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Catalyst-free MOCVD growth of aligned ZnO nanotip arrays on silicon substrate with controlled tip shape

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Abstract

Quasi-aligned zinc oxide nanotip arrays have been grown by MOCVD without using catalyst. The tip shape was controlled systematically by varying the gas flow rate, demonstrating a technique for growing tip arrays of ZnO on silicon. This technology can be large-scale on the wafer level and it has the potential to be directly integrated with clean room silicon technology. The diameter of these ZnO nanowires or nanotips could be controlled by the varying of source flow rate, providing a simple but unique way of fabricating ZnO nanotip arrays for application in field emission and nanogenerators.

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Keywords: A. ZnO nanotip; B. MOCVD; C. Scanning and transmission electron microscopy

1. Introduction

One-dimensional (1D) ZnO nanostructures are one of the most important semiconducting nanomaterials for applications in optics [1], electronics [2], mechanics [3], and biomedical-sensing nanodevices [4]. Among the known 1D nanomaterials, ZnO has several key advantages. Firstly, ZnO exhibits both semiconducting and piezoelectric properties that can form the basis for electromechanically coupled sensors and transducers. Relying on the coupling of piezoelectric and semiconducting properties of ZnO as well as the formation of a Schottky barrier between the metal tip and ZnO, a power nanogenerator has been demonstrated [3]. Secondly, ZnO is a wide band gap (3.37 eV) semiconductor material with a large excitation binding energy (60 meV) [5], which has attracted intensive attention for applications as ultraviolet (UV) and blue light-emitting diodes and laser diodes [1]. Thirdly, ZnO is a biocompatible material, and it is possible to be used for biochemical and biomedical applications [6]. Finally, ZnO exhibits the most diverse and abundant configurations of nanostructures know so far [7–14].

Recently, the study of field emission from ZnO 1D nanostructures has attracted much attention [15–18]. As we know, the main requirements for field emitters are low threshold field, high current density, and good stability. To get a lower threshold field, the emitters should possess a low work function or surface electron affinity or high-field enhancement factor, or both. So the needle or tip shape of the nanowire can drastically increase the aspect ratio and the field enhancement factor, leading to a dramatic reduction in the threshold field [19]. To achieve this goal, controlled growth of aligned ZnO nanowires with needle-like shape is needed. The vapor–liquid–solid (VLS) process is the most widely used technique for growing aligned ZnO, in which gold is the most frequently chosen metal catalyst [20–23]. However, as limited by the clean room requirements for silicon technology, gold is not the choice of metal for integrating with silicon. Therefore, seeking a catalyst-free growth techniques of ZnO nanowires is important. In this paper, we report the synthesis of aligned zinc oxide nanotip arrays on silicon (111) substrates by a catalyst free, metal–organic chemical vapor deposition (MOCVD) process. The ZnO nanotips have a needle shape at the nanowire tips and

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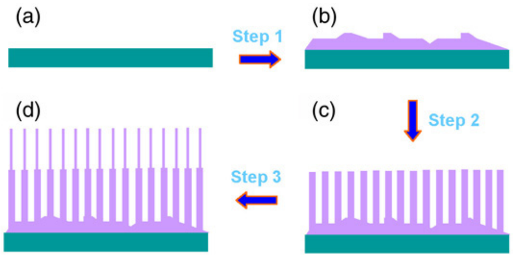

Fig. 1. Schematic diagram of the growth process for the aligned ZnO nanotip arrays.

the nanotips are well separated from each other, which are a potential candidate for field emission and other applications.

2. Experimental

A vertical chamber low-pressure MOCVD system was used for the synthesis of the ZnO nanostructure materials. The Si (111) wafer was used as the substrate and no metal catalyst was introduced. The Si wafers were cleaned with acetone in an ultrasonic bath and etched by piranha solution (2:1 mixture of concentrated H_2SO_4 30% H_2O_2) at room temperature for 20 min. High-purity diethyl zinc (DEZn) (99.999%) and N_2O (99.999%) were used as the zinc and oxygen sources, respectively, and nitrogen as the carrier gas. The precursor temperature of DEZn was set at 0 or 10 °C. The base pressure of the reactor chamber was 10^{-5} Torr and the working pressure was set to 60 or 80 Torr. The ZnO nanowires were grown by the following procedure. Three growth steps were used to grow aligned ZnO nanotips, as shown in Fig. 1. In the first step (Fig. 1(a)), a thin ZnO film layer with thickness of ∼100 nm was firstly grown on the Si substrate with substrate temperature of ∼400 °C. Then the gases were cut off and the substrate temperature was increased to 650 °C, and the ZnO layer was annealed for 10 min. In the secondly step, all of the gases were turned on again, and 20 min later, ZnO nanowires had grown at the substrate temperature of 650 °C (Fig. 1(c)). In the third step, we decreased the flow rate of Zn source gas (diethyl zinc), to finally get ZnO nanowires with needle shape (Fig. 1(d)).

The growth products were characterized with high-resolution field emission scanning electron microscopy (SEM) Leo 1530 FEG at 3 kV capable of tilt, energy dispersive x-ray spectroscopy (EDS) attached to the SEM. The samples were transferred to a carbon coated copper grid and characterized using field-emission transmission electron microscopy (TEM) Hitachi HF-2000 at 200 kV.

3. Results and discussion

The morphology of the as-grown ZnO nanowires and nanotips was characterized by the scanning electron microscopy (SEM). Fig. 2 shows a SEM image of the ZnO nanowires which were grown in the second growth step. The image reveals that aligned ZnO nanowires with average diameters of ∼60 nm were grown on the silicon substrate, and the top surface of the ZnO nanowires is flat. The inset is a top-view SEM image of the ZnO

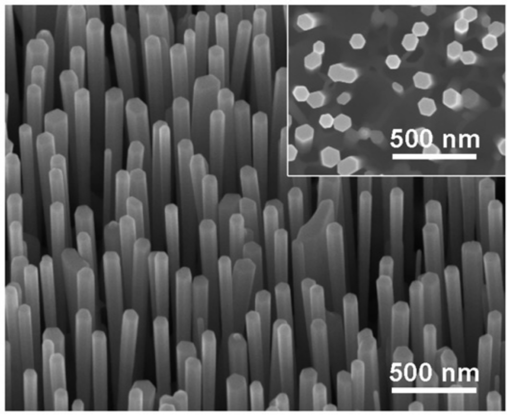

Fig. 2. A 30° tilted view SEM image of the zinc oxide nanowire arrays. Inset: top-view SEM image of the zinc oxide nanowire arrays.

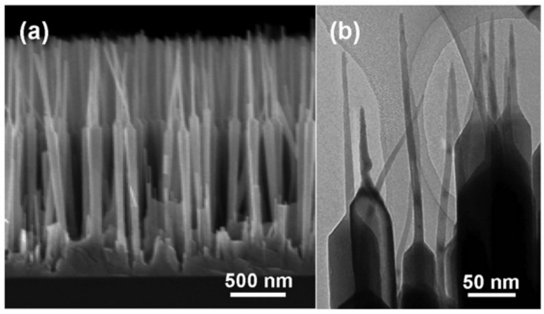

Fig. 3. (a) Cross-section view SEM image of the vertical aligned ZnO nanotip arrays. (b) Low magnification TEM image of the ZnO nanotips.

nanowires, indicating that every ZnO nanowire has a hexagonal morphology. Fig. 3(a) shows a cross section SEM image of the ZnO nanotips which were grown in the third growth step, demonstrating that the nanotips are vertically aligned. The diameter in the top region (tip region) is much smaller than that of the bottom region (wire region), resulting in a much higher aspect ratio. Specially, the ZnO nanotips are very uniform in each segment, the length of the entire wire and the tip region are rather uniform. Importantly, they were well separated from each other. Fig. 3(b) shows a low magnification transmission electron microscopy (TEM) image of the ZnO nanotips, also indicating that every ZnO nanotip has a needle shape. The diameter of the nanotip decreases abruptly from bottom to top with a sharp slope.

The internal structures of the ZnO nanotips were fully studied by high resolution TEM (Fig. 4). Fig. 4(a) is a low magnification TEM image of an individual ZnO nanotip. Fig. 4(b) is the enlarged TEM image from the rectangular-enclosed area of Fig. 4(a). The Fig. 4(c) is the corresponding SAED pattern of the ZnO nanotip, indicating that the ZnO nanotip is single crystalline and the growth direction is [0001]. Fig. 4(d) is the high resolution TEM image of the tip region of the zinc oxide nanotip corresponding to the rectangle region D in Fig. 4(b). Two sets of space fringes of 0.52 nm and 0.28 nm are indexed to (0001) and ($01\bar{1}0$), respectively. Fig. 4(e) is a high-resolution TEM (HRTEM) image of the shoulder region which was taken from the rectangle region *E*

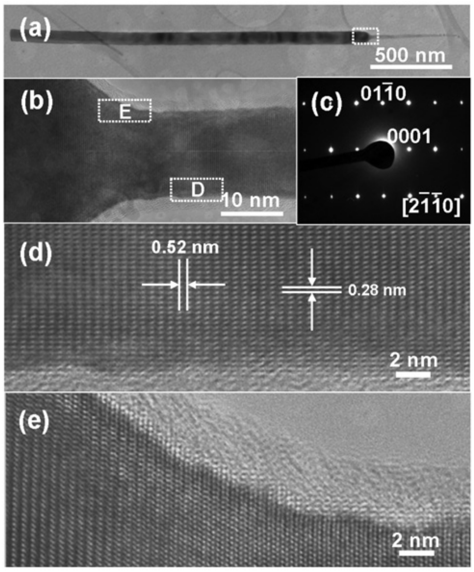

Fig. 4. (a) Low magnification TEM image of an individual ZnO nanotip. (b) Enlarged TEM image from the rectangle-enclosed area of (a). (c) Corresponding SAED pattern of the ZnO nanotip indicates the ZnO nanotip is single crystalline with [0001] growth direction. (d) High resolution TEM image of the tip region of the zinc oxide nanotip corresponding to the rectangle region *D* in (b). (e) High resolution TEM image of the shoulder region that was taken from the rectangle region *E* in (b).

in Fig. 4(b); dislocation and stacking faults were not observed in the shoulder region of the tip, depicting that the ZnO nanotip is single-crystal and free of dislocations.

No catalyst was used in our growth process. In addition, the SEM and TEM study shows no nanoparticles at the ends of the zinc oxide nanotips. The formation of the segmented tip-shape structure may be dominated by the source flow or temperature change in the growth process, which will thus change the supersaturation.

The aligned growth of the ZnO on Si (111) substrates is likely attributed to the hexagonal symmetry and the lattice mismatch between the ZnO (0001) buffer layer and Si substrate. Due to a lattice mismatch between ZnO and Si, the ZnO buffer is grown as uniform island shapes on Si substrates. Subsequently, the ZnO nanowires are grown on these islands.

The growth of the nanowires are driven by a much faster growth along [0001] than that along either the ⟨01-10⟩ or ⟨2-1-10⟩. But the ratio of growth rates along [0001] to that of along ⟨01-10⟩ or ⟨2-1-10⟩ could very much depend on the growth temperature. When the temperature increased from 400 to 650 °C, the relative growth rate along [0001] could be much faster, leading to the formation of the needle shape.

4. Summary

In summary, quasi-aligned zinc oxide nanotip arrays have been grown by MOCVD without using catalyst. The tip shape was controlled systematically by varying the gas flow rate, demonstrating a technique for growing tip arrays of ZnO on silicon. This technology can be large-scale on the wafer level and it has the potential to be directly integrated with clean room silicon technology. The diameter of these ZnO nanowires or nanotips could be controlled by varying of source flow rates, providing a simple but unique way of fabricating ZnO nanotip arrays for application in field emission and nanogenerators.

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