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Low-temperature growth of ZnO nanorods in anodic aluminum oxide on Si substrate by atomic layer deposition

Ching-Jung Yang, Shun-Min Wang, Shih-Wei Liang, Yung-Huang Chang, and Chih Chen[a)]
Department of Material Science and Engineering, National Chiao Tung University, Hsinchu 30050, Taiwan, Republic of China

Jia-Min Shieh
National Nano Device Laboratories, Hsinchu 30078, Taiwan, Republic of China

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Low-temperature growth of self-organized ZnO nanorods on Si substrate is achieved using anodic aluminum oxide and atomic layer deposition at 250 °C without catalyst or seed layer. Photoluminescence spectrum indicates that the ZnO nanorod arrays exhibit a blue/green luminescence at 480 nm. In addition, the nanorod arrays demonstrate excellent field-emission properties with a turn-on electric field of 6.5 V μm^{-1} and a threshold electric field of 9.8 V μm^{-1}, which are attributed to the perfectly perpendicular alignment of ZnO nanorods to the Si substrate. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2431786]

In recent years, one-dimensional (1D) semiconductor nanostructures have attracted considerable interest due to their unique physical and chemical properties.[1–10] Because ZnO has a high melting point of 1975 °C and is thermally and chemically stable at high temperature, 1D ZnO nanostructure is a potential candidate for field emitters with possible long lifetime. In addition, ZnO is a wide and direct band-gap semiconductor possessing high excited binding energy of 60 meV, and it is therefore quite suitable as photodetectors,[11] field-effect transistors,[7] and other optoelectronic devices.[12–15]

Various techniques for fabricating ordered ZnO nanorod or nanotube arrays have been reported. Generally speaking, they can be categorized as follows: metal-organic chemical-vapor deposition,[11,12] infrared irradiation,[10] thermal evaporation through vapor-liquid-solid,[4,9,15] vapor-solid (VS) mechanisms,[6] electrochemical deposition,[15] and template technology.[3,16] Previously, atomic layer deposition (ALD) has been employed to deposit a seed layer in the VS method to prepare ZnO nanorod or nanotube arrays.[2,6] Moreover, anodic aluminum oxide (AAO) has been widely used as a template to prepare 1D self-aligned nanostructure because the AAO pores have high aspect ratio. ALD is known to have superb capability in filling pores with high aspect ratios. However, the fabrication of ALD ZnO nanorods using AAO templates on Si substrate has not been reported.

In this letter, ALD is employed to fabricate ZnO nanorods at 250 °C using an AAO template on a Si substrate. Highly ordered arrays of ZnO nanorods can be obtained with an average diameter of 70 nm and a periodicity of 90 nm. Their photoluminance and field-emission properties were measured. This approach provides low-temperature growth of ZnO nanorods with excellent photoluminance and field-emission properties.

To prepare AAO on a Si substrate, 20 nm Ti films were sputtered on *p*-type (100) silicon substrates to serve as an adhesion layer. Subsequently, a 1.5 μm Al film was deposited by a thermal evaporation coater. The Al film was treated with a two-step anodization process using 0.3*M* oxalic acid ($H_2C_2O_4$) electrolyte to form a highly ordered nanoporous AAO structure.[17] As shown in Fig. 1(a), the newly prepared AAO possessed an average diameter of 70 nm and a periodicity of 90 nm, and its nanopores have an aspect ratio of around 9. Then ALD technique was employed to deposit ZnO in the AAO nanostructure. $Zn(C_2H_5)_2$ (DEZ) and H_2O were used as the precursors. ZnO deposition was achieved at 250 °C for 550 cycles with DEZ pulse time of 1 s, purge time of 1.5 s, H_2O pulse time of 1 s, and H_2O purge time of 1.5 s. Since surface reaction control occurs in the ALD process, ZnO can be deposited layer by layer into the AAO nanopores. After deposition, the ZnO film filled the AAO nanopores and covered its surface, as shown schematically in Fig. 1(b). With slight polishing, the ZnO film on the AAO surface can be removed, as shown schematically in Fig. 1(c). The final step was to remove the AAO selectively by a solution of 0.4 wt % $NaOH_{(aq)}$, leaving the ZnO nanorod arrays standing perpendicular to the Si substrate, as shown schematically in Fig. 1(d).

The nanostructure and morphology of the ZnO nanorods were examined by field-emission scanning electron microscope (JSM-6500F). Photoluminescence (PL) spectroscopy was performed at room temperature, using a continuous wave He–Cd laser of 325 nm wavelength as the excitation source. The measurements were conducted by simple diode configuration and carried out in a high vacuum chamber at 10^{-6} torr. The distance between the specimen and the anode

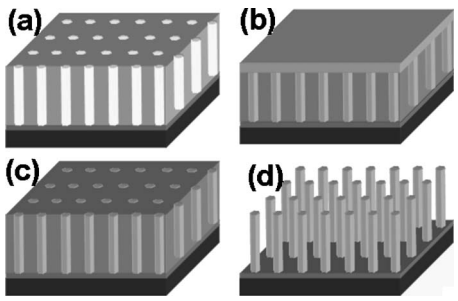

FIG. 1. Schematic diagram of fabricating ZnO nanorod arrays: (a) AAO on a Si substrate, (b) after the deposition of ZnO by ALD, (c) after the polishing step, and (d) after the selective etching of the AAO template.

[a)]Electronic mail: chih@faculty.nctu.edu.tw

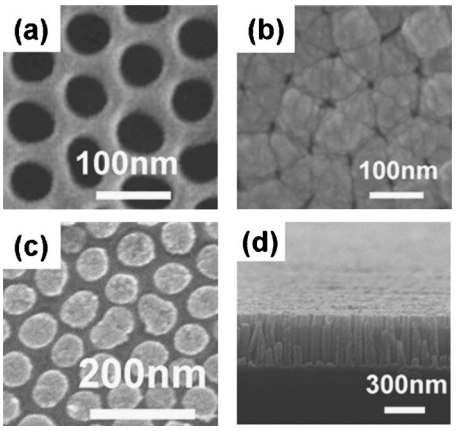

FIG. 2. SEM images showing (a) AAO template before the deposition of ZnO, (b) after the deposition of ZnO at 250 °C by ALD, (c) plan view of ZnO nanorods after removal of the AAO template, and (d) cross-sectional view of ZnO nanorods in (c). Every ZnO nanorod stands perpendicular to the Si substrate.

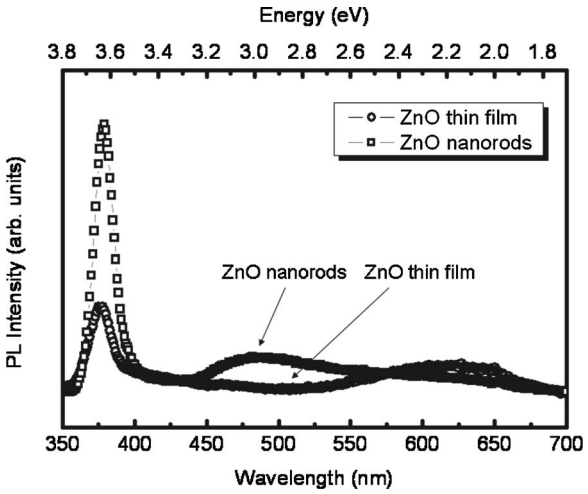

FIG. 3. Room-temperature PL spectra for ZnO nanorod arrays and ZnO film on Si substrates.

was about 100 μm, and it was controlled by a precise screw meter. The specimen was biased with a positive voltage sweeping from 0 to 1000 V at room temperature to extract electrons from the ZnO emitters. A voltage source, Keithley 237, was used for providing the sweeping electric field (E) and monitoring the emission current density (J).

With the aid of AAO and ALD, highly ordered and vertical arrays of ZnO nanorods can be prepared. Figure 2(a) shows the plan-view scanning electron microscopy (SEM) image for the AAO nanopores on a Si substrate before the deposition of ZnO. The AAO nanopores were 70 nm in diameter and their periodicity was 90 nm. After the deposition of ZnO by ALD at 250 °C, all the nanopores were filled by the ZnO film and the film became continuous, as shown in the plan-view SEM image in Fig. 2(b). After polishing and selective etching, the ZnO nanorods remained perpendicular to the Si substrate and could be observed clearly, as illustrated in the plan-view SEM image in Fig. 2(c). We observe that the AAO nanopores can be filled completely by ZnO. It is worth noting that the nanorods remained separate and did not touch each other after the removal of the AAO template. Figure 2(d) shows the cross-sectional view of the ZnO arrays. The height of the nanorods was 470 nm. Some of the ZnO nanorods near the front edge were broken during the cleavage process for the preparation of cross-sectional SEM samples. ZnO nanorods with uniform height can be fabricated by this approach. Further, they were vertically aligned to each other. Therefore, this approach demonstrates an excellent way for fabricating self-organized, uniform height, and straight ZnO nanorod arrays on Si substrates.

Compared with the ZnO film prepared by ALD without template, the PL of ZnO nanorods was significantly enhanced. Figure 3 shows the PL spectra for a 180-nm-thick ZnO film and the ZnO nanorod arrays. The film was prepared at the same conditions of 550 cycles and 250 °C. For both the ZnO film and nanorods, strong excitation emission was observed in the ultraviolet region with a peak at 379 nm. However, the PL intensity for the nanorods was much higher. Shen *et al.*[18] studied the PL spectrum of ZnO nanorod arrays and suggested that both photon-to-electron conversion efficiency and photonic performance were enhanced because of decreasing diameters and increasing surface areas for nanorod configuration. As a result, ZnO nanorods exhibited higher PL intensity than that of the ZnO film. From the PL spectrum, it is found that ZnO films had red visible emission located around 625 nm. In contrast, the nanorod arrays possessed a blue/green luminescence centered around 480 nm. From the literature,[19–21] the peak at 480 nm is indicative of transitions between oxygen vacancy and interstitial oxygen, common lattice defects related to oxygen and zinc vacancies. With the Ti film serving as the adhesion layer, better quality of ZnO nanorods can be fabricated. As reported by Kim *et al.*,[22] the Ti layer may react with the deposited ZnO to form Zn_2TiO_4, which has the same crystal structure of wurtzite and has small lattice mismatch with ZnO. The mismatch may be as small as 0.722% for ZnO (110) on Zn_2TiO_4 (202). Nevertheless, the orientations of the nanorods in this study are not clear at this moment, and further study is required to clarify this issue.

Furthermore, these ZnO nanorods possess excellent field-emission properties. Figure 4 shows the emission current density against the applied field for these ZnO nanorod arrays. The turn-on field and the threshold field in this letter were defined as the electric field required to produce current densities of 10 μA cm^{-2} and 10 mA cm^{-2}, respectively. A turn-on field of 6.5 V μm^{-1} was obtained for these ZnO nanorods. The field-emission data were analyzed using the

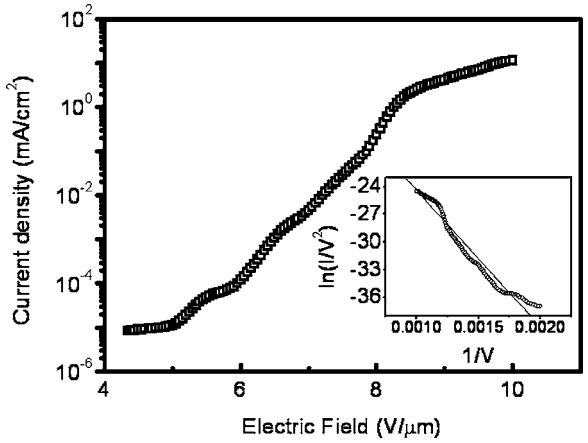

FIG. 4. Measured field-emission current density as a function of the electric field applied to ZnO nanorod arrays. The inset shows the corresponding Fowler-Nordheim plots.

Fowler-Nordheim model.[23] The total current I as a function of the local field at the emitter surface F is approximated by $I \propto (F^2/\Phi)\exp(-B\Phi^{3/2}/F)$, with $B=6.83\times10^9$ V m^{-1} eV$^{-3/2}$, and Φ is the work function of ZnO, which is 5.3 eV. F is usually taken as $F=\beta E=\beta V/d$, where V is the applied potential, d is the distance between anode and sample, β is the field enhancement factor, and $E=V/d$ is the macroscopic field. The inset of Fig. 4 shows the Fowler-Nordheim plot for the fabricated ZnO nanorods. By plotting $\ln(1/V^2)$ against $1/V$, a straight line was obtained for the nanorods. The linear behavior of this plot indicates that these nanorods possess field-emission behavior that follows the Fowler-Nordheim description quite well. According to previous studies,[15,24] field-emission properties including low emission threshold and high current density will be greatly improved if the 1D nanostructures are perfectly aligned and stay perpendicular to their substrate. For the nanorods fabricated by this approach, almost every single nanorod grew perpendicularly to the Si substrate. In addition, owing to the AAO template, the nanorods did not touch each other, resulting in extremely low screen effect. As a result, these ZnO nanorods demonstrate excellent field-emission properties that pose substantial potential for possible application in photoelectronic devices.

In summary, high-quality self-aligned ZnO nanorods have been prepared on Si substrate using the AAO template and ALD process on Si substrates without any catalyst or seed layer at temperature as low as 250 °C. Results from PL spectrum indicated that a strong excitation emission was observed at 379 nm and a blue/green luminescence was located around 480 nm. Field-emission measurements on the ZnO nanorods showed a low turn-on field emission of 6.5 V μm^{-1} at a current density of 10 μA cm^{-2}. The observed excellent field-emission quality may be attributed to the fact that every nanorod was perpendicular to the Si substrate. This approach provides a well-controlled method for fabricating large-scale self-aligned ZnO nanorods for many important applications in the field of nanotechnology.

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