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2007 Nanotechnology 18 235604

(http://iopscience.iop.org/0957-4484/18/23/235604)

IOP PUBLISHING NANOTECHNOLOGY
Nanotechnology **18** (2007) 235604 (5pp) doi:10.1088/0957-4484/18/23/235604

Growth of well-aligned ZnO nanowire arrays on Si substrate

F Fang[1,2], D X Zhao[1,4], J Y Zhang[1], D Z Shen[1], Y M Lu[1], X W Fan[1], B H Li[1] and X H Wang[3]

[1] Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, 16 East Nan-Hu Road, Open Economic Zone, Changchun 130033, People's Republic of China
[2] Graduate School of the Chinese Academy of Sciences, People's Republic of China
[3] National Key Laboratory of High Power Semiconductor Laser, Changchun University of Science and Technology, 7089-WeiXing Road, ChangChun, 130022, People's Republic of China

E-mail: dxzhao2000@yahoo.com.cn

Received 12 March 2007, in final form 16 April 2007
Published 16 May 2007
Online at stacks.iop.org/Nano/18/235604

Abstract
Well-aligned ZnO nanowire arrays have been successfully synthesized on Si(100) substrate by a vapour transport process. A ZnO thin film was used as the nucleation sites, which can control the growth orientation of the nanowires. By observation of the initial process of nanowire growth, a vapour transport solid condensation mechanism was proposed for ZnO nanowire growth, in which the role of ZnO thin film was to provide nucleation sites for nanowire growth. It was also found that the nanowire density could be adjusted by varying the thickness of the ZnO thin film. The synthesized ZnO nanowires, which had a single-crystalline wurtzite structure, had diameters of 50–120 nm and lengths of around 5 μm. The strong ultraviolet emission and weak deep level emission reflect the high optical quality of the nanowires.

1. Introduction

The potential applications of nanostructured materials in microelectronic and optoelectronic devices has been a major focal point in recent nanoscience research [1–3]. Among these materials, the ZnO nanostructure, having a direct band gap of 3.37 eV and a large exciton binding energy of 60 meV, could be used to realize practical applications in the areas of laser emission, field emission, and nanoscale heterojunctions [4, 5]. Synthesis of well-aligned ZnO nanowire arrays is integral to many applications, including light-emitting diodes and laser diodes.

Recently, well-aligned ZnO nanowires were grown on sapphire substrate [6–8]. Owing to the large lattice mismatch and the difference in the crystal structure between ZnO and Si, metal catalysts (such as Au) have been used to assist and control the ZnO growth process on Si substrate. Hence, the remains of catalysts may be a source of contamination that will influence the purity of the products. Until now, most catalyst-free methods could only be used to synthesize disarrayed nanostructures [9–12].

In this work, we report a simple physical vapour deposition method to synthesize well-aligned ZnO nanowires on Si(100) substrate. A thin film of ZnO was used as the nucleation template to control the growth direction of the ZnO nanowires. Moreover, we can regulate the nanowire density by changing the thickness of the ZnO thin film. A detailed description of the probable growth mechanisms of the ZnO nanowires is discussed.

2. Experimental details

The ZnO nanowires were fabricated via a simple vapour-phase transport process in a horizontal tube furnace. A mixture of commercial ZnO and graphite powders in a certain weight ratio (1:1), serving as source material, was loaded in a quartz boat. The synthesis was carried out at 990 °C under a constant flow of Ar(99.99%) with a flow rate of 100 sccm for 30 min. The substrates (Si and ZnO/Si) were laid above the source material with a vertical distance of 4 mm. A thin layer (70 nm) of ZnO was deposited on the Si surface by electron beam evaporation. After deposition a white grey layer was found only on the ZnO thin film coated substrate surface. No product

[4] Author to whom any correspondence should be addressed.

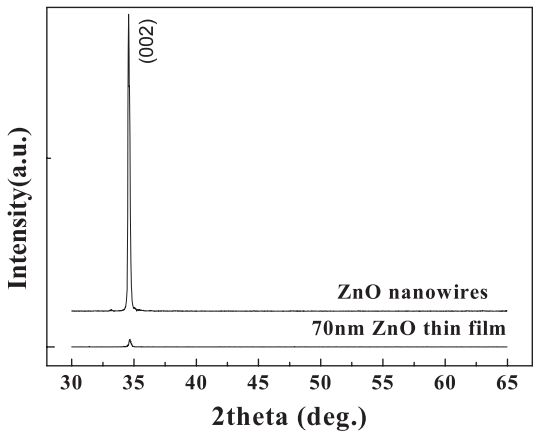

Figure 1. XRD results of the ZnO thin film (with 70 nm thickness) and the synthesized ZnO nanowire arrays.

was found on the bare Si substrate. The as-grown samples were then investigated by field-emission scanning electron microscopy (FESEM), energy-dispersive x-ray spectroscopy (EDX) attached to an SEM, transmission electron microscopy (TEM), and x-ray diffraction (XRD). Photoluminescence (PL) measurements were performed using a He–Cd laser line of 325 nm as the excitation source.

3. Results and discussion

Figure 1 shows the XRD results of the ZnO thin film and the as-grown ZnO nanowires on the film. Both the thin film and the final product are *c*-oriented. It can be confirmed that only the ZnO(002) peak appears. The intensity of the (002) peak of the ZnO nanowires is very strong, about 40 times higher than that of the thin film. The calculated lattice constants along the *c*-axis estimated from each (002) peak are 5.193 and 5.176 Å for the ZnO nanowires and the ZnO thin film. Compared to the lattice parameter of bulk ZnO (5.206 Å), these values indicate a low strain level in the nanowires.

The morphology of the final product on the ZnO thin film/Si substrate is shown in figure 2. Aligned ZnO nanowires are found to be synthesized on the *c*-oriented ZnO thin film. The ZnO nanowires have diameters ranging from 50 to 120 nm and lengths around 5 μm. The inset of figure 2(c) shows a magnified top-view image of a single nanowire, which indicates that the top of the nanowire is flat with a hexagonal shape. No catalyst 'ball' is seen at the top end of the nanowire. The EDX analysis also indicates that there are only zinc and oxygen elements on the ZnO nanowires with almost stochiometric content (Zn:O = 0.52:0.48). To further investigate the structural characteristics of the product, a high-resolution transmission electron microscopy (HRTEM) image of a single ZnO nanowire is shown in figure 3. Clear lattice fringes indicate the single-crystalline structure of the ZnO nanowires. The lattice spacing of approximately 0.26 nm between adjacent lattice planes, which corresponds to the distance between two (002) crystal planes, further confirms the ⟨0001⟩ growth direction.

Based on our previous report, it suggests that our nanowires grow via a vapour transport solid condensation mechanism with the ZnO film acting as a seed layer for nucleation [13]. The ZnO nuclei are formed from the oxidation of zinc vapour, which is produced by the carbonthermal reduction of ZnO powder. We have grown some samples (with the same ZnO film thickness, 70 nm) for a very short time (1, 2, and 5 min corresponding to figures 4(a)–(c)) to detect the

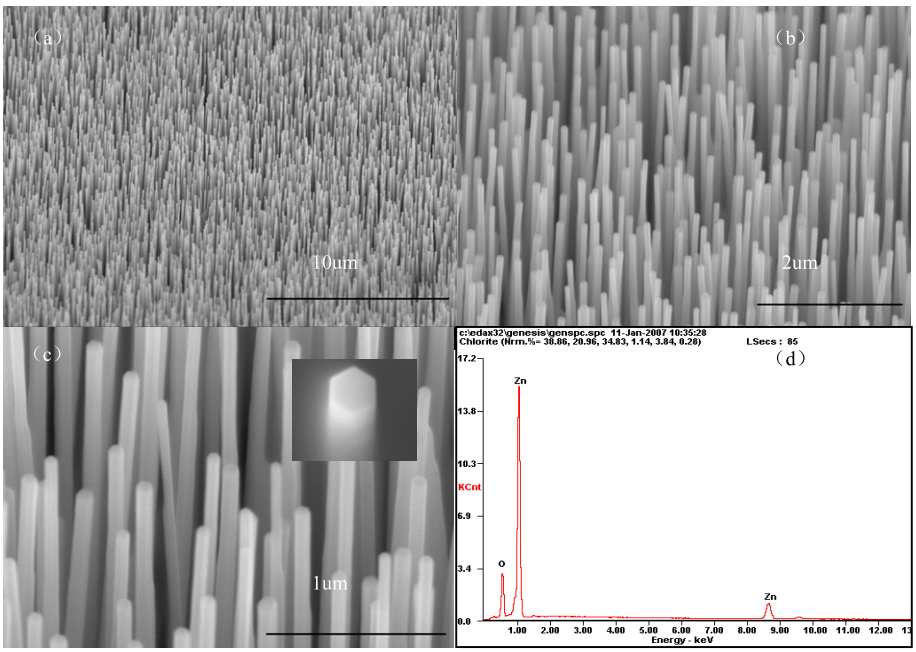

Figure 2. ((a)–(c)) FESEM images and (d) an EDX spectrum of the ZnO nanowires formed on ZnO thin film (with 70 nm thickness)/Si substrate. The inset in (c) shows the faceted hexagonal shape of the nanowires.

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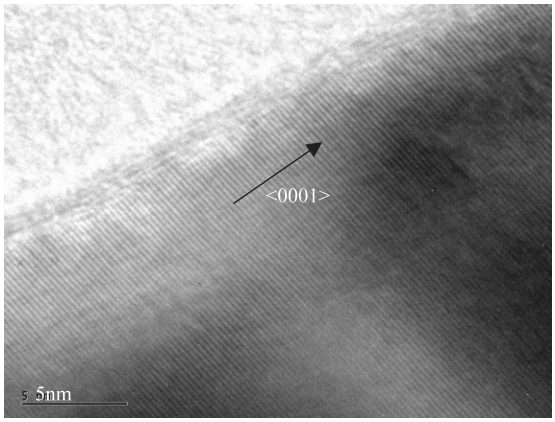

Figure 3. HRTEM image of an individual ZnO nanowire whose lattice spacing shows growth in the ⟨0001⟩ direction.

initial period. With increasing growth time, the ZnO nanowires nucleate and incubate bigger islands on the surface of these thin films (figures 4(a) and (b)). Furthermore, hexagonal rod-like structures nucleated at the top of these bigger islands before the completion of in-plane grain growth (figure 4(c)) [10]. The thin film is *c*-oriented, which is the preferential growth direction of ZnO nanowires. In the subsequent development of the growth to 30 min, well-aligned ZnO nanowire arrays with hexagonal cross sections seem to predominately grow along the normal direction of the thin film [8]. As shown in figure 4(c), each nuclear site usually forms only one nanowire. But when the nuclear sites are close to each other (see the black circle), two nanowires will be combined into one nanowire, with a larger diameter, in the following growth process.

Professor Yang's group has used the thickness of the metal catalyst to control the diameter of the nanostructure as well as the areal density [7]. In order to identify the effect of the thickness of the ZnO thin film, three nanowire samples are grown using the same gas flow, substrate temperature and quantity of reactants but with different catalyst film thicknesses (the thicknesses of the ZnO thin films are 20, 70, and 400 nm corresponding to samples A, B, and C). All samples are well-aligned ZnO nanowires. As shown in figures 5(j)–(l), sample A coated with 20 nm thick ZnO film has a lower density than the other samples (the densities are 8 μm^{-2}, 15 μm^{-2}, and 13 μm^{-2}, respectively, for samples A, B, and C). Corresponding to the above samples, different thicknesses of the ZnO thin film layers are annealed in the furnace without powder using similar growth conditions (figures 5(d)–(i)). The high annealing temperature (990 °C) causes the ZnO layer to assemble and ball into bigger islands. During this process, 20 nm thick ZnO film is too thin to coat the whole substrate. Therefore, some bare Si substrate will appear. Our experiment has confirmed that nanowires cannot be directly grown on Si substrate. Because the growth temperature is higher than 900 °C, the Zn adatoms can only stay on the substrate for a very short time. If there is no special nucleation site on the substrate, the Zn atoms will re-evaporate from the substrate without being oxidized (the boiling point of Zn is 907 °C). Therefore, no product could be found on bare Si substrate [14]. As a result, the nanowires growing from the 20 nm thick ZnO film will lead to a low density. With increasing thickness, the ZnO film can coat the whole substrate and the thicker 400 nm ZnO film will form relatively larger seeds than the 70 nm thick ZnO film. The nanowires growing from the 70 nm thick ZnO film which has smaller ZnO seeds implies the formation of denser areas [15].

In the metal catalyst assisted process, the nanowires grow from the supersaturated metal–Zn alloy droplet. The diameter of the wires is related to the size of the catalyst droplets. Unlike the metal catalyst, our ZnO thin film acts only as the nucleation site. There is no definite relationship between the thickness of the thin film and the diameter of the nanowires. Figures 5(j)–(l) show that there is no distinct change in the diameter of the three samples.

The optical properties of the ZnO nanowires are investigated by PL spectroscopy, and are found to be quite similar to the PL spectra of ZnO nanowires fabricated using a Au catalyst [7]. From the room temperature PL spectrum of ZnO nanowires in figure 6, a strong sharp ultraviolet (UV) near-band-emission is observed with a peak centred at 380 nm, which is explained by 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 emission in ZnO is not yet clearly understood but is generally attributed to structural defects, single ionized vacancies, and impurities [18]. As our ZnO nanowires use a thin film ZnO layer as a self-catalyst, the unintentional incorporation of metal impurities into the nanowires can be avoided. In addition, as determined from the TEM study, ZnO was single crystalline, and had no observable structural defects, such as dislocations and stacking faults. It is suspected that oxygen vacancies, which commonly exist in ZnO nanowires as point defects, led to the deep-level emission [11]. This deduction is in accordance with the EDX result, which shows stochiometrically less oxygen than zinc in the product. The excellent optical properties, evident as strong and sharp excitonic emission and low deep level emission, indicate that the ZnO nanowires are of high optical quality.

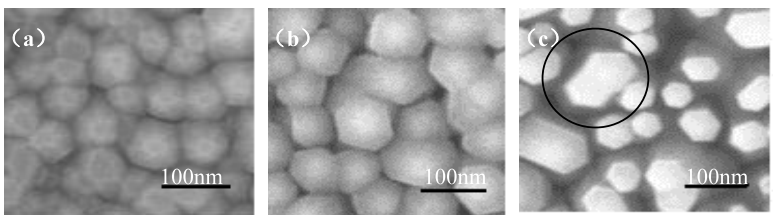

Figure 4. FESEM images of the ZnO nanowires grown on ZnO thin film (with 70 nm thickness)/Si substrate at 990 °C (a) for 1 min, (b) for 2 min, and (c) for 5 min.

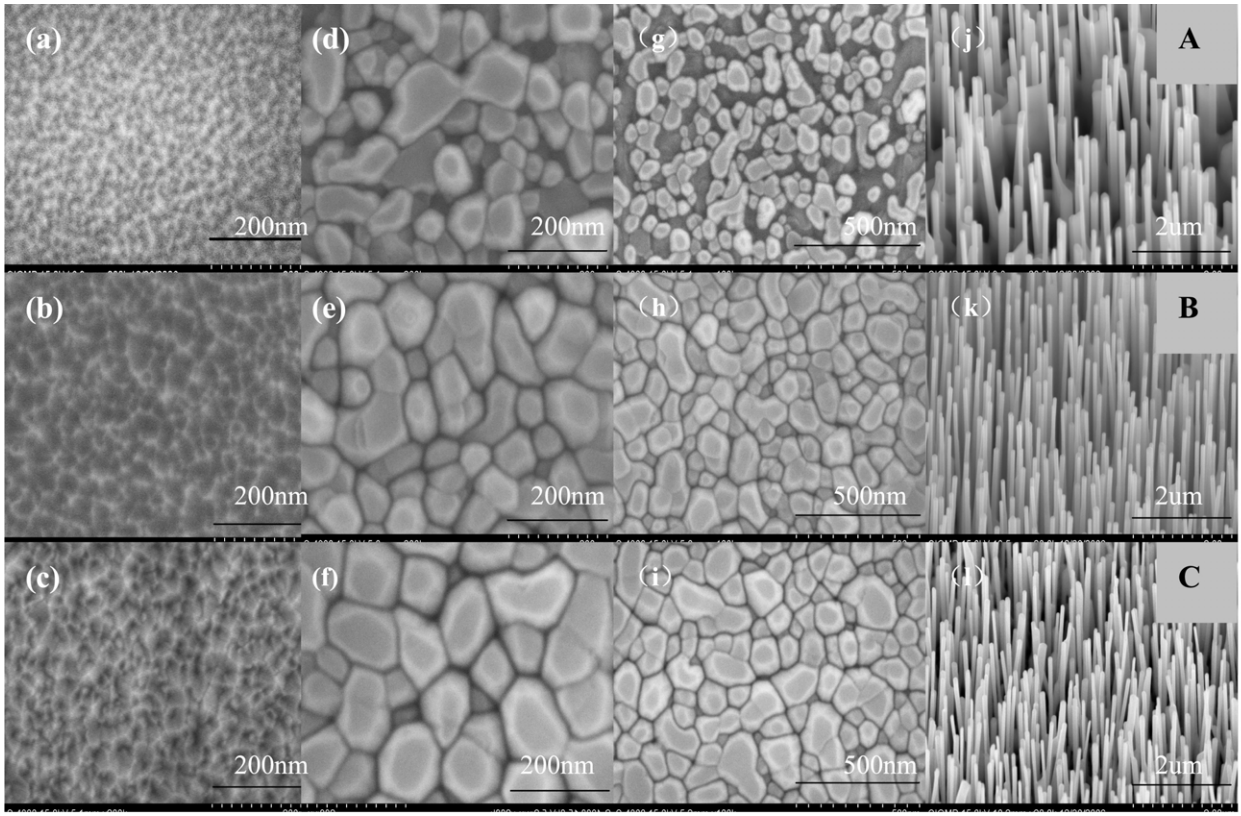

Figure 5. FESEM images of the ZnO thin film with different thickness 20 nm, 70 nm, and 400 nm, respectively and the as-grown ZnO nanowires on these films: ((a)–(c)) per-annealed ZnO thin film, ((d)–(i)) as-annealed ZnO thin film, ((j)–(l)) as-grown ZnO nanowires on the film with the ZnO thin film thickness 20 nm, 70 nm, and 400 nm, respectively.

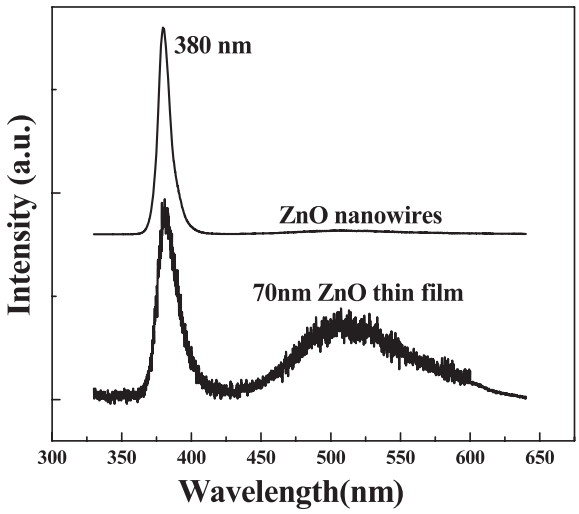

Figure 6. PL spectrum of ZnO thin film (with 70 nm thickness) and synthesized ZnO nanowire arrays.

4. Conclusion

In conclusion, well-aligned ZnO nanowire arrays were grown on Si substrate by a carbonthermal reaction using a thin ZnO film to promote nucleation and control the growth orientation of the nanowires. The density of the nanowires was regulated by changing the thickness of the ZnO thin film. The synthesized ZnO nanowires had high crystalline and excellent photoluminescent properties. We believe such well-aligned ZnO nanowire arrays on low-cost silicon substrates could be used in nanoscale optoelectronic applications.

Acknowledgments

This work is supported by the Key Project of National Natural Science Foundation of China under Grant Nos 60336020, 50532050, the '973' program under Grant No. 2006CB604906, the Innovation Project of Chinese Academy of Sciences, the National Natural Science Foundation of China under Grant Nos 60429403, 60506014, 50402016, 60676059 and 10674133.

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