Surface roughness and strain effects on ZnO nanorod growth

Department of Materials Science and Engineering, Pohang University of Science and Technology (POSTECH), Pohang 790-784, Korea
S.-W. Han
Institute of Proton Accelerator, Institute of Science Education and the Division of Science Education, Chonbuk National University, Jeonju 561-756, Korea

(Received 14 January 2006; accepted 22 May 2006; published online 19 June 2006)

Vertically aligned ZnO nanorods were fabricated on Al$_2$O$_3$(001) substrates with various GaN interlayers by a catalyst-free metal-organic chemical vapor deposition. We observed that the shape and quality of ZnO nanorods grown on the GaN interlayers were considerably sensitive to the surface roughness of the interlayers. We also investigated orientation-dependent residual strain in the ZnO nanorods grown on Al$_2$O$_3$ substrates using polarized x-ray absorption fine structure (XAFS) measurements at Zn K edge. The XAFS revealed that the residual strain relaxation of Zn–O pairs in $ab$ plane played a key role in the ZnO nanorod growth. © 2006 American Institute of Physics. [DOI: 10.1063/1.2215631]

ZnO nanorod arrays have attracted considerable attention for their practical applications to nanometer-scale electronics and photonics as well as fundamental academic research. Since Park and Yi demonstrated potential applications of the ZnO nanorods for ultraviolet light emitting diodes, the heterostructures of ZnO nanorods/GaN were intensively studied. Previous studies have reported that the crystallinity and alignment of the ZnO nanorods grown on Al$_2$O$_3$ substrates were enhanced by using GaN interlayers. This can be understood in terms of strain relaxation by the GaN interlayers. It is well known that the growth and crystal quality of a film are affected by the lattice constants, surface roughness, and crystal quality of substrates. However, there was no report of the surface roughness contribution of substrates to the ZnO nanorod growth. In this letter, we demonstrate the influence of the surface roughness on the ZnO nanorod growth.

There were many attempts to understand the growth mechanism of ZnO nanorods. However, the growth mechanism is still an ongoing argument. The Stranski-Krastanov island growth mode can be a realistic idea for the ZnO nanorod growth. In the island growth mode, there should be seeds on the ZnO growing surface. The surface roughness, lattice mismatch, and surface energy difference of crystals may have an effect on the nanorod growth. We investigated whether or not structural stress due to lattice mismatch at the interface of the ZnO nanorods and substrates play a role in the ZnO nanorod growth. We employed polarized x-ray absorption fine structure (XAFS) which can describe the angles and distances of neighboring atoms from a probe atom to investigate the orientation-dependent residual strain in ZnO nanorods.

ZnO nanorod arrays were fabricated using metal-organic chemical vapor deposition (MOCVD) on Al$_2$O$_3$(001) substrates with various GaN interlayers. The conditions of the GaN interlayers are summarized in Table I. The substrate temperature was maintained at 350–500 °C and the growth rate was about 10 nm/ min. To investigate the structural residual strain in ZnO nanorods, we synthesized the ZnO nanorods with average length of 0.1, 0.2, and 1.0 μm by MOCVD on the Al$_2$O$_3$ substrates. High-resolution x-ray diffraction (XRD) and high-resolution transmission electron microscopy (TEM) revealed that the ZnO nanorods were well-ordered single crystals. The XRD measurements were made with a conventional x-ray source using Cu Kα$_1$ radiation in air. The XAFS measurements at Zn K edge (9659 eV) were performed at beamline 3C1 of PLS at room temperature with a fluorescence mode. Incident x-ray energy was selected with a three-quarters tuned Si(111) double monochromator.

Figure 1 demonstrates field emission scanning electron microscope (SEM) images of ZnO nanorods grown on various GaN interlayers. In (a) ZnO nanorods directly grown on Al$_2$O$_3$ substrates had a wurtzite (WZ) structures with average diameter of 70 nm. (b)–(f) show the ZnO nanorods synthesized on $n$-GaN interlayers and (f) demonstrates the nano-

---

Author to whom correspondence should be addressed; electronic mail: swhan@chonbuk.ac.kr
rods on p-GaN interlayer. The average diameter and density of the nanorods on the n-GaN interlayer in (b) were about 50 nm and 414/μm². From the ZnO nanorods grown on Al₂O₃ substrates with and without GaN interlayers, we observed a ZnO film underneath of the ZnO nanorods. This growth mechanism suggests that the ZnO nanorod growth can be also influenced by a surface electrical potential. That the ZnO crystals became a film for the GaN surface roughness larger than 0.3 nm was a very surprising result. It should be noted that the growth conditions, such as the flow rates of diethylzinc and oxygen reactants, substrate temperature, chamber pressure, and others, remained the same during the nanorod growth for all specimens of (a)–(f). TEM measurements shown in Fig. 2 revealed that structural distortion and disorders were absent near the interlayer surfaces. Structural details were carefully characterized using XRD, as shown in Fig. 2(c). The results are summarized in Table I. The analysis showed that both the surface roughness and residual strain full widths at half maximum (FWHM–2θ) of the GaN interlayers were dominant over the shape and quality of the ZnO nanorods. With the FWHM–2θ value in the specimen (e), the residual strain of ~0.003 Å in the GaN interlayer was estimated with Δd=nλcosθΔθ/2sin²θ, where Δθ=(FWHM–2θ)/2, based on Bragg’s law, 2d sin θ = nλ. The small amount of the strain corresponds well to the TEM results. The strain was about just 1% of the surface roughness of the GaN interlayer. This implied that the surface roughness plays a more critical role than the strain of the GaN interlayers in the ZnO nanorod growth. The critical roughness of 0.3 nm is about Ga–Ga (N–N) bond length. As the GaN surface roughness is smaller than 0.3 nm, the surface is Ga terminated or N terminated. However, for the roughness of greater than 0.3 nm, the GaN film has a mixed surface with terminating both Ga and N atoms. As Zn and O atoms deposited on the mixed surface, the two atoms can sit on the same ab plane rather than stacking Zn and O layers in turn. The resultant ZnO crystals cannot be high quality nanorods. This growth mechanism suggests that the ZnO nanorod growth can be also influenced by a surface electrical property as well as the surface roughness and structural differences.

![Figure 2](image1.jpg)

**FIG. 2.** (A) and (B) TEM images from the GaN interlayers of (c) and (d) in Fig. 1, respectively. The inset is the expansion of dashed box. (C) X-ray diffraction of ZnO and GaN (002) peaks from ZnO nanorods on Al₂O₃ substrates with and without GaN interlayers. (a)–(e) indicate sample configurations corresponding to the SEM images in Fig. 1. The inset shows the Φ scan on the ZnO (101) diffraction peak from the samples (a) and (b). The data of (a) were intentionally shifted by 10° along the x axis for clarity.

![Figure 3](image2.jpg)

**FIG. 3.** Normalized x-ray absorption coefficient from ZnO nanorods/Al₂O₃ with different lengths as a function of incident x-ray energy at the Zn K edge with the geometry of the c axis aligned, (a) parallel and (b) perpendicular, to the electric field vector (ê) of the incident x rays. (c) XAFS (kF) from ZnO nanorods with lengths of 0.1 μm (first, fourth), 0.2 μm (second, fifth), and 1.0 μm (third, sixth) as a function of the photoelectron wave vector, k = (2m(E–E₀))/h, where m is the electron rest mass, E is the incident photon energy, and E₀ is the edge energy. In (c) the first three are for ê||c and the last three are for ê⊥c. (d)–(g) are amplitude of Fourier transformed XAFS from (c) as a function of the distance from a Zn atom. For the Fourier transformation, a Hanning window with a window sill width of 0.5 Å⁻¹ was used. Data in the range of r=1.2–3.3 Å were fitted.

**TABLE I.** Different conditions of GaN interlayers on the Al₂O₃ substrates. The thickness (t) and rms roughness (r) were determined by SEM and atomic force microscopy, respectively. D is the nanorod density, c is the lattice constant determined by GaN (002) and Al₂O₃ (006) diffraction peaks with the x-ray wavelength of 1.5407 Å. Full widths at half maximum of θ–2θ (FWHM–2θ) scans and FWHM of θ rocking were determined at the GaN and ZnO (002) diffraction peaks. The characteristics of the GaN interlayers were determined before the ZnO nanorods were deposited. The denotations of (a)–(e) indicate the corresponding SEM images in Fig. 1.

<table>
<thead>
<tr>
<th>GaN interlayers</th>
<th>ZnO nanorods</th>
</tr>
</thead>
<tbody>
<tr>
<td>t (nm) r (nm) c (Å) FWHM–2θ (°) FWHM–θ (°)</td>
<td>c (Å) FWHM–2θ (°) FWHM–θ (°) D (μm²)</td>
</tr>
<tr>
<td><strong>(a)</strong> no GaN</td>
<td>0.16 5.1867 0.01 0.08 5.2085 0.10 2.70 115</td>
</tr>
<tr>
<td><strong>(b)</strong> 2555</td>
<td>0.22 5.1887 0.01 0.09 5.2060 0.02 0.97 348</td>
</tr>
<tr>
<td><strong>(c)</strong> 3500</td>
<td>0.31 5.1890 0.02 0.11 5.2061 0.03 1.21 414</td>
</tr>
<tr>
<td><strong>(d)</strong> 1043</td>
<td>0.35 5.1916 0.14 2.20 5.2057 0.04 0.84 575</td>
</tr>
<tr>
<td><strong>(e)</strong> 136</td>
<td>0.35 5.1916 0.14 2.20 5.2053 0.04 1.01 490</td>
</tr>
</tbody>
</table>
strain because the zinc and oxygen ion bondings to the substrate surface are greatly affected by the surface charges. Therefore, the surface roughness effect on the ZnO nanorod growth can be different depending on synthesis methods.

Without the GaN interlayers, the ZnO nanorods had a substantial amount of residual strain and mosaicity, as shown in Table I. We also observed that the nanorods without the interlayers were randomly distributed in the \( ab \) plane shown in the inset of Fig. 2(c). The structural strain can be orientation dependent. Figures 3(a) and 3(b) show the fluorescence XAFS data collected with the incident x-ray electric field parallel and perpendicular to the nanorod length direction. The XAFS data were analyzed with the UWXAFS package\textsuperscript{15} using standard procedures.\textsuperscript{15,16} The polarized XAFS data without atomic background are presented in Fig. 3(c). To minimize uncertainty only the XAFS data in the \( k \) range of 2.5–10.5 \( \AA^{-1} \) were used for further analysis. Figures 3(d) and 3(e) show the magnitudes of the Fourier transformed XAFS data from the ZnO nanorods with different lengths. It should be noted that the peaks shifted by about 0.4 \( \AA \) on the \( \tau \) axis from their true bond lengths due to the phase shift of the backscattered photoelectrons. The both sets of the XAFS data Fourier transformed to \( r \) space were simultaneously fitted to the theoretical XAFS calculations\textsuperscript{1} with the same parameters, as shown in Figs. 3(f) and 3(g). The fits included single- and multiscattering paths. The data were fitted with a fully occupied model of a WZ structure, varying the bond lengths and Debye-Waller factors (\( \sigma^2 \), including thermal vibration and static disorders). The fit results are summarized in Table II.

From the XAFS data analysis, we observed that the \( \sigma^2 \)'s of Zn–O pairs in the ZnO nanorods with length of 0.1 \( \mu \)m had a substantial amount of disorders, compared with ZnO powder and high quality ZnO nanorods.\textsuperscript{15} As the nanorod length became greater than 0.1 \( \mu \)m, the extra disorder in the Zn–O(2) pairs (located near \( ab \) plane) disappeared. However, the extra disorder in the Zn–O(1) pairs (located along \( c \) axis) was observed in even 1 \( \mu \)m nanorods. We did not observe any extra disorders from all Zn–Zn pairs, comparing to ZnO powder counterpart. XAFS results strongly suggested that the structural strain in Zn–O(2) pairs due to the lattice mismatch should be first relaxed for the ZnO nanorod growth, and that the strain relaxation in \( ab \) plane was the ZnO nanorod seeds of the Stranski-Krastanov growth mode.

In conclusion, the growth mechanism of vertically well aligned ZnO nanorods grown on various GaN interlayers by MOCVD was studied. As the surface roughness of the GaN interlayers was increased, the density of ZnO nanorods increased, and the nanorod quality was degraded. Polarized XAFS measurements of ZnO nanorods revealed that the structural strain in Zn–O(2) pairs disappeared for the nanorod length greater than 0.1 \( \mu \)m. Our observations present strong evidence that the structural stress due to the lattice mismatch between nanorods and substrates, and the surface roughness of the layer underneath of the nanorods dominantly influence forming ZnO nanorods.

This work was supported by the Korea MOCIE through the New Technology R&D Program, the Korea MOST through PEPF User Program as a part of the 21C Frontier R&D Program, and the Korea MOEHRD (KRF-2005-042-C00055). The XAFS data were collected at 3C1 beamline of the Pohang Light Source.

<table>
<thead>
<tr>
<th>Rod length (( \mu )m)</th>
<th>Zn–O(1) ( d ) (( \AA ))</th>
<th>( \sigma^2 (\AA^2) )</th>
<th>Zn–O(2) ( d ) (( \AA ))</th>
<th>( \sigma^2 (\AA^2) )</th>
<th>Zn–Zn(1) ( d ) (( \AA ))</th>
<th>( \sigma^2 (\AA^2) )</th>
<th>Zn–Zn(2) ( d ) (( \AA ))</th>
<th>( \sigma^2 (\AA^2) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>1.939(5)</td>
<td>0.0052(5)</td>
<td>2.018(7)</td>
<td>0.0045(6)</td>
<td>6.3209(3)</td>
<td>0.0088(3)</td>
<td>6.3255(4)</td>
<td>0.0085(4)</td>
</tr>
<tr>
<td>0.2</td>
<td>1.939(6)</td>
<td>0.0049(6)</td>
<td>2.024(7)</td>
<td>0.0027(6)</td>
<td>6.3209(5)</td>
<td>0.0089(4)</td>
<td>6.3259(2)</td>
<td>0.0090(3)</td>
</tr>
<tr>
<td>1.0</td>
<td>1.939(5)</td>
<td>0.0055(5)</td>
<td>2.018(6)</td>
<td>0.0028(6)</td>
<td>6.3206(5)</td>
<td>0.0085(4)</td>
<td>6.3257(4)</td>
<td>0.0085(4)</td>
</tr>
</tbody>
</table>