Structural Properties of ZnO Nanowires Grown by Chemical Vapor Deposition on GaN/sapphire (0001)

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ABSTRACT

ZnO nanowires were grown on 2-µm-thick GaN templates by thermal chemical vapor deposition without employing any metal catalysts. The GaN template was predeposited by metalorganic chemical vapor deposition on a c-plane sapphire substrate. The diameters of the resulting nanowires are in the range 40-250 nm depending on growth time. The ZnO nanowires were vertically well-aligned with uniform length, diameter, and distribution density as revealed from electron microscopy. X-ray diffraction spectra show that ZnO grows in single c-axis orientation with the c-axis normal to the GaN basal plane, indicating a heteroepitaxial relationship of (0002)ZnO||(0002)GaN. The lattice constant of the c-axis of the ZnO nanowires with the diameter of 40 nm is 5.211 Å, which is larger than that of bulk ZnO, 5.207 Å. In the ZnO nanowires there exists a residual tensile strain, which decreases with increasing the diameter of nanowires, along the c-axis. The tensile strain might be from the surface stress of nanowires.

INTRODUCTION

Zinc oxide (ZnO), which exhibits a direction bandgap of 3.37 eV and a large exciton binding energy of 60 meV [1], is of considerable technological importance because of its potential use in short-wavelength devices, such as ultraviolet light-emitting diodes and laser diodes. It has the same crystal structure type as GaN, and the lattice mismatch is 1.8% on the c-plane. The thermal expansion coefficients of ZnO are $\alpha_a = 6.5 \times 10^{-6}$ K$^{-1}$ and $\alpha_c = 3.0 \times 10^{-6}$ K$^{-1}$, along the a- and c-axis, respectively [2], close to those of GaN, which are $\alpha_a = 5.59 \times 10^{-6}$ K$^{-1}$ and $\alpha_c = 3.17 \times 10^{-6}$ K$^{-1}$ [3]. This opens up the applications of ZnO/GaN heterostructures. Growth of high-quality ZnO crystals is important not only for basic studies but also for application. Fabrication of low-dimensional semiconductor structures such as nanowires [4-6], nanotubes [7-9] and nanorods [10-12] is an interesting subject due to their optoelectronics, bio-sensor device and other technological applications [13-14]. In this paper, we report on the structural properties of ZnO nanowires grown on GaN templates by chemical vapor deposition (CVD).
EXPERIMENT

The ZnO nanowires used in this study were grown on GaN templates by CVD without employing any metal catalysts. The GaN template was predeposited by metalorganic chemical vapor deposition on a c-plane sapphire substrate. Zinc shots (99.9999%) were placed in a quartz boat as the Zn source in the center of a quartz tube in a furnace. The quartz tube was kept at 1 atmosphere pressure by flowing high purity Ar (99.99%) with a flow rate of 100 sccm and heated up to 850°C. When the temperature reached this synthesis temperature, high purity oxygen (99.9999%) was introduced with a flow rate of 5 sccm for the growth of the ZnO nanowires. In this series of samples, the growth times of the process were 10, 30, 60, and 120 min. before terminating oxygen flow and cooling down to room temperature. The morphology of the ZnO nanowires was examined by a JEOL JSM-7000F field emission scanning electron microscopy (SEM). The microstructural observations were carried out by a JEOL JEM-2010 high-resolution transmission electron microscopy (TEM). X-ray diffraction (XRD) experiments were carried out on a Bede triple-axis diffractometer system, using Cu $K\alpha_1$ ($\lambda = 1.5406 \text{ Å}$) radiation.

RESULTS AND DISCUSSION

The diameters of the resulting ZnO nanowires grown on 10, 30, 60, and 120 min. are 40±5, 80±5, 150±20, and 250±50 nm, respectively. Figure 1 shows the SEM image of ZnO nanowires grown by CVD on the GaN template under the growth time of 10 min. The ZnO nanowires were vertically well-aligned with uniform length, diameter, and distribution density. Figure 2 shows a high resolution TEM image of a single nanowire grown under the growth time of 10 min. along with the associated selected area diffraction pattern (SADP). These data confirm the single-crystal nature of the wires. From this image, the lattice constants of $a$- and $c$-axis are 0.325 and 0.521 nm, respectively.

Figure 1. SEM image of ZnO nanowires grown on GaN template under the growth time of 10 min.
Figure 2. High resolution TEM image and SADP (inset) of ZnO nanowires grown on GaN template under the growth time of 10 min.

Figure 3 shows XRD θ−2θ scan results of ZnO nanowires grown on GaN template under different growth time. There are only two distinct diffraction peaks for each sample. One diffraction peak corresponds to GaN (0002) and the other corresponds to ZnO (0002). Thus, the ZnO nanowires grow in single c-axis orientation with the relationship of (0002)_{ZnO}\|\langle0002\rangle_{GaN}. However, the peak position of ZnO nanowires shifts to higher diffraction angle with increasing growth time. From the XRD results, the lattice constants of the c-axis of the ZnO nanowires grown under 10, 30, 60, and 120 min. are c = 5.211, 5.210, 5.209 and 5.208 Å, respectively. However, the lattice constant of the c-axis of bulk ZnO is 5.207 Å [15], which is smaller than that of the ZnO nanowires used in this study. Thus, in these ZnO nanowires there exists residual tensile strain along the c-axis. Table I lists the diameter of the resulting ZnO nanowires and residual strain, estimated from ε = (c-c_0)/c_0. Here, c_0 and c indicate the lattice constants of unstrained and strained crystal, respectively. The residual tensile strain decreases with increasing the diameter. Nanometer-sized materials have a high surface-to-volume ratio. Chen et al. reported that the critical diameter of ZnO nanorod exhibiting the bulk properties is about 620 nm [16], which is larger than that of the ZnO nanowires used in this study. Thus, the residual tensile strain might be from the surface stress.

![Figure 3](image-url)
Table I. The diameters and residual strain of the resulting ZnO nanowires grown on GaN template under different growth time.

<table>
<thead>
<tr>
<th>Growth time (min.)</th>
<th>Diameter (nm)</th>
<th>Strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>40±5</td>
<td>0.08%</td>
</tr>
<tr>
<td>30</td>
<td>80±5</td>
<td>0.06%</td>
</tr>
<tr>
<td>60</td>
<td>150±20</td>
<td>0.04%</td>
</tr>
<tr>
<td>120</td>
<td>200±50</td>
<td>0.02%</td>
</tr>
</tbody>
</table>

CONCLUSIONS

The ZnO nanowires grown by catalyst-free CVD on GaN template are vertically well-aligned with the relationship of (0002)\text{ZnO}||(0002)\text{GaN}. In the ZnO nanowires there exists a residual tensile strain, which might be from the surface stress of nanowires.

ACKNOWLEDGMENTS

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REFERENCES