nanowire arrays with hexagonal cross sections, growing along the normal direction of the thin films. Different from Ref. 9, which claims Ga atoms as nuclei sites, we propose that as long as the whole system is in a proper condition, the transported zinc particles can nucleate directly on the thin films without the help of foreign atoms. In most cases, each nucleus forms one single nanowire which has an average diameter of 60 nm, and grows on the substrate randomly. If two nuclei are close to each other, the two nanowires growing from them will meet and combine to one nanowire during the growth, whose average diameter is about 120 nm.

Fig. 3 shows the photoluminescence (PL) spectrum of the nanowire arrays measured at room tem-

perature on a fluorescence spectrophotometer using a Xe lamp with an excitation wavelength of 275 nm. Only a strong sharp ultraviolet (UV) emission at 370-390 nm is observed with a peak at 380 nm. This emission corresponds to the recombination of free excitons between conductive band and valence band and is called near band-edge emission [17]. This UV peak, with the full width at half maximum (FWHM) as narrow as 15 nm, is much sharper than the result given by Ref. 12, indicating the high purity and similarity of our nanowires. In addition, compared to Refs. 9 and 12, the disappearance of green emission at ~510 nm, which is attributed to the recombination of a photogenerated hole with a singly ionized charge state of oxygen vacancy [18], implies the rare existence of oxygen vacancies in our ZnO nanowires.

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