Selective growth of vertical ZnO nanowires on ZnO:Ga/Si₃N₄/SiO₂/Si templates

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High density vertical single crystal ZnO nanowires were selectively grown on ZnO:Ga/Si₃N₄/SiO₂/Si templates at various temperatures by a two-step oxygen injection process of self-catalyzed vapor-liquid-solid (VLS) technology. It was found that tips of the ZnO nanowires are hexagonal. It was also found that average length of the ZnO nanowires increased while the average tip diameter of the ZnO nanowires decreased as the growth temperature increased. Furthermore, it was found that the ZnO nanowires grown at 500 °C were “tube-shaped” while the ZnO nanowires grown at 700 °C were “cone-shaped.” Photoluminescence (PL), x-ray diffraction (XRD), and energy dispersive x-ray (EDX) results all indicate that the quality of our ZnO nanowires is good. © 2005 American Vacuum Society. [DOI: 10.1116/1.2101600]

I. INTRODUCTION

In recent years, one-dimensional (1D) nanostructures, such as nanotubes, nanowires, nanobelts, nanorods, nanocables, and nanoribbons have stimulated great interest for scientific research and development due to their importance in fundamental physics. The 1D nanostructures are also potentially useful in both nanoscale electronic and optoelectronic devices. Although many studies have been performed on Si and III-V nanowire systems, only few reports on 1D oxide systems can be found in the literature. These 1D oxide systems include SnO₂, SiO₂, GeO₂, ZnO, indium tin oxide (ITO), and Al₂O₃. Among them, ZnO is an n-type semiconductor with a large exciton binding energy of 60 meV and a wide band gap energy of 3.37 eV. ZnO emits short-wavelength light at room temperature, conducts transparently and is piezoelectric. Previously, Huang et al. reported the successful gas phase synthesis of ZnO nanowires on a patterned Au catalyst by vapor-liquid-solid (VLS) reaction at high temperatures (i.e., 900–925 °C). Geng et al. modified this VLS technology and successfully grew ZnO nanowires on the Si substrate.

Very recently, Tseng et al. developed a low-temperature VLS process and demonstrated the selective area growth of ZnO nanowires at 550 °C. They also reported that crystal quality and diameter of the as-grown ZnO nanowires depend strongly on the amount of Zn powder and the oxygen flow rate. To realize a feasible device such as field emission display, we need to control crystal quality and diameter of the as-grown ZnO nanowires. Tseng et al. found that one can increase the diameter of the ZnO nanowires either by increasing the amount of Zn powder or by increasing the oxygen flow rate. However, it is still difficult to grow well-aligned single crystal ZnO nanowires and even more difficult to control the tip size of the ZnO nanowires. In this study, we report the growth of high density vertical single crystal ZnO nanowires on ZnO:Ga/Si₃N₄/SiO₂/Si templates by two-step oxygen injection method without catalysts. The optical properties and structural characteristics of the ZnO nanowires will be reported. The growth mechanism will also be discussed.

II. EXPERIMENTS

The synthesis technique used in this study is a modified self-catalyzed VLS method based on the evaporation of a Zn

Fig. 1. FE-SEM image shows the ZnO nanowires were selectively grown on ZnO:Ga/Si₃N₄/SiO₂/Si templates.
metallic source with a 2-step gas flow control. The evaporation process was carried out in a quartz tube located in a horizontal tube furnace. The diameter and length of the quartz tube were 5.0 and 70 cm, respectively. Zinc metal powder with a purity of 99.9% purchased from Strem Chemicals was used as the zinc vapor source. Prior to the growth of ZnO nanowires, we first oxidized Si substrates by thermal oxidation to achieve 30-nm-thick SiO₂ films, followed by plasma enhanced chemical vapor deposition (PECVD) of 50-nm-thick Si₃N₄ films on top of the SiO₂ films. We subsequently deposited 50-nm-thick Ga-doped ZnO films on top of the Si₃N₄ films by rf sputtering. From x-ray diffraction (XRD) measurements, it was found that the sputtered ZnO:Ga films were preferred to be oriented in the (002) direction. Standard photolithography and wet etching were then performed to define the stripe patterns with a stripe width of 10 μm on the templates. The spacing between the stripes was also 10 μm. During wet etching, the ZnO:Ga/Si₃N₄/SiO₂/Si templates were dipped in HCl (2%) for 3 min to remove the exposed regions of the ZnO:Ga layers. We then placed the patterned ZnO:Ga/Si₃N₄/SiO₂/Si templates together with zinc vapor source on an alumina boat, and inserted them into the quartz tube of furnace. Streams of argon and oxygen gases were then intro-

Fig. 2. Cross section FE-SEM micrographs of the results from the two-step oxygen injection method for deposition zinc oxide nanowires on the ZnO:Ga/Si₃N₄/SiO₂/Si substrate with various growth temperatures of (a) 500 °C, (b) 550 °C, (c) 600 °C, (d) 650 °C, and (e) 700 °C. The insets at the top left corner shows the same sample top view images.
duced into the furnace. The first step was to lead an argon flow of 54 sccm into the reaction system as the experiment began. When the furnace temperature reached 420 °C, an oxygen flow of 0–3 sccm was added into the argon flow as the second step, until the end of experiment. It should be noted that oxygen was the only oxidizer during the synthesis. Thus, properties of the deposited ZnO nanowires should depend strongly on oxygen flow rate and the reaction time. We have varied the growth conditions and found that the optimal growth condition was to keep oxygen and argon flow rates at 0.8 and 54.5 sccm, respectively. We then grew the ZnO nanowires under such a condition with various growth temperatures.

It should be noted that we carefully controlled the positions of the patterned ZnO:Ga/Si_{3}N_{4}/SiO_{2}/Si template, zinc vapor source, and alumina boat so that they were located at the same horizontal level and were heated at the same temperature. We also kept the distance between zinc vapor source and patterned ZnO:Ga/Si_{3}N_{4}/SiO_{2}/Si template at 20 mm with the zinc vapor source placed at the upstream side. A mechanical pump was then used to evacuate the system and a programmable temperature controller was used to precisely control the furnace temperature with an accuracy of ±1 °C. During the growth of ZnO nanowires, the pressure inside the quartz tube, growth temperature and growth time were kept at 10 Torr and 30 min, respectively. A Philips PW3710 x-ray diffractometer and a JEOL JEM-2100F transmission electron microscopy (TEM), operated at 200 kV, were then used to characterize the crystallographic and structural properties of the as-grown ZnO nanowires. Surface morphologies of the samples and size distribution of the nanowires were characterized by a LEO 1530 field emission scanning electron microscope (FESEM), operated at 5 keV. Photoluminescence (PL) properties of these as-grown ZnO nanowires were also characterized by a Jobin Yvon-Spex fluorolog-3 spectrophotometer. A Xe lamp emitting at 254 nm was used as the excitation source during PL measurements.

### III. RESULTS AND DISCUSSION

Figure 1 shows FESEM image of the ZnO nanowires grown at 550 °C viewed with a 30° title angle. It can be seen clearly that high density vertical ZnO nanowires with uniform diameter and uniform length were selectively grown on the sputtered ZnO:Ga layer. In other words, no nanowires could be grown directly on the Si_{3}N_{4} layer where the sputtered ZnO:Ga layer was etched. The inset of Fig. 1 shows an enlarged image of this sample. It should be noted that we clearly observed the boundary of these ZnO nanowires while no disordered ZnO nanowires were found. Figures 2(a)–2(e) show FESEM images of the ZnO nanowires grown at 500 °C, 550 °C, 600 °C, 650 °C, and 700 °C, respectively. The insets of Figs. 2(a)–2(c) show top view FESEM images of the ZnO nanowires grown at 500 °C, 550 °C, and 600 °C, respectively. It can be seen that tips of the ZnO nanowires are hexagon, which is probably due to the wurtzite structure of ZnO single crystal. For the ZnO nanowires grown at 650 °C and 700 °C, it was found that tips of the nanowires all topple down. Thus, top view FESEM images of these two samples are not available. Although high density vertical ZnO nanowires were observed in all these five samples, it was found that diameter and length of these nanowires were different.
Figures 3(a) and 3(b) show average length and average tip diameter, respectively, of the ZnO nanowires grown at different temperatures. It can be seen clearly from Fig. 3(a) that the average length of the ZnO nanowires increased as the growth temperature increased. On the other hand, average tip diameter of the ZnO nanowires decreased as the growth temperature increased, as shown in Fig. 3(b). The root diameter of the ZnO nanowires grown at different temperatures is also shown in Fig. 3(a). Compare these root diameter values with the tip diameter values shown in Fig. 3(b). It was found that the root diameter (i.e., 300–400 nm) and tip diameter (i.e., around 400 nm) were about the same for the ZnO nanowires grown at 500 °C. However, the ratio between root diameter and tip diameter increased as the growth temperature was increased. For the ZnO nanowires grown at 750 °C, it was found that the root diameter (i.e., 80–120 nm) was about five times larger than the tip diameter (i.e., around 20 nm). In other words, the ZnO nanowires grown at 700 °C were “tube-shaped.” In contrast, the ZnO nanowires grown at 500 °C were “cone-shaped.”

Figure 4 shows XRD spectra of these samples. It was found that only one strong ZnO (002) XRD peak with small linewidth could be observed in these spectra. Such a result indicates that these ZnO nanowires were all well oriented with pure wurtzite structure. Figure 5 shows room temperature PL spectra measured from the ZnO nanowires grown on ZnO:Ga/Si$_3$N$_4$/SiO$_2$/Si with various growth temperatures. It can be seen clearly that the all PL spectra exhibit a strong peak located at approximately 376 nm with long tails in the long wavelength region. The strong PL peak can be attributed to the recombination of free excitons through the exciton-exciton collision process. Deep level emissions (i.e., green-yellow bands) are also observed as the long tails shown in Fig. 5. It has been suggested that deep level emissions are related to the singly ionized oxygen vacancy in ZnO. Previously, it has been shown that defect related emissions are originated from radiative transitions between oxygen vacancy related shallow donors. Since the acceptor level (i.e., Zn vacancy) and the donor level are located at 2.5 and 0.05–0.19 eV below the conduction band edge, respectively, the strong excitonic emission and the very weak deep level emission again indicate that quality of our ZnO nanowires is good. Hu et al. proposed a model called self-catalyzed VLS growth. They suggested that Zn deposits vaporize in the form of liquid droplet. Liquidized zinc is involved in ZnO whisker growth. The Zn droplets then react with O$_2$ to form ZnO. The melting temperature of ZnO is 1975 °C, so the formation of ZnO on the Zn liquidized droplets proceeds by the VLS mechanism. Zn not only acts as a reactant but also provides an energetically favorable site for the absorption of O$_2$. Therefore, no transition metal need be added as a catalysts. Yao et al. reached a similar conclusion. However, they believed that Zn suboxides played the same role in the nucleation of ZnO nanowires as Zn, because both Zn and Zn suboxides have low melting temperatures (approximately 419 °C for both Zn and ZnO$_x$, where $x < 1$).
High density vertical single crystal ZnO nanowires were selectively grown on ZnO:Ga/Si3N4/SiO2/Si templates at various temperatures by a two-step oxygen injection process of self-catalyzed VLS technology. It was found that the length, top diameter, and root diameter of these ZnO nanowires all depend strongly on the growth temperature. PL, XRD, and EDX results all indicate the quality of our ZnO nanowires is good.

**IV. SUMMARY**

The diameter of the ZnO nanowire was related to the Zn vapor pressure. The Zn vapor pressure was determined by the growth temperature. In the high temperature regime, ZnO nanowires show higher growth rate, meanwhile their length are longer and diameter are decreased.

Figure 6 shows energy dispersive x-ray (EDX) spectrum of the ZnO nanowires grown at 550 °C. It was found that the nanowires contain 58% zinc and 42% oxygen. The small amount of copper and carbon signals should originate from TEM copper grids and the carbon adhesion film. Figure 7 shows the cross-sectional HRTEM image of the ZnO nanowires grown at 550 °C. The brightness contrast observed in this image could be attributed to the diffraction patterns originated from various crystallographic planes. We thus believe that the sputtered ZnO layer should have a grainy and columnar structure while the ZnO nanowires were grown along the columnar grains of the sputtered ZnO layer. Selected area electron diffraction (SAED) image of the ZnO nanowires grown at 550 °C is shown in the lower right portion of Fig. 8. Such a diffraction pattern also indicates that our ZnO nanowires are single crystal with wurtzite structure. HRTEM image taken from the tip portion of the ZnO nanowires grown at 550 °C is shown in the upper left portion of Fig. 8. It can be seen clearly that the ZnO crystal lattices are well oriented with no observable defects in this region. The 0.52 nm lattice spacing observed from this figure is equivalent to two ZnO (002) crystal planes. Such a result indicates our ZnO nanowires are structurally uniform and defect free. It also suggests that the ZnO nanowires grown on ZnO:Ga/Si3N4/SiO2/Si templates are potentially useful in various optical and electrical applications.