Soft-x-ray spectroscopy probes nanomaterial-based devices

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Synchrotron radiation-based spectroscopic techniques provide information about the characteristic electronic structure of nanostructured materials.

Synchrotron radiation is a photon light source generated by high-energy electrons that are centripetally accelerated in the magnetic fields of a storage ring, as shown in Figure 1. This radiation is extremely intense over a broad range of wavelengths extending from the infrared through visible light and ultraviolet into the soft and hard x-rays of the electromagnetic spectrum.

The wavelength of soft x-rays (1–10 nm) is most suitable for the analysis of nanomaterials. Such analysis provides information about the materials’ electronic structures that can be used to optimize nanomaterial-based devices.

Among the soft-x-ray spectroscopic techniques, x-ray absorption spectroscopy (XAS) and x-ray emission spectroscopy (XES) probe the energy distribution of electronic states in atoms, molecules, and solid state materials. The basic concepts, shown in Figure 2, involve the interaction of x-rays and matter as explained by molecular orbital theory. In XAS, the absorption of photons excites electrons from deep core levels, such as 1s, of a selected atom in a molecule to unoccupied states, leaving behind a core hole. In XES, the core hole is filled by a valence electron causing the emission of an x-ray photon. XES gives information about chemical bonding in the molecule. By combining XAS and XES, one can obtain information about unoccupied states (conduction band) and occupied states (valence band). The difference in energy between the conduction band and the valence band is called the band gap.

As semiconductor devices become smaller and smaller, the dimensions of new electronics components are reaching nanometer scale. Understanding the fundamental properties of these new devices, such as their electronic structures and band gaps, provides opportunities to design advanced materials and to fabricate devices for future applications. In certain semiconductors, when electrons fall from the conduction band to the valence band, they emit light that is commercially exploited for devices such as light-emitting diodes (LEDs) and semiconductor lasers.

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Here we present the XAS and XES electronic structures of two technologically important materials, zinc oxide (ZnO) and indium nitride (InN).

Figure 3 presents the XAS and XES spectra of nanostructured (∼150nm) and bulk ZnO. The oxygen (O) K-edge absorption spectrum reveals the unoccupied O 2p states, and the O K-edge emission spectrum reveals the occupied O 2p states. In this XAS spectrum, energies are assigned to the following hybridized states:

- ∼530–539 eV is O 2p with Zn 4s,
- ∼539–550 eV is O 2p with Zn 4p,
- and energies above 550 eV are O 2p with Zn 4d.

Similarly, one can assign three distinct features in the XES spectrum to particular hybridized bonding states:

- ∼526 eV is O 2p with Zn 4p,
- the low energy shoulder in the 522–524 eV region is O 2p with Zn 4s,
- and the single-band shape at 520 eV is mainly O 2p with Zn 3d.

Nanostructured ZnO exhibited stronger s-p-d hybridization compared to bulk ZnO because the features at 520 eV and 523 eV are enhanced. A well-defined band gap occurs at ∼3.3 eV, which is in agreement with the 3.4 eV found for bulk ZnO.

InN is another intriguing but poorly studied material. Due to its low dissociation temperature and the high equilibrium vapor pressure of nitrogen, InN is the most difficult compound to synthesize among Group III nitrides. Furthermore, it has been found recently that the band gap of InN is ∼0.7–0.9 eV and not ∼1.9 eV as it has long been believed. Figure 4 displays the nitrogen (N) K-edge XAS for InN film and nanobelts recorded at different incidence angles. The ribbon-like nanobelts have widths of ∼20–80 nm, width to thickness ratios of 2–10, and lengths of ∼15 μm.

The electronic structures of the film and nanobelts occur at the same energy and exhibit similar spectral profiles, which indicates that the local symmetry and chemical states are similar. The intensities of these features are quite different, however, implying the stronger anisotropy of the p-state in the conduction band of the thin film.

Bonding symmetry of a molecule can be probed using polarized radiation. When a chemical bond interacts with radiation of large incidence angle, the bond’s σ-bond character is dominant. Thus, a strong absorption is observed for the transition from N 1s to the unoccupied p_x states. Similarly, for a grazing incidence angle, the strong absorption is dominated by the transition from N 1s to the unoccupied p_z state that corresponds to the π-bond character. In Figure 4, C corresponds to p_z final states while A, B, and D correspond to p_x final states. This implies stronger in-plane and weaker out-of-plane bonding of the crystal structure. For wurzite InN, three In-N bonds lie in the bilayer (σ-bond) and one In-N bond lies along the c axis (π-bond). The observed anisotropy may influence the optical and transport properties in the ab plane and along the c axis.

Two distinct features appear in the valence band (see Figure 5). The feature at ∼393 eV, the top of valence band, is N 2p-In 5p states, and the low-energy feature at ∼388–390 eV is N 2p – In 5s states. The band gap is ∼0.8 eV. One advantage of XES is that it helps to distinguish whether the material contains a direct or an indirect band gap. For a direct band gap, one expects emission to occur at the highest energy for the lowest possible excitation energy. As excitation energy increases, the emission should

![Figure 3](image1.png)  
**Figure 3.** X-ray absorption and x-ray emission spectra of zinc oxide (ZnO) showing the conduction and valence bands near the Fermi level, the band gap at absolute zero. arb.: arbitrary.

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move to lower energies. In Figure 6, the peak shift to lower energy with increasing incident energy indicates a direct band gap. XAS and XES provide information about the electronic structure and orbital character of both the conduction and valence bands of materials. These techniques also indicate a material’s overall electronic structure as well as its energy scale in the conduction and valence bands. Studying the In$_{1-x}$Ga$_x$N and In$_{1-x}$Al$_x$N alloys and their nanostructures, and in particular understanding how composition and size affect p-d hybridization, will be a big challenge for next-generation devices.

**Figure 5.** X-ray absorption and x-ray emission spectra illustrate the band gap of indium nitride (InN) thin film and nanobelts. *arb.*: arbitrary, *N*: nitrogen.

**Figure 6.** Nitrogen (N) K-emission spectra for excitation energies (a) below and (b) far above the absorption threshold. The shift of the main peak indicates that the band gap is direct rather than indirect. *arb.*: arbitrary, *hv*: photon energy, InN: indium nitride.

**References**


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