Electronic structure of In$_2$O$_3$ from resonant x-ray emission spectroscopy


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The valence and conduction band structures of In$_2$O$_3$ have been measured using a combination of valence band x-ray photoemission spectroscopy, O K-edge resonant x-ray emission spectroscopy, and O K-edge x-ray absorption spectroscopy. Excellent agreement is noted between the experimental spectra and O 2p partial density of states calculated within hybrid density functional theory. Our data are consistent with a direct band gap for In$_2$O$_3$. © 2009 American Institute of Physics. [DOI: 10.1063/1.3070524]

Indium oxide (In$_2$O$_3$) and Sn-doped In$_2$O$_3$ are important optoelectronic materials. Early experimental work suggested that In$_2$O$_3$ has a direct band gap of 3.75 eV, although a weaker absorption onset at 2.62 eV was also observed and tentatively assigned to indirect transitions. However, ab initio band structure calculations have consistently failed to find the pronounced upward dispersion of the topmost valence bands required by the indirect gap hypothesis. The “band gap” of In$_2$O$_3$ (presumed to be the lowest energy gap) has therefore been widely quoted to be approximately 3.75 eV, corresponding to the onset of strong optical absorption. On the other hand, the valence band onset in photoemission experiments on nominally undoped In$_2$O$_3$ is found about 2.8 eV below the Fermi level, a value inconsistent with a band gap of 3.75 eV. Recent theoretical work has shown that the separation between weak and strong optical onsets arises from the fact that transitions from the first six valence bands into the conduction band (CB) are either symmetry forbidden or have very low dipole intensity and has set an upper limit of 2.9 eV for the band gap of In$_2$O$_3$.

We report here a resonant x-ray emission spectroscopy (RXES) study of the electronic structure of In$_2$O$_3$. This technique involves coupled x-ray absorption and x-ray emission processes and is used here to investigate the O 2p partial density of states (PDOS), below and above the Fermi level of In$_2$O$_3$. RXES was also used to probe the bulk valence band dispersion of In$_2$O$_3$. We directly compare the experimental spectra with hybrid density functional theory (DFT) calculations of the band structure. We find excellent agreement between the x-ray absorption and emission spectra and the calculated O 2p PDOS. Furthermore, examination of the resonant emission spectra provides evidence of a lack of an indirect band gap, in agreement with the DFT calculations.

In$_2$O$_3$ thin films were grown by radio frequency magnetron sputtering onto doped Si substrates to a thickness of 400–500 nm using pure Ar as the sputter gas and a 400 °C substrate temperature. Carrier concentrations were estimated as $n = 3 \times 10^{19}$ cm$^{-3}$ from transport measurements.

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Band structure calculations of bcc bixbyte structure $\text{In}_2\text{O}_3$ were performed within the framework of hybrid DFT using the recently proposed HSE03 functional for exchange and correlation. All the calculations are performed using the Vienna \textit{ab initio} simulation package (VASP), and the projector augmented wave (PAW) method has been used to model the electron-ion interaction. The hybrid functionals allow for an approximate treatment of the quasiparticle effects, while the PAW method yields all-electron wave functions. Further details can be found elsewhere.

Figure 1 presents (i) the O $K$-edge XES spectrum recorded with excitation energies above the absorption threshold, (ii) the O $K$-edge XAS spectrum, and (iii) the valence band (VB) XPS spectrum, all plotted on a common binding energy scale. The XPS spectrum agrees with recent measurements of high quality $\text{In}_2\text{O}_3(100)$ samples reported elsewhere. We note that the location of the valence band peak ($\sim 4.5\text{ eV}$ below $E_F$) for both XES and XPS are in agreement. We observe a peak in the O $K\alpha$ XES spectrum at 17 eV below $E_F$. This lies at the binding energy of the In 4$d$ shallow core level and is due to In 4$d$–O 2$p$ hybridization. The sensitivity of XES to hybridized states has been well established in metal oxides.

Also included in Fig. 1 is the computed total DOS and O 2$p$ PDOS of bixbyte $\text{In}_2\text{O}_3$, calculated within the DFT-HSE03; these are plotted below VB-XPS and the normalized O $K$-edge XES and XAS spectra, respectively. The occupied and unoccupied contributions were first convoluted separately with a Gaussian with widths of 0.37 and 0.20 eV, respectively, corresponding to the experimental energy resolutions of the XES and XAS spectra. This enabled a fairer comparison with the experimental spectra. To obtain a common binding energy axis, the O 2$p$ PDOS was then rigidly shifted to match the VB peaks of both the XPS and XES. An additional shift of $-1\text{ eV}$ was required for the unoccupied PDOS due to the influence of the core hole with the final state of the XAS process, providing an estimate of the core-hole binding energy. The experimental spectra are well reproduced by the first principles calculation, most notably: the location of the calculated In 4$d$–O 2$p$ hybrid states and the XAS spectral shape.

For weakly correlated systems and excitation energies close to the absorption edge, resonance effects are known to influence the shape of the emission spectra due to $k$-selectivity. As a result, it is possible to evaluate the nature of the band gap and VB dispersion with RXES. For instance, RXES spectra of GaN, InN, and ZnO (Ref. 15) are consistent with direct band gaps and an upward dispersing VB. Figure 2 displays the raw RXES spectra of the O $K$ edge of $\text{In}_2\text{O}_3$, as a function of incident energy. As the incident energy is increased from the absorption onset to the main absorption peak, little or no change in the corresponding emission peak is observed. This is in contrast to the RXES spectra from the direct gap materials GaN, InN, and ZnO, where clear changes in the spectral shape and XES peak positions are observed.

Figure 3(a) displays the emission spectra for incident energies of $h\nu=530.2\text{ eV}$ and $545.0\text{ eV}$. These excitation energies correspond to the onset of O $K$-edge absorption
well above the threshold, respectively. The emission spectra were also divided by $E^3$ (where $E$ is the photon energy) to correct for the photon density of states’ contribution to the transition rate. The above-threshold emission spectrum corresponds to the incoherent contribution. If this is subtracted from the threshold emission spectrum, the difference is then the coherent contribution to the RXES. (The above-threshold emission spectrum was weighed to ensure the largest non-negative sum difference between the onset and above-threshold emission spectra.) This difference spectrum is also plotted in Fig. 3(a). Figure 3(b) displays the DFT+HSE03 band structure near the Brillouin zone center of bcc In$_2$O$_3$ ($\Gamma$-H high symmetry points). The onset of the absorption spectrum corresponds to the CB maximum, which lies at the zone center (i.e., the $\Gamma$-point). As a result, the coherent k-selective contribution to the onset RXES spectrum corresponds from the $\Gamma$-point. No difference is observed between the spectral shape and energetic position of the coherent RXES (near the $\Gamma$-point) and the above-threshold RXES. Referring to the DFT in Fig. 3(b), this is consistent with the VB maximum (VBM) being located at the zone center. We note that this finding is in contrast to our results from CdO which has an indirect gap, where the combination of the $pd$-repulsion and crystal symmetry results in a significant difference between the VBM and VB near the $\Gamma$-point.

In conclusion, the electronic structure of In$_2$O$_3$ has been investigated by XES, XAS, XPS, and RXES. Direct comparison between the O K-edge XES and XAS, and the hybrid DFT calculated O 2p PDOS reveals excellent agreement in terms of the spectral shape and the relative peak positions. The O K-edge RXES results experimentally rule out the possibility of an indirect band gap.

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