Determination of micro-structural properties with x-ray absorption fine structure


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ABSTRACT

The structural properties including bonding lengths and their disorders of the nanomaterials are fundamental to understand their properties. Diffraction is a canonical method to measure the crystalline structure. However, it has a limit to detect the structures from the materials which are not well crystallized or amorphous. Extended X-ray absorption fine structure (EXAFS) can describe the atomic species, bonding lengths and coordination number around a selected species atom, independent of the crystallinity, size or shape of specimens. We accurately determined the local structural properties of ZnO nanostructures with EXAFS and illustrated the growth mechanism of vertically aligned ZnO nanorods.

Keywords: EXAFS, structure, disorder, ZnO, nanorod

1 INTRODUCTION

The physical and chemical properties of a material are mainly determined by the elements and their bonds in the material. Therefore, the knowledge of the structural properties of the material is fundamental to understand the properties of the material. X-ray and neutron diffractions are typical methods to measure the structural properties. However, the diffractions detect the average structure of a crystal only. Diffraction cannot effectively determine the structures of the none-crystalline materials because the disorder on the local scale is averaged out in the average periodic structure measured by diffraction. As a particle size becomes a nano-meter scale, its properties can be different from those of its bulk counterpart due to the size and surface effects, and also structural disorder/distortion [1-3]. The structural properties of nanomaterials cannot be accurately determined by diffraction because nanomaterials do not contain enough scattering source atoms and, moreover, have a large amount of structural distortions and disorders. Even tunneling electron microscopy cannot effectively determine the structural properties of nanostructures. We employed extended x-ray absorption fine structure (EXAFS) to determine the local structural properties of ZnO nanomaterials. EXAFS can describe the average local structural properties, such as bonding length, bonding length disorder, atomic species, and coordination numbers around a selected species atom in a matter [1].

As x-rays pass through a material, they are partially scattered, absorbed and the last transmit. The x-ray absorption coefficient can be determined, measuring either transmission or fluorescence. The intensity of transmitted x-rays is determined by the incident x-ray intensity and total x-ray absorption, as

\[ I_t(E) = I_0(E)e^{\mu(E)t}. \]  

where \( I_t \) and \( I_0 \) the intensities of the incident and transmitted x-rays, \( \mu \) x-ray absorption coefficient, \( t \) thickness of the specimen and \( E \) incident x-ray energy. The total x-ray absorption is obtained, as

\[ \mu(E)t = \ln \left( \frac{I_0(E)}{I_t(E)} \right). \]

For fluorescent x-rays, the fluorescent x-ray intensity is

\[ I_f = \frac{I_0(E)e(\epsilon(E)\mu(E))}{\mu_f(E) + \mu_f(E)\sin \theta_f / \sin \theta_i} \left[ 1 - e^{-\mu_f(E)\sin \theta_i + \mu_f(E)\sin \theta_f} \right]. \]

where \( I_f \) fluorescent intensity of x-rays, \( \epsilon(E) \) fluorescence efficiency, \( \mu_f(E) = \mu(E) + \mu_0(E) \) total fluorescence coefficient (\( \mu_0 \) background x-ray absorption coefficient), \( \theta_i \) and \( \theta_f \) the angles of the incident and fluorescent x-rays, and \( E_c \) fluorescence x-ray energy. As \( \mu(E) >> \mu_f(E) \) and \( \mu(E) >> \mu_0(E) \), the fluorescence intensity becomes

\[ I_f = I_0 \left( \frac{\epsilon(E)\mu(E)t}{\sin \theta_i} \right). \]

Finally, the x-ray absorption coefficient from the fluorescence x-rays is

\[ \mu(E) = \frac{I_f(E)\sin \theta_i}{I_0(E)\epsilon(E)t}. \]
neighboring atoms around the x-ray absorbing atom. Equation 6 demonstrates that the structural properties of neighboring atoms around a selected species atom can be determined by EXAFS measurements.

![Figure 2. Vertically aligned ZnO nanorods grown on (a) Al2O3 and (b) GaN/Al2O3 substrates.](image)

### 2 EXPERIMENTAL DETAILS

The ZnO nanorods were synthesized on -Al2O3 (0001) substrates with and without GaN interlayers by a catalyst-free metal-organic chemical-vapor (MOCVD) procedure [4, 5]. DEZn (diethylzinc, Zn(C2H5)2) and high purity oxygen (99.9999%) were used as zinc and oxygen precursors. During ZnO nanorod growth, the substrate temperature and chamber pressure were maintained at 350 - 400 °C and 0.3 - 0.4 Torr, respectively. The precursor ratio of oxygen to DEZn was kept at about 300 : 1. The growth rate of the ZnO nanorods was about 0.01 µm per minute and the diameter of the nanorods was about 50 nm. Figures 2 demonstrate the ZnO nanorods grown on Al2O3 and 2µm-µGaN/Al2O3 substrates. EXAFS measurements were performed at PNC-CAT of Advanced Photon Source, Argonne National Laboratory and Pohang Light Source, Korea. The EXAFS were collected with a fluorescence mode at 30 K and room temperature. The incident x-ray energy was selected with a three-quarter tuned Si(111) double-monochromater. The details of EXAFS measurements are described elsewhere [1].

### 3 RESULTS AND DISCUSSION

The local structural properties of the ZnO nanorods were measured with EXAFS. Figures 1 show the total x-ray absorption for ZnO powder with a transmission mode, and the polarization-dependent x-ray absorption coefficients for ZnO nanorods with a fluorescence mode. The EXAFS data were analyzed with the UWXAFS package [6] using standard procedures [1,7], and photoelectron back-scattering functions calculated with the FEFF8 code [8]. After the atomic background absorption µ₀ was determined using AUTOBK (part of the UWXAFS package), the EXAFS function, \( \chi(E) = \frac{\mu(E)}{\mu_0(E)} - 1 \), was obtained. Figure 3 shows the EXAFS(\( \chi \)) data from ZnO powder and nanorods at the Zn K-edge for \( \hat{e} \parallel \hat{c} \) and \( \hat{e} \perp \hat{c} \), as a function of the
The observed X-ray absorption near-edge structure (XANES) and EXAFS can be summarized from the ZnO powder and nanorods. The data from the ZnO powder and nanorods were used to determine the structural parameters and validate the theoretical calculations. The EXAFS data from the ZnO powder and nanorods were concurrently fitted with the same parameters, as shown in Figs. 4 (b) and (c). The fits included single- and multi-scattering paths. The data were fitted with a fully occupied model of a wurtzite (WZ) structure, varying the bond lengths and Debye-Waller factors (σ², including thermal vibration and static disorder). The two sets of EXAFS data measured at the electric field of the incident x-ray parallel and perpendicular to the c-axis can independently determine the distance and the distance distribution from the probe Zn atom to one O(1) located just below the Zn atom along the c-axis, three O(2)s located about 19° off from the Zn ab-plane, six Zn(1)s located at −55° off from the ab-plane, and six Zn(2)s located in the ab-plane. These four sets of bonds are critical to understand the structural properties of the ZnO nanorod crystals.

Due to the structural stress due to the lattice mismatch between the ZnO and substrates, the nanorods directly grown on Al₂O₃ substrates showed a substantial amount of disorder in the bond length of the Zn-O pairs. The EXAFS measurements demonstrated that the relaxation of the structural strain between the Zn-O pairs in the ab-plane was a necessary condition for the ZnO nanorod growth.

The magnitude of the Fourier transformed EXAFS measurements from the ZnO nanorods directly grown on Al₂O₃ substrates is shown in Fig. 4 (d).

**Figure 3.** EXAFS ( ) from ZnO powder (1st), ZnO nanorods with a length of 1.0 µm grown on Al₂O₃ substrates (2nd and 3rd) measured with a polarized x-ray mode at room temperature, and ZnO nanorods with a length of 0.4 µm grown on n-GaN/Al₂O₃ substrates (4th) measured with an unpolarized X-ray mode at 30 K.

**Figure 4.** Magnitude of Fourier transformed EXAFS measurements from the data at the Zn K-edge from (a) ZnO powder, and (b) and (c) 1.0-µm long ZnO nanorods/Al₂O₃.
as a function of distance from a zinc atom at room temperature. (d) The EXAFS for ZnO nanorods with a length of 0.4 μm at 30 K. For the Fourier transformation, a Hanning window with a windowsill width of 0.5 Å-1 was used. Data in the range of $\tilde{r} = 1.2 - 3.3$ Å were fitted.

4 CONCLUSIONS

Vertically aligned ZnO nanorods were synthesized by catalyst-free MOCVD on Al$_2$O$_3$ substrates with and without n-GaN interlayers. The structural properties of the ZnO nanorods were studied by using EXAFS. Polarized EXAFS revealed that the structural strain effectively affected on the bond length disorder of the Zn-O(1) pairs. The structural strain along the c-axis of the ZnO nanorods was propagated through a pre-grown ZnO film to the ZnO nanorods and observed even in the 1-μm long nanorods. However, the structural strain in the ab-plane was disappeared as the ZnO formed into a rod. From the EXAFS study, we found that the relaxation of the structural strain in the ab-plane is a necessary condition of ZnO nanorod growth and that the disorder of the Zn-O(1) pairs located along the c-axis determined the crystal quality.

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<table>
<thead>
<tr>
<th>Rod length</th>
<th>Zn-O(1)</th>
<th>Zn-O(2)</th>
<th>Zn-Zn(1)</th>
<th>Zn-Zn(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder</td>
<td>d (Å)</td>
<td>$\sigma^2$(Å$^2$)</td>
<td>N</td>
<td>d(Å)</td>
</tr>
<tr>
<td>1.0 μm</td>
<td>1.904(5)</td>
<td>0.004(1)</td>
<td>3</td>
<td>1.980(5)</td>
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<tr>
<td>0.1 μm</td>
<td>1.939(5)</td>
<td>0.0052(5)</td>
<td>3</td>
<td>2.018(7)</td>
</tr>
<tr>
<td>0.1 μm</td>
<td>1.91(1)</td>
<td>0.006(1)</td>
<td>3</td>
<td>1.98(1)</td>
</tr>
<tr>
<td>0.4 μm</td>
<td>1.90(1)</td>
<td>0.003(1)</td>
<td>3</td>
<td>1.98(1)</td>
</tr>
</tbody>
</table>

Table 1. Coordination number (N), bond length (d) and Debye-Waller factor ($\sigma^2$) of ZnO powder and ZnO nanorods on n-GaN/Al2O3 substrates obtained from the fits. The EXAFS data were measured at $T = 30$ K. $S_0^2$ of 0.95(5) was used in the data fits. For the model calculations, the WZ structure with $a = b = 3.234$ Å, $c = 5.240$ Å and the crystalline symmetry $z$ of oxygen = 0.370 were used.

REFERENCES