Polarization-dependent DANES study on vertically-aligned ZnO nanorods

Chengjun Sun\(^1\), Chang-In Park\(^2\), Zhenlan Jin\(^2\), In-Hui Hwang\(^2\), S. M. Heald\(^1\), and Sang-Wook Han\(^2\)*

\(^1\)X-ray Science Division, Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60440, USA
\(^2\)Department of Physics Education and Institute of Fusion Science, Jeonbuk(Chonbuk) National University, Jeonju 54896, Korea

*Email: shan@jbnu.ac.kr

Abstract. The local structural and local density of states of vertically-aligned ZnO nanorods are examined by using polarization-dependent diffraction anomalous near edge structure (DANES) measurements from c-oriented ZnO nanorods at the Zn K edge at the geometry of the incident x-ray electric field parallel and perpendicular to the x-ray momentum transfer direction. Orientation-dependent local structures determined by DANES are comparable with polarization-dependent EXAFS results. Unlike other techniques, polarization-dependent DANES can uniquely describe the orientation-dependent local structural properties and the local density of states of a selected element in selected-phased crystals of compounds or mixed-phased structures.

1. Introduction
Anomalous x-ray scattering techniques have been widely used to determine local structural properties in the crystalline regions of matters, particularly, including phase-mixture structures and textured structures [1-4]. Polarization-dependent diffraction anomalous fine structure (DAFS) can describe the orientation-dependent local structural and the chemical properties of a probing atom because the atomic form factor square of \(|f_0 + f' + if''|^2\) depends on x-ray electric field directions. The Thomson scattering factor of \(f_0\) is independent of the orientation of crystalline structures, whereas the resonant anomalous scattering amplitude of \(f' + if''\) is contributed by crystalline orientations due to the interaction of incident x-ray electric field and electron-hole dipoles [1-4]. Polarization-dependent diffraction anomalous near edge structure (DANES) can uniquely describe the chemical valence state and the local electron density of states of probing atoms within selected-phased crystals in a specimen. Previous studies have mostly focused on DAFS compared to EXAFS [1-4]. In this paper, we demonstrate polarization-dependent DANES measurements from vertically-aligned ZnO nanorods, comparing with simultaneously-measured XANES. The direct comparison of DANES and XANES measured from single-crystal ZnO nanorods will prove that DANES alone can probe the chemical valence state and the local density of state of a selected element within selected-phased crystals.

Wurtzite-phase ZnO nanorods have been intensively studied as building blocks for nanodevice applications, including light emitting diodes, solar cells, piezoelectric devices, sensors, and actuators [5]. The observation of quantum confinement effects from ZnO nanorods perpendicular to the nanorod length [6] suggested that the behavior of electrons in nanorods depends on the direction. Furthermore, previous studies with polarization-dependent XAFS measurements from ZnO nanorods demonstrated that the bond lengths of ZnO pairs parallel and perpendicular to the nanorod length direction were elongated and shrunken, respectively, compared to those of ZnO powder [8]. Since XAFS detects an average structural properties of a specimen, it cannot determine the local structural properties of selected-phased crystals. The orientation-dependent local structural properties and the local density of
states in crystalline regions are often critical in understanding of fundamental properties of materials, including superconductivity and orientation-dependent magnetization [9].

Figure 1. (a) and (b) SEM images of vertically-aligned ZnO nanorods and (c) schematic of polarization-dependent DANES geometry.

Figure 2. XRD from the ZnO(0002) planes as a function of momentum transfer, q, at the electric field of incident x-rays perpendicular to the nanorod length direction at the incident x-ray energies of 9.4, 10.0, and 10.36 keV, respectively. The inset shows the θ-rocking curve at the ZnO(0002) diffraction peak at the incident x-ray energy of 9.4 keV.

2. Experiment
For polarization-dependent DANES measurements, wurtzite-phase ZnO nanorods are synthesized on α-Al₂O₃ substrates using a catalyst-free metal organic chemical vapor deposition (MOCVD). The details of ZnO nanorod growth by using MOCVD are described elsewhere [5]. The structural properties of ZnO nanorods are examined by using field-emission scanning electron microscopy (SEM, S-5500, Hitachi) and x-ray diffraction (XRD) measurements. SEM images demonstrate that ZnO nanorods are vertically-well oriented with a uniform distribution on the substrate surface, as shown in Figs. 1 (a) and (b). From the SEM images, the mean length and diameter of ZnO nanorods are determined to be 1.4 µm and 80 nm, respectively. High-resolution XRD measurements (data not shown) from the nanorods using a conventional tube x-rays with the Cu Kα₁ radiation show the ZnO lattice constant c of 5.2098 Å with the residual strain of 0.038 Å. The mosaicity of the nanorods are determined to be 3.70 ± 0.06° by θ-rocking at the ZnO(0002) diffraction, as shown in the inset of Fig. 2. SEM images from the nanorods shown in Fig. 1 (a) suggest that the mosaicity is mainly contributed by the orientation of the nanorods. DANES
measurements at the ZnO(0002) diffraction peak from the ZnO nanorods are performed with the electric field of incident x-rays parallel (\(\vec{\varepsilon} \parallel \vec{c}\)) and perpendicular (\(\vec{\varepsilon} \perp \vec{c}\)) to the ZnO nanorod length at the Zn K edge, as shown in Fig. 1 (c). The incident x-ray energy is selected by the Si(111) double crystal monochromator at the 20BM beamline of the Advanced Photon Source (APS). Near the ZnO(0002) peak, the two-dimensional measurements of \(\theta - 2\theta\) and energy scans are performed. XANES data are simultaneously taken with the DANES measurements to directly compare the two techniques. For the \(ab\)-and \(c\)-polarized DANES measurements, the \(c\)-axis of ZnO nanorods is vertically and horizontally placed by rotating the sample to 90°, respectively, as shown in Fig. 1 (c) because the x-ray is horizontally polarized. The polarization-dependent XANES measurements are performed with a fluorescence mode.

Figure 3. Polarization-dependent DAFS from ZnO nanorods at the Zn K edge at the incident x-ray electric fields (a) parallel and (b) perpendicular to the nanorod length.

3. Results and Discussion

When the angle between the incident and the out-going x-rays with a parallel geometry (\(\varepsilon \parallel \vec{c}\)) approaches to the Brewster angle of 90°, the intensity of diffraction decreases to zero by an angle dependent factor of \(\cos(\theta_i + \theta_f)\). The lattice constant \(c\) of ZnO is \(\sim 5.21\) Å corresponding to the x-ray momentum transfer of \(q \sim 2.41\) Å\(^{-1}\) and to the incident angle of \(\sim 14.26\)° at the x-ray energy of 9659 eV. At the Zn K edge (9659 eV), the angle dependent factors are estimated to be 0.76 and 0.8 at 9400 eV and 10360 eV, respectively, for the parallel geometry. The angle dependent factor does not affect the resonant anomalous scattering intensity because it gradually increases from 0.76 to 0.8 when incident x-ray energy increases from 9400 eV to 10360 eV. The diffraction angle changes from \(\sim 13.3°\) to \(\sim 14.7°\) within the x-ray energy range and the change of the diffraction angle does not affect XANES spectra much. Figure 2 shows XRD from the ZnO(0002) planes at different x-ray energies of 9400, 10000, and 10360 eV for below, just above, and far above the Zn K edge, respectively. XRD obviously shows the contribution of resonant anomalous scattering, \(f' + if''\), near the absorption edge. Polarization-dependent XRD measurements as a function of incident x-ray energy near the absorption edge can determine the orientation-dependent local structural properties around a probing atom due to the absorption factor of \(f''\). DANES spectra are obtained by taking the total intensity of the XRD peaks as a function of the incident x-ray energy.
Figure 3 shows polarization-dependent DANES on the ZnO(0002) diffraction peak as a function of incident x-ray energy near the Zn K edge. The peak intensities dramatically decrease at the absorption edge and gradually increased above the edge for both polarizations, due to the anomalous scattering factor of $f'$. The polarization-dependent intensities agree well with the theoretical prediction of DAFS [1-4]. The small oscillations above the absorption edges are owing to the absorption terms of $f''$ which is dependent of the angle between the incident x-ray electric field and the direction of a neighboring atom [8]. The oscillations in DAFS above an absorption edge are originated from the local structures around probing atoms in crystalline sites, similar to EXAFS which detects average local structural properties of a whole specimen [1-4]. From the absorption contribution to diffraction intensity near the absorption edge, the chemical valence states and the local density of states can be determined because $f''$ corresponds to the electron transitions from a core shell to the empty outermost orbitals of a probing atom. Thus, DANES can describe the local density of states in the outermost orbitals.

Figure 4. Polarization-dependent DANES from ZnO nanorods at the Zn K edge with polarization-dependent XANES at the incident x-ray electric field (a) parallel and (b) perpendicular to the nanorod length.

Figures 4 (a) and (b) show a direct comparison of polarization-dependent DANES and XANES. The DANES is considerably similar to the XANES. However, we observe a shift of DANES from XANES. The minimum position of DANES is shifted by ~2.0 eV from the maximum position of XANES for both polarization. The shift is ascribed to the Kramers-Kronig relation of $f(E)$ and $f''(E)$. Polarization-dependent XANES data from vertically-aligned ZnO nanorods shows the typical XANES from a ZnO film [10] and vertically-aligned ZnO nanorods [7]. XANES from ZnO with $c$-polarization ($\hat{e} \parallel \hat{c}$) is quite different that with $ab$-polarization ($\hat{e} \perp \hat{c}$) owing to oxygen positions in the Zn-O tetrahedron; one oxygen in the $c$-axis and the other three oxygen atoms in nearly the $ab$-plane. The polarization-dependent XANES data corresponds to the average distribution of the local density of states of Zn atoms in ZnO nanorods, whereas polarization-dependent DANES corresponds the orientation-dependent local density of states of Zn atoms in ZnO crystals. Since the ZnO nanorods are single crystals, the DANES is nearly identical to the XANES that corresponds to the local density of states and the chemical valence state of a probing atom. This result demonstrates that polarization-dependent DANES can determine the
orientation-dependent local density of states and the chemical valence state of probing atoms in selected-phased crystalline sites.

4. Conclusions
We demonstrate that polarization-dependent DANES measurements from vertically-aligned ZnO nanorods at the Zn K edge can be a probe to determine the orientation-dependent local density of states and the chemical properties of probing atoms in crystalline sites, comparing to simultaneously-measured XANES. Polarization-dependent DANES can detect orientation-dependent local structure and density of states around a selected element in selected-phased crystals, whereas polarization-dependent XANES can provide average information of a whole specimen. The direct comparison of polarization-dependent DANES and XANES measurements on single-phase ZnO nanorods demonstrates that the DANES will be considerably useful to determine the local structural and the local density of states of a selected element in complex-phase structures and mixed-phase nanostructures.

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