Patterned growth of ZnO nanofibers

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Received September 12, 2008

A simple method is adopted to grow ZnO nanofibers laterally among the patterned seeds designed in advance on silicon substrate. The preparation of seed lattices is carried out by lithographing the metal zinc film evaporated on the substrate. A layer of aluminum is covered on the zinc layer to prevent the ZnO nanorods vertically growing on the top surface. After oxidation, the patterned ZnO/Al_2O_3 spots are formed at the sites for the horizontal growth of ZnO nanofibers by the vapor phase transportation (VPT) method using the zinc powders as source material.

OCIS codes: 160.0160, 220.0220, 250.0250.

doi: 10.3788/COL20090703.0238.

Zinc oxide (ZnO) is a kind of II-VI compound semiconductor with wurtzite structure and has attracted great interest for its direct band gap of 3.4 eV and a large exciton-binding energy of 60 meV which provides opportunities for many applications such as ultraviolet (UV) lasers[1], gas sensors[2], UV detectors[3], transparent electrodes[4], optical fiber sensors[5], and optical nonlinearity research[6]. By controlling the experiment conditions, the vapor phase transportation (VPT) method has been employed to fabricate various ZnO nanostructures[7−10]. It is still in challenge to align one-dimensional (1D) nanostructures horizontally and further to construct the nanodevices. Silicon is one of the ideal substrates for the growth of ZnO, and it also has the potential in the integration of optoelectronic devices. In this letter, we attempt to fabricate ZnO pattern as seeds for laterally growing ZnO nanofibers. It is expected to bring some ideas for nanodevice fabrication.

The schematic process to fabricate the patterned ZnO nanofibers is shown in Fig. 1. The silicon substrate was put into a tube furnace under the temperature of 1000 °C to form a film of SiO_2 on the surface. Then a thick film of zinc and a comparatively thin film of aluminum were evaporated onto the substrate successively. The square seeds for the patterned growth of ZnO nanofibers were preparing by lithography on this Zn/Al film. Then this patterned substrate was placed into the tube furnace under the temperature of 300 °C for 12 h to oxidize the Zn and Al into ZnO and Al_2O_3. The ZnO on the lateral of the squares would play the role of seeds for the growth of ZnO nanofibers, while the top Al_2O_3 and the interval SiO_2 layer were not favorable for the ZnO growth. The ZnO nanofibers were synthesized by the VPT method similar to our precious work[8]. A few zinc powders were put into the bottom of a slender one-end-sealed quartz tube as start materials and the pretreated silicon wafer was placed at the down stream from the source region as a collector. During the reaction, the source temperature was kept at 720 °C and the substrate temperature was kept at 450 °C. A carrier gas consisting of 150-sccm Ar and 10-sccm O_2 was applied to stabilize the circumstance for reaction and a steady pressure in the airtight furnace was maintained at 0.1×10^5 Pa by a vacuum pump. After 30-min sintering, the sample was taken out and rapidly cooled down to room temperature. The reaction can be simply expressed as

$$2Zn + O_2 \rightarrow 2ZnO.$$

The patterned substrate for growing ZnO nanostructures was observed by an optical microscope. The morphology of the as-grown ZnO nanofibers was observed by a scanning electron microscope (SEM) and the crystal structure of the nanofibers was characterized by a transmission electron microscope (TEM). The optical property of ZnO nanofibers was measured by a photoluminescence (PL) spectroscopy.

Figure 2 shows the optical microscope image of the Zn/Al pattern on the silicon substrate. The dimension

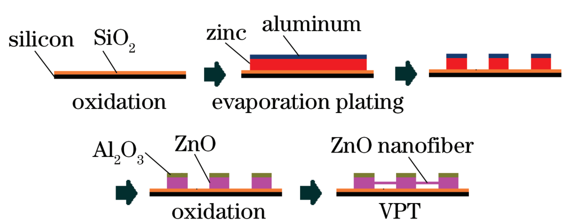

Fig. 1. Outline of the process for fabricating patterned ZnO nanofiber on the substrate.

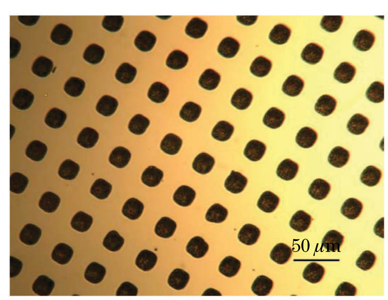

Fig. 2. Microscope image of the Zn/Al pattern on the silicon substrate.

of the spots are uniformly 20 × 20 (μm). In fact the size and shape of pattern can be accurately controlled by mask design according to the concrete need in practice.

The SEM images of the ZnO nanofibers synthesized on the patterned substrate are shown in Fig. 3. In Fig. 3(a), several nanofibers with homogeneous diameter of hundreds of nanometers can be clearly seen connecting the nodes. The small agglomerations of Al_2O_3 could be observed on the node, which actually constrained the perpendicular growth of ZnO from the top of the node to a certain extent. This enables us to further fabricate the electrodes on the nodes by plating other metals. Figures 3(b) and (c) clearly show an individual nanofiber linking two adjacent nodes. In the present case, unfortunately, some unnecessary ZnO nanostructures still appear on the top and the intervals of the nodes. So an improvement is required in the future work, such as introducing other amorphous compounds to prevent the ZnO nanostructure growth on these areas.

Figure 4 illustrates a typical high-resolution TEM image. From the image, we can estimate an inter-spacing of 0.52 nm which is consistent with the lattice constant c of ZnO. This indicates that the legs are of wurtzite structure of ZnO growing along [0001] direction.

As a potential photonic material, it is important to evaluate the optical property of the ZnO nanofiber. As shown in Fig. 5, the PL spectrum illustrates a strong UV emission band peaked at 380 nm which originates from the band edge excitonic recombination[11] and an obvious green emission which is attributed to the electron transfer from the singly ionized oxygen vacancy state to the photo-excited hole in the valence band[12]. The strong UV emission proves that our ZnO nanostructures have a

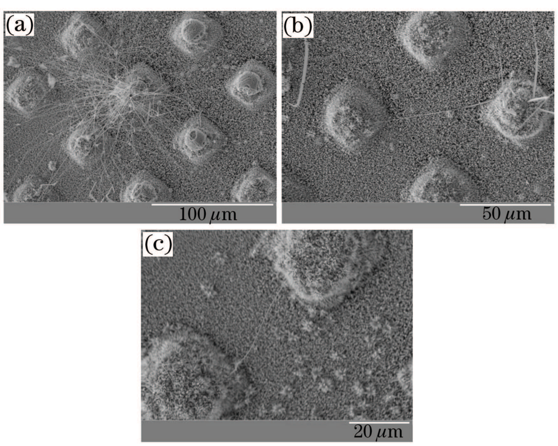

Fig. 3. SEM images of the ZnO nanofibers laterally growing among the nodes.

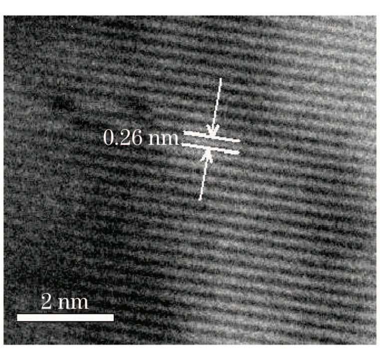

Fig. 4. High-resolution TEM image of the ZnO nanofiber.

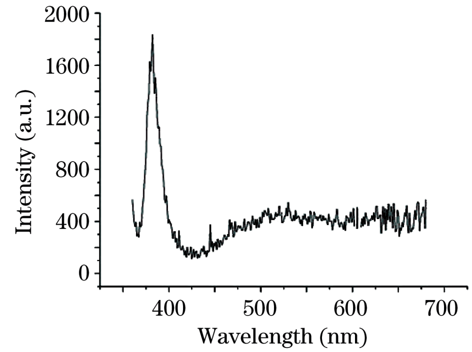

Fig. 5. PL spectrum of the ZnO nanofiber.

good crystal quality with little defects.

In conclusion, the patterned ZnO nanofibers were fabricated by combination of lithography and VPT. The size and shape of pattern could be controlled by mask in lithography. The ZnO nanofibers grew from the lateral of the nodes and connected the adjacent nodes. The nanofibers have uniform size and good crystal quality. The PL spectrum reveals the good optical property of the ZnO nanofibers. This growth process is expected to provide a method to fabricate the precise patterns for nanodevice construction.

This work was supported by the National Natural Science Foundation of China (No. 60725413, 60576008, and 10674023), the National "863" Program of China (No. 2006AA03Z313), and the National "973" Program of China (No. 2007CB936300).

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