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Polarization-dependent soft-x-ray absorption of highly oriented ZnO microrod arrays

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Abstract

Polarization-dependent x-ray absorption measurements were performed on crystalline ZnO three-dimensional arrays consisting of highly oriented microrods as well as on particulate thin films consisting of monodisperse spherical nanoparticles. Strong anisotropic effects have been observed for the highly oriented ZnO rods, but not for the isotropic spherical nanoparticles. Full-potential calculations of the orbital-resolved x-ray absorption of a ZnO wurtzite periodic crystal, including Zn 3d among the valence states, show very good agreement with the experimental findings. Comprehensive fundamental knowledge of the electronic structure of ZnO is obtained by probing and demonstrating the orbital symmetry of oxygen and its contribution to the conduction band of this important II–VI semiconductor.

(Some figures in this article are in colour only in the electronic version)

Zinc oxide represents an important basic material (II–VI semiconductor) due to its low cost, its wide band gap as well as its electrical [1], optoelectronic [2] and luminescent properties [3]. ZnO is of great importance for fundamental research as well as being relevant in various fields of industrial and high-technology applications. Recently, a low-threshold lasing action has been observed at room temperature in highly oriented ZnO nanorod arrays [4]. From a fundamental point of view, it is crucial to probe and understand the electronic structure of such novel materials to enable tailoring of their physical properties as well as development of novel and improved devices.

In this letter, we report a polarization-dependent x-ray absorption spectroscopy (XAS) study performed on highly oriented ZnO microrods. The most striking features of x-ray spectroscopic characterization are:

(1) the atomic and site selectivity due to transitions involving core levels; and
(2) the orbital and symmetry selectivity by virtue of dipole selection rules and the use of polarized x-rays from synchrotron radiation sources.

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In order to probe the orbital character and symmetry as well as its contribution to the conduction band of ZnO, we have compared the XAS spectra to the prediction of an *ab initio*, full-potential calculation of a periodic crystal, wurtzite ZnO.

The thermodynamically stable crystal structure of ZnO is wurtzite (hexagonal crystal system) and occurs in Nature as the mineral zincite (crystal class 6_{mm}). Such ionic and polar structure can be described as a hexagonal close packing (HCP) of oxygen and zinc atoms in space group $P6_3mc$ with zinc atoms in tetrahedral sites (point group 3_m). The occupancy of four of the eight tetrahedral sites of the HCP array controls the structure. The unit cell contains two formula units and the typical crystal habit exhibits two types of low-index surface: (i) polar surfaces $(00\bar{1})$ (O terminated) and (001) (Zn terminated) and (ii) non-polar surfaces $(\bar{1}00)$; and C_{6v}-symmetric ones parallel to the c-axis. In addition, there is no centre of inversion in the wurtzite structure and therefore an inherent asymmetry is present which allows anisotropic growth along the c-axis. The velocities of ZnO crystal growth in different crystal directions are reported to be $[\bar{1}00]\rangle[\bar{1}01]\rangle[001] \approx [00\bar{1}]$ (see [10]).

A novel approach to materials chemistry has been developed which contributed to the fabrication of purpose-built nano/microparticulate thin films from aqueous solution [5], with a better control over size, shape and orientation of crystallites on substrates. Three-dimensional arrays of highly oriented nanorods [6], microrods [7], microtubes [8] and nanocomposites [9] of 3d metal oxides have been created on various substrates. Such well-defined and well-ordered materials should contribute to the required enhanced fundamental knowledge of the relation between structure and physical properties.

The experiments were performed at the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory, beamline 7.0.1, which is equipped with a spherical grating monochromator [11]. The x-ray absorption spectra were measured by recording the total electron yield from the samples while scanning the photon energy over the O K-edge region at a resolution of 0.2 eV. The XAS experiments were carried out on two different (isotropic and anisotropic) homogeneous and crystalline zincite ZnO (wurtzite) thin-film samples, i.e. ZnO spheres, which consist of monodisperse spherical particles 150 nm in diameter (figure 1(a)), and ZnO microrods consisting of monodisperse, anisotropic and highly oriented crystallites (figure 1(b)) grown along the c-axis and perpendicular to a transparent conducting glass substrate (F-SnO_2) [7]. The microrods, 10 μm in length and 1.5 μm in width, are oriented normal to the substrate surface.

The calculation of the electronic structure was based on a first-principles, full-potential linearized augmented-plane-wave (FPLAPW) method [12]. The scalar-relativistic Hamiltonian was formulated within the local density approximation to the density functional theory, and we chose the exchange–correlation potential of Perdew *et al* [13], derived from the generalized gradient expansion. Experimental values [14] of the ZnO lattice constants and the internal lattice parameter were used: $a = 3.249$ Å, $c = 5.205$ Å and $u = 0.382$. The importance of considering the 3d states in transition metals as valence states for obtaining accurate hybridization is well known and has been discussed in detail in [15] for instance. In the present calculation only the Zn 3p states (and deeper-lying Zn levels) and the O 1s state are treated as core states. The partial density of states (DOS) was calculated using the modified tetrahedron method [16], whereupon the XAS was calculated according to Neckel *et al* [17] with a Lorentzian broadening of 0.2 eV.

The polarization-dependent x-ray absorption measurements are shown in figure 2. The vertical dashed lines are drawn to guide the eyes. The variations in the spectral shape continue up to 30 eV above the absorption threshold. The resolved absorption features are indicated as a_1–a_8. Prior to a_1, no polarization dependence is observed in the x-ray absorption spectra for either sample. However, at higher photon energies, strong anisotropic effects are observed for the ZnO microrods (bottom spectra). Measuring in grazing incidence geometry, i.e. incidence

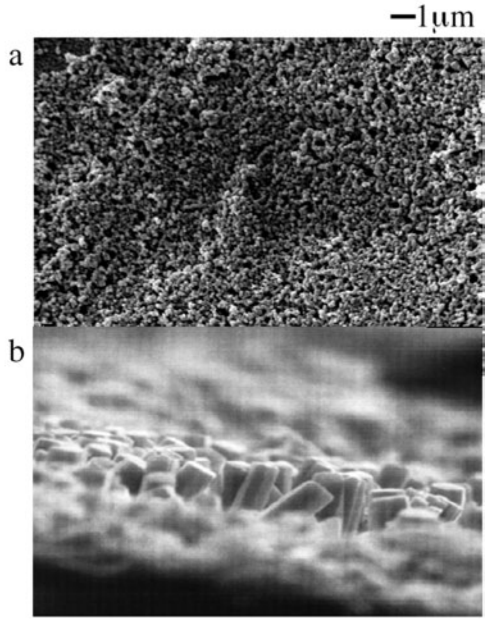

Figure 1. SEM micrographs of crystalline ZnO: (a) particulate thin film consisting of monodisperse spherical nanoparticles (top view); and (b) a three-dimensional array consisting of highly oriented microrods (cross section). A scale bar (1 μm) is given at the top.

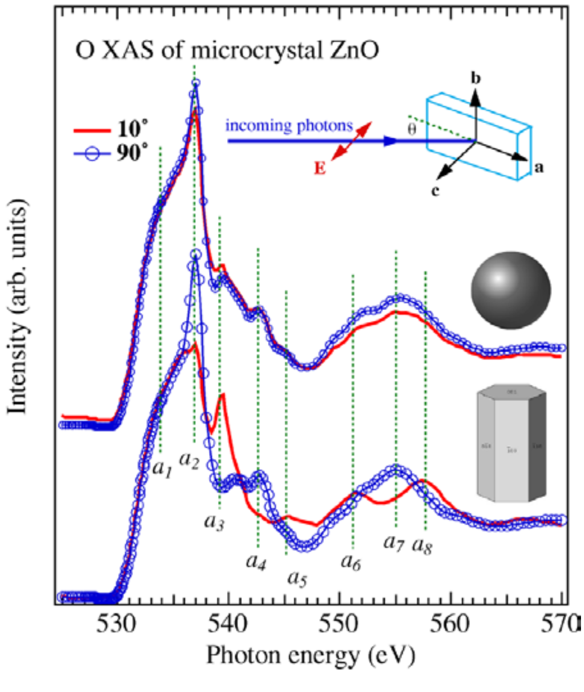

Figure 2. Polarization-dependent x-ray absorption spectra of zincite ZnO particulate thin films with isotropic (spherical) and anisotropic (rod-like) morphology. The inset illustrates the XAS experimental geometry, where $\boldsymbol{a}$-, $\boldsymbol{b}$-axes define the sample surface plane, the $\boldsymbol{c}$-axis is along the growth direction of the ZnO rods, $\boldsymbol{E}$ is the polarization of incoming photons and θ indicates the angle of incidence to the sample surface: 10° ($\boldsymbol{E} \parallel \boldsymbol{c}$, solid curves) or 90° ($\boldsymbol{E} \perp \boldsymbol{c}$, dots).

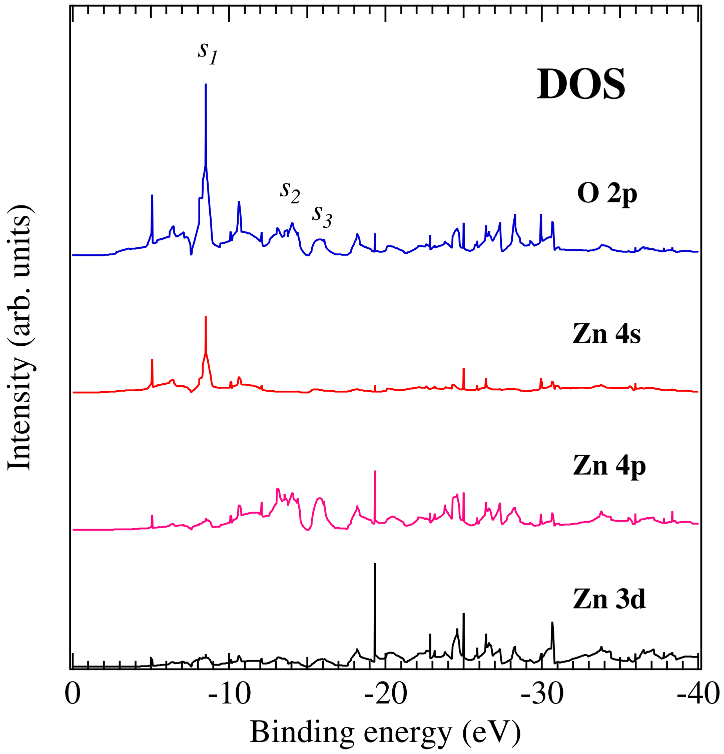

Figure 3. The calculated partial DOS of the unoccupied valence states O 2p as well as Zn 3d, 4s and 4p of zincite ZnO.

angle $\theta = 10°$, where the absorption features a_3, a_5 and a_8 are stronger, the excitation to the state along the c-axis of the wurtzite structure is enhanced. At normal incidence geometry, i.e. $\theta = 90°$, where the absorption features a_2, a_4 and a_7 are stronger, the excitation to the in-plane state is enhanced. No significant change is observed for the isotropic samples of ZnO consisting of spherical particles as a function of the polarization angle. However, all the absorption features, observed in either detection geometry, are averaged out. The experimental findings suggest a strong correlation between the electronic structure and the geometrical structure of the crystalline ZnO arrays.

Figure 3 shows the calculated partial DOS of the unoccupied valence states O 2p as well as Zn 3d, 4s and 4p. The similarity between the O 2p DOS and Zn 4s DOS in the binding energy region below 10 eV suggests a strong hybridization of Zn 4s with O 2p states. Feature s_1 located at the binding energy of 8.5 eV shows a strong Zn 4s character. Minor contributions from Zn 4p and 3d are observed. In the region 10–20 eV, Zn 4p-hybridized O 2p states become dominant as indicated by features s_2 and s_3. Above 20 eV, the contribution from Zn 3d becomes significant. Hybridizations of both Zn 4p and 3d with O 2p states are observed.

The calculated XAS spectra of the wurtzite periodic crystal as well as the experimental data recorded for the oriented microrod sample are shown in figure 4. The calculation takes into account the partial DOS and the dipole-allowed transition probability of the oxygen p_{x+y} and p_z states. For comparison, the measured XAS spectra are shown on a binding energy scale using an O 1s binding energy of 528.5 eV. An excellent agreement is obtained between the experimental and the calculated results. The anisotropic effects of DOS in x–y plane or along

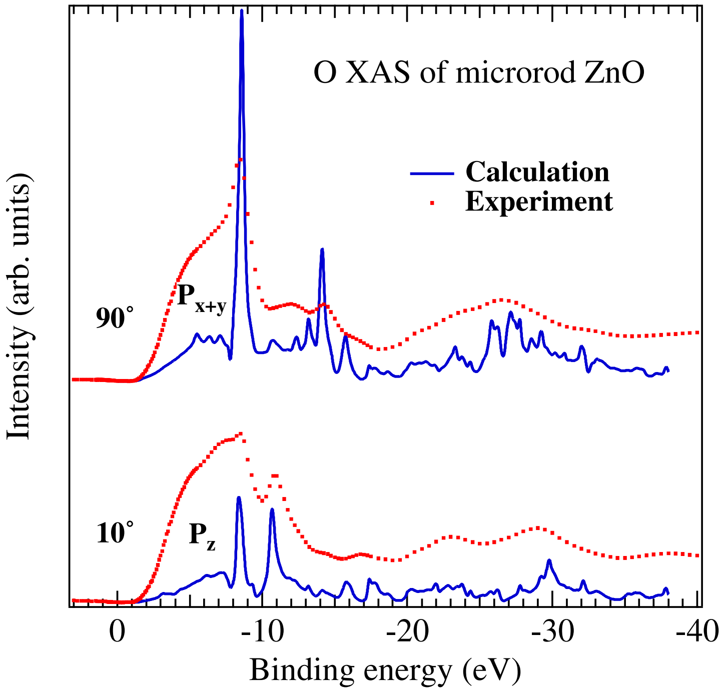

Figure 4. Experimental (dots) and calculated (curves) x-ray absorption spectra of zincite ZnO. The calculations of the XAS spectra include the DOS and the probability of transition to the O p_{x+y} and p_z states.

z-axis are clearly observed. The oxygen 2p DOS has relatively strong in-plane character at binding energies of around 8.5, 14 and 27 eV, and out-of-plane character at binding energies of around 11 and 30 eV.

In conclusion, we have measured the polarization-dependent XAS spectra of ZnO thin-film samples with isotropic and anisotropic morphology grown by controlled aqueous chemical growth. Strong anisotropic effects on the c-elongated oriented microrod sample have been observed. This is in very good agreement with the orbital-resolved calculations of the XAS spectra of a ZnO wurtzite periodic crystal. Such results demonstrate that designing materials with the appropriate morphology and orientation, i.e. *purpose-built* materials, enables one to reach a better fundamental understanding of nano/microscale materials and their physical properties. Probing the orbital symmetry of oxygen and resolving its contribution to the conduction band of this important large-band-gap II–VI semiconductor is of crucial importance for the understanding of its optoelectronic properties.

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