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Synthesis of ZnO nanorod on bare Si substrate using metal organic chemical vapor deposition

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Abstract

We have synthesized the ZnO nanorod on bare silicon substrate using the simple metal organic chemical vapor deposition technique. We investigated the effect of substrate temperature on the growth of ZnO films or nanorods on Si(1 0 0) substrate. The substrate temperature affects deposition process, revealing that ZnO nanorods were obtained at the temperature of 500°C. The results showed that the as-prepared nanorods are composed of ZnO with an average diameter of 50–120 nm.

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In recent years, there has been increasing interest in quasi one-dimensional nanostructural systems, because of their numerous potential applications in various areas, such as materials sciences, electronics, optics, magnetism and energy storage. Specifically, zinc oxide (ZnO) is recognized as one of the most promising oxide semiconductor materials, because of its good optical, electrical, and piezoelectrical properties. It can be used in many areas, such as field emission displays, solar cells, and gas sensors.

Recently, a great deal of attention has been focused on the study of ZnO low-dimensional materials. However, not much work has been reported regarding synthesizing one-dimensional ZnO materials. ZnO columns or nanowires were synthesized by electrodeposition method [1–3]. Single-crystalline ZnO nanowires have been synthesized using high-temperature vapor–liquid–solid growth methods [4,5]. Single-crystalline ZnO nanobelts have been prepared by thermal evaporation of the ZnO powders [6].

High-quality ZnO nanomaterials grown on Si substrate, will pave the way for integration of future opto-electronic devices with developed silicon integrated circuit technology. ZnO nanorod or whiskers are grown on copper metallized Si substrate by radio frequency sputter deposition method [7] and on sapphire substrate by the chemical vapor depositon method [8]. Although ZnO nanorods were demonstrated to have been grown directly on fused silica substrate

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by the chemical vapor deposition method using evaporated zinc acetylacetonate hydrate ($Zn(C_5H_7O_2)_2 \cdot xH_2O$) [9], there are rare reports on the growth of ZnO nanorod on silicon substrate.

In this paper, we demonstrate the deposition of ZnO nanorods on bare Si substrate by the simple metal organic chemical vapor deposition (MOCVD) technique, using $Zn(C_2H_5)_2$ and O_2 system. We use a silicon substrate in growing ZnO film for future optical-electronic integration. We investigate the effect of substrate temperature, revealing that growth temperature plays an important role in growing ZnO nanorods.

The ZnO films or nanorods were deposited on p-type silicon with (1 0 0) orientation. The substrates were cleaned with organic solvents and dried before loading into the system. We used a $Zn(C_2H_5)_2$ (99.9999% purity DEZ (diethylzinc)) and O_2 (99.999% purity) system and used Ar (99.999% purity) as a carrier gas of DEZ source. Fig. 1 shows a schematic diagram of the MOCVD reactor used in our experiments. Mass flow controllers separately controlled the flow of Ar and O_2 gases and the gas flow ratio of Ar to O_2 was in the range of 1–2. The substrate temperature was varied as a process variable ranging from 250°C to 500°C. The deposition time was set to 10 min.

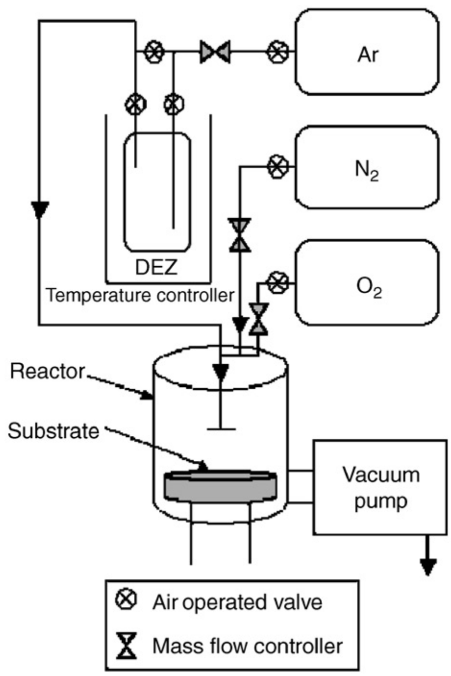

Fig. 1. Schematic diagram of the MOCVD system.

The as-grown morphologies of the product were observed with a Hitachi S-4200 field emission scanning electron microscope (FE-SEM) equipped with an energy-dispersive X-ray (EDX) spectroscope. Fig. 2 shows SEM images at substrate temperatures of 250°C, 300°C, 400°C, and 500°C, revealing that increasing the substrate temperature increased the grain size of ZnO thin films in the temperature range of 250–400°C. The cross-sectional SEM images indicate that the surface roughness of ZnO films increase by increasing the substrate temperature and thus, increasing the grain size. Fig. 2d shows the ZnO rods grown on silicon substrate. Most of the nanorods are slightly curved and the orientation of the rods appears to be randomized. By comparing Fig. 2c with Fig. 2d, it is noteworthy that as the temperature increases from 400°C to 500°C, the ZnO morphology changes from a thin film to a nanorod. The previous report also reveals that growth of ZnO whiskers is influenced by the substrate temperature [8].

In order to address the composition of the products grown at 500°C, we have used a Rigaku (Tokyo, Japan) D/max-2400 X-ray diffractometer (XRD) with CuKα radiation ($\lambda = 1.5405$ Å). Figs. 3a and b show the SEM image and the XRD patterns of ZnO nanorods grown directly on the silicon substrate at 500°C. The XRD pattern reveals the appearance of Si peaks. The position of the XRD peaks shows good agreement with those of the hexagonal ZnO with lattice constants $a = 0.3250$ nm and $c = 0.5207$ nm [10]. An EDX was also used to reveal the composition of the product grown at 500°C, indicating that the nanorods are composed of ZnO (not shown here). To reveal the crystallinity of the ZnO nanorod, a transmission electron microscopy is underway.

The right-hand side of Fig. 2d shows the cross-sectional SEM images, indicating that ZnO nanorods are found on top of ZnO thin

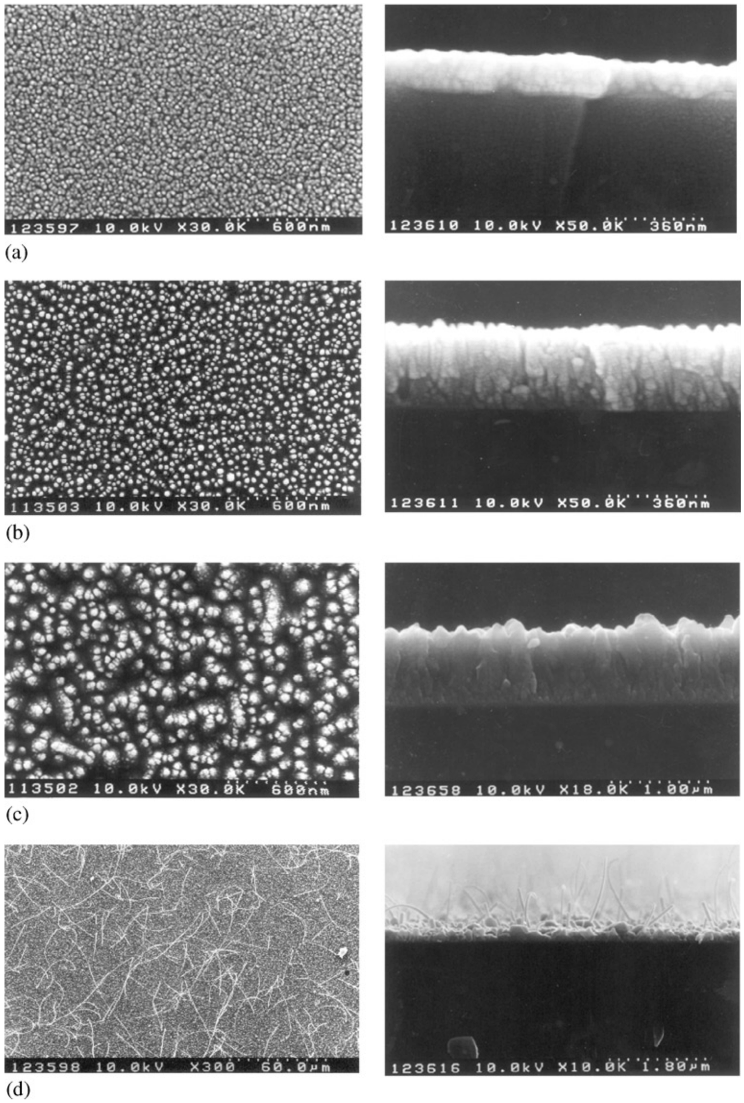

Fig. 2. SEM images of top view (left) and cross-sectional view (right) of ZnO films deposited at (a) 250°C, (b) 300°C, (c) 400°C, and (d) 500°C.

films. Fig. 3a reveals that ZnO nanorods are directly grown on Si substrate. The sample of Fig. 3a is processed by a different process condition from that of Fig. 2d. The formation mechanism of ZnO thin films or ZnO rods is currently unknown. Further systematic study is necessary to reveal the detailed mechanism of ZnO nanorod formation. The SEM images reveal that the diameter of ZnO nanorod ranges from 40 to 120 nm. Fig. 4 shows the SEM image of a ZnO nanorod, the diameter of which is measured to be about 110 nm.

In summary, we have successfully synthesized uniform ZnO nanorods in bulk quantities directly on the Si substrate using the MOCVD technique. We reveal that the growth temperature plays a key role in growing the ZnO nanorods. The crystallinity of ZnO thin films improved and the

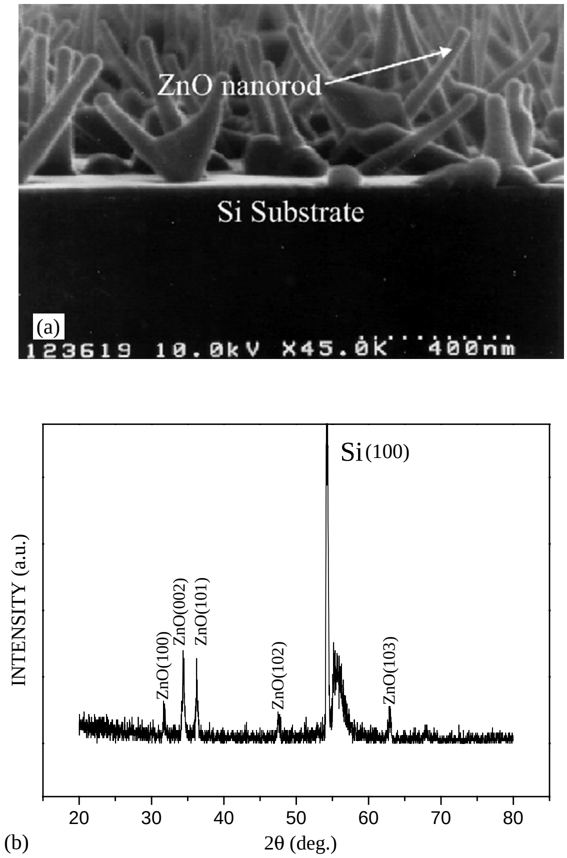

Fig. 3. (a) SEM images and (b) X-ray rocking curves of ZnO nanorods grown directly on silicon substrate at 500°C.

surface smoothness decreased by increasing the growth temperature. ZnO rods are found to be grown at a temperature of 500°C.

Fig. 4. SEM image of a ZnO nanorod, indicating a diameter of 110 nm.

Acknowledgements

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