

The influence of growth temperature on ZnO nanowires

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Abstract

ZnO nanowires have been successfully synthesized on Si(100) substrate by a simple physical vapor deposition method. Thin film ZnO layer used as the nucleation site can avoid the contamination from the metal catalysts, and it can also control the growth direction of ZnO nanowires. Well-aligned ZnO nanowire arrays along the normal direction of the substrate can be obtained by controlling different growth temperature, which was demonstrated by XRD and FESEM analysis. A strong ultraviolet emission at room temperature was observed in all ZnO nanostructures. In addition, the growth mechanisms of the ZnO nanowires with different growth temperature is discussed in details.

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1. Introduction

The potential applications of nanostructure in microelectronic and optoelectronic devices are the major focuses of recent nanoscience researches [1–3]. Among these, the ZnO nanostructure, having a direct band gap of 3.37 eV and a large exciton binding energy of 60 meV, could realize practical applications in the areas of laser emission, field emission, and nanoscale heterojunction [4–6]. Synthesis of well-aligned ZnO nanowire arrays is integral to many applications, such as, light-emitting diodes and laser diodes.

Recently, well-aligned ZnO nanowires have been fabricated on different substrates, such as an expensive sapphire substrate, which show a good lattice match with ZnO [7,8]. But such substrates cannot be commonly utilized in current silicon based optoelectronic technology. Due to the large lattice mismatch and different crystal structure between ZnO and Si, the metal catalysts (such as Au) have been used to assist the growth process of ZnO nanowires. Hence, the remains of catalysts may be a contaminative

source that will degrade the purity of the products. However, most catalyst-free methods can only be used to synthesize disarrayed nanostructures until now [9–12].

In this work, we report well-aligned ZnO nanowires grown on Si(100) substrate by using a simple physical vapor deposition method. The contamination from the metal catalysts can be avoided by using a thin film ZnO layer as the nucleation site, and it can also control the growth direction of ZnO nanowires. In addition, a detailed understanding about the probable growth mechanisms of the ZnO nanowires with different growth temperature is presented.

2. Experimental

The ZnO nanowires were fabricated via a simple vapor-phase transport process in a horizontal tube furnace. A mixture of commercial ZnO and graphite powders in a certain weigh ratio (1:1) was loaded in a quartz boat served as source material. The furnace was heated up to the desired temperature (930, 960, and 990 °C, respectively) under a constant flow of Ar (99.99%) of 100 sccm for 30 min. The substrates were laid above the source material with a vertical distance of 4 mm. Before being loaded, the Si(100) substrates were cleaned by organic solvent, etched by HF

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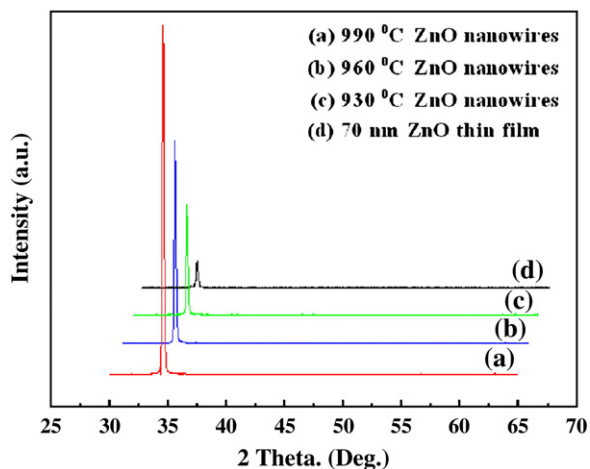


Fig. 1. XRD results of the synthesized ZnO nanowire arrays ((a), (b), and (c)) and 70 nm ZnO thin film (d).

acid and washed with deionized water. The thin layer of ZnO was deposited on Si(100) surface by electron beam evaporation method with the thickness of 70 nm. After deposition each substrate surface was covered with a white gray layer. The as-grown samples were then investigated by the field-emission scanning electron microscopy (FESEM), the energy-disperse X-ray (EDX) attached to the SEM and the X-ray diffraction (XRD). Photoluminescence (PL) measurement was performed using a He–Cd laser line of 325 nm as excitation source.

3. Result and discussions

Fig. 1 shows the XRD results of the ZnO thin film and the as-grown ZnO nanowires on the film. Both thin film and final products are *c*-oriented, which can be confirmed by only ZnO (002) diffraction peak appeared in the spectra. With increasing growth temperature, the (002) peak intensity of ZnO nanowires becomes stronger. In contrast to the nanowires, the thin ZnO film has a weaker intensity of (002) peak. The calculated lattice constants along the *c*-axis estimated from each (002) peaks are 5.193 Å, 5.191 Å, 5.193 Å and 5.176 Å in Fig. 1(a)–(d). Compared to the lattice constant of bulk ZnO (5.206 Å), these values indicate low strain level that exists in nanowires.

Morphologies of these as-grown samples obtained at different growth temperature were analyzed by SEM shown in Fig. 2. Both ZnO nanowires grown at the temperature of 930 °C and 990 °C have the typical diameter about 100 nm. The average lengths of three samples are 15 μm, 5 μm and 5 μm, corresponding to the growth temperatures at 930 °C, 960 °C, and 990 °C, respectively. The nanowires grown at relatively low temperature are too long to stand straightly. The ZnO nanowires grown at 960 °C are as well-aligned as the sample grown at 990 °C. Unlike other samples, its single wire has two typical diameters: 200 nm at top and 400 nm at bottom. At low magnification (Fig. 2(a), (d), and (g)), the nanowires have denser areas with increasing growth temperature. All samples have the flat and hexagonal shape at the top of nanowires shown in the inset of Fig. 2(i) (an amplified top image of a single nanowire). Unlike the metal catalyst assisted process, no catalyst “ball” can be seen at the top end. The EDX analysis also indicates that there is no any other metal element on the ZnO nanowires, and the synthesized nanowires consist of zinc and oxygen elements only (not shown here).

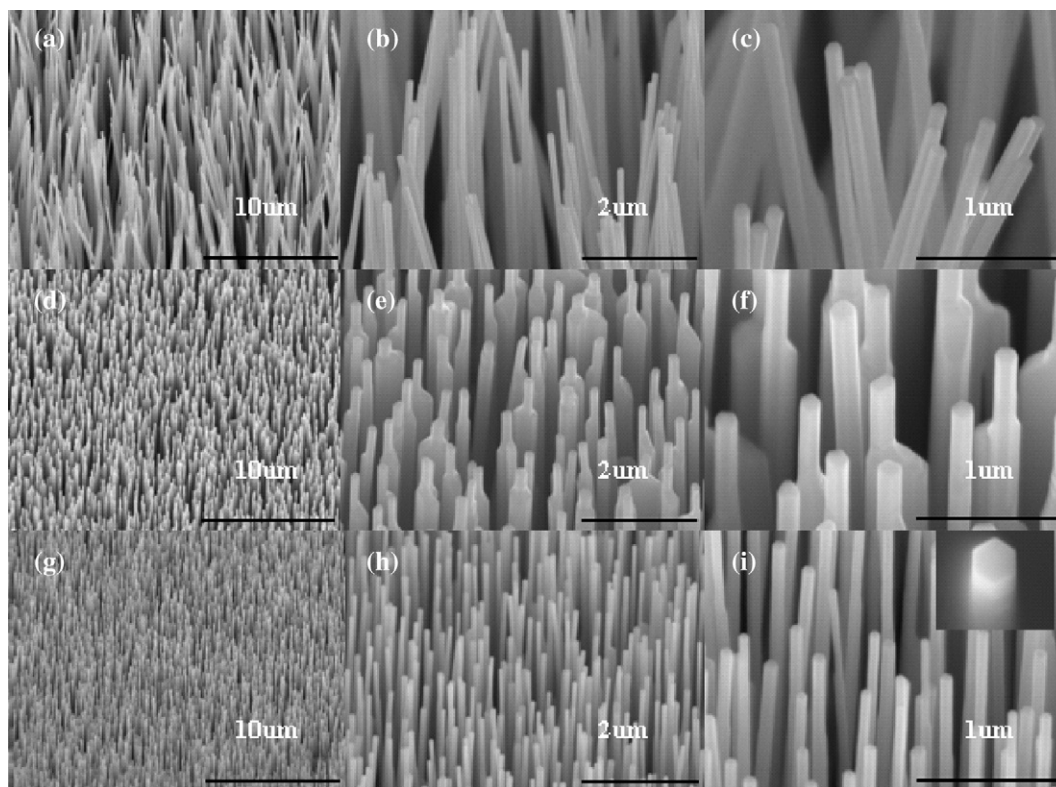


Fig. 2. The titled view of FESEM images of the ZnO nanowires at different temperature: (a)–(c) for 930 °C, (d)–(f) for 960 °C, (g)–(i) for 990 °C. The inset in (i) shows the faceted hexagonal shape of the nanowires.

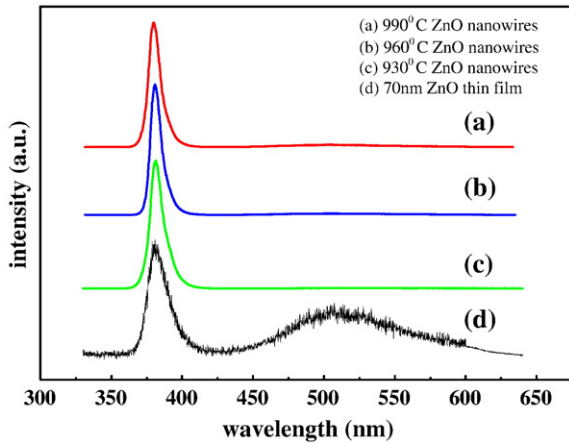


Fig. 3. PL spectrum of the synthesized ZnO nanowire arrays ((a), (b), and (c)) and 70 nm ZnO thin film (d).

Since no metal catalyst is used in our synthesis, the widely used VLS mechanism cannot be used to interpret the growth process. It suggests that our nanowires grow via a vapor transport solid condensation mechanism with the ZnO film acting as a seed layer for nucleation [13]. The ZnO nuclei form by the oxidation of supersaturation zinc vapor, which was produced by the carbonthermal reduction of ZnO powder. In this mechanism, ZnO nuclei are firstly formed on the surface of ZnO film and finally grow to nanowires. Benefited from the perfect lattice match, the ZnO nuclei were formed epitaxially on the *c*-oriented ZnO thin film/Si substrate. Combined with the fact that [0001] is the preferential growth direction for ZnO nanowires, ZnO nanowire arrays are expected to synthesize vertically to the substrate surface in our experiment. The analysis is in well agreement with the XRD and FESEM results.

Growth temperature is a critical experimental parameter for the formation of different morphologies of ZnO nanostructures: it determines how much the reactive vapor could be generated and the surface diffusion length of the adsorbed vapor species [14]. The effects of surface diffusion and the condensation of vapor will affect the growth rate in different growth temperature. As shown from the FESEM images, the length of nanowires grown at 930 °C is three times longer than other samples during the same growth time. At high temperature (990 °C) the growth species has enough energy to diffuse and move to the energetically favorable plane of growth but the ample energy can also cause a high rate of desorption and re-evaporation which leads to distributed, dense, and short nanowire arrays. If the heating temperature is low (930 °C), the energy for Zn vapor is not sufficient and the atoms are deposited exactly where they land, creating a rough uneven film with nuclei clusters [15]. These nuclei clusters will lead to several ZnO nanowires assembling in the following growth process (as shown in Fig. 2(a)–(c)). The phenomena of nuclei assembling also exist in the medial temperature (960 °C) growth process. Because the temperature is higher than 930 °C, the number of nuclei assembled in each nuclei cluster is fewer. The closing nuclei devoured each other to become a larger grain in the initial growth stage. The nanowires growing from them will lead to larger diameter. In addition, the growth of larger diameter nanowires will need more vapor, hence, it will be heavily suffered by changes in the amount of Zn vapor source. With the decreases of source vapor, the nanowire diameter seems to reduce in size to compensate for the lack of vapor. This is the reason why a single wire has two typical diameter.

The optical properties of the ZnO nanowires are investigated by PL spectra. Fig. 3 exhibits room-temperature PL spectrum of ZnO nanowires, a strong and sharp ultraviolet (UV) near-band-emission located at 380 nm is observed in all samples, which is attributed to the recombination of free excitons [16,17]. Meanwhile, the deep-level green emission is very weak compared with the UV peak. The origin of the deep level in ZnO is not yet clearly understood, nevertheless, it is generally considered as single ionized vacancies, and impurities [18]. Since our ZnO nanowires use a thin film ZnO layer as self-catalysts, which the unintentional incorporation of metal impurities into nanowires can be avoided. It is suspected that oxygen vacancies, which exist commonly in ZnO nanowires as point defects, led to the deep-level emission. The above results show that there are no distinct differentiations among all as-grown samples. However, the excellent optical properties (evident in strong and sharp excitonic emission with low deep-level emission) indicate that all the samples have high optical quality compared to the ZnO thin film.

4. Conclusion

By controlling growth temperature, well-aligned ZnO nanowire arrays along the normal direction of the substrate can be acquired by carbonthermal reaction. Utilize a thin ZnO film to promote nucleation and control the growth orientation of the nanowires. Growth temperature is the critical experimental parameter for the formation of different morphologies of ZnO nanowires. Of course, the favorable growth temperature for alignment can be changed by varying the other parameters (such as deposition pressure, or the oxygen partial pressure). We will carry out further investigation to obtain controllable ZnO nanowires for applications.

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