

## Supplementary information for: Mid-wave to near-IR optoelectronic properties and epsilon-near-zero behavior in indium-doped cadmium oxide

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### Additional Discussion of In:CdO and Y:CdO Orbital Hybridization

Density functional theory (DFT) calculations would most directly support the claim of better hybridization of In-donor and CdO-conduction-band-edge states compared to Y-donors. While this is beyond the scope of this manuscript, first-principles calculations by Yang, *et al.* support this reasoning.[1] Aside from this, a simpler approach is to compare electron affinities of CdO (5.9 eV), In<sub>2</sub>O<sub>3</sub> (5.5 eV), and Y<sub>2</sub>O<sub>3</sub> (2eV). [2]–[4] These values describe how the metal orbitals which dominate the conduction band edge behave in a high-oxygen-coordination environment.

In:CdO and Y:CdO are “dilute alloys” of CdO and In<sub>2</sub>O<sub>3</sub> or CdO and Y<sub>2</sub>O<sub>3</sub>, respectively. To fabricate In:CdO, two oxides with similar electron affinities are combined, so their conduction band (CB) edges are close in energy. Further, the CB edges are similar in orbital type because In and Cd have closed d shells and two 5s valence electrons (In also has a 5p valence electron). The similarity in orbital type and energy enables In and Cd orbitals to hybridize readily in In:CdO such that the bottom of the CB will have strong In and Cd character. This hybridization likely allows a higher solubility limit for In in CdO than Y in CdO, enabling higher carrier density.

Conversely, Y:CdO fabrication brings together two oxides with CB edges that are vastly different in energy and orbital type (Y has two 5s electrons, but also one 4d valence electron—d orbitals are much different from s and p orbitals). These differences inhibit Y and Cd orbitals from readily hybridizing in Y:CdO, so the bottom of the CB will not have strong Y character. In other words, to an electron moving along the CB of Y:CdO, the electronic landscape “looks like” undoped CdO. Effectively, more electrons are introduced to CdO by doping, but the electronic structure near the CB remains more or less the same, as if no doping has occurred. This may explain the higher peak mobility in Y:CdO than In:CdO. This concept is analogous to “modulation doping” in semiconductor devices where dopants are spatially separated from the carriers to improve mobility and reduce impurity scattering. Here, dopants are not separated in real space, but rather reciprocal space.

## Additional Figures

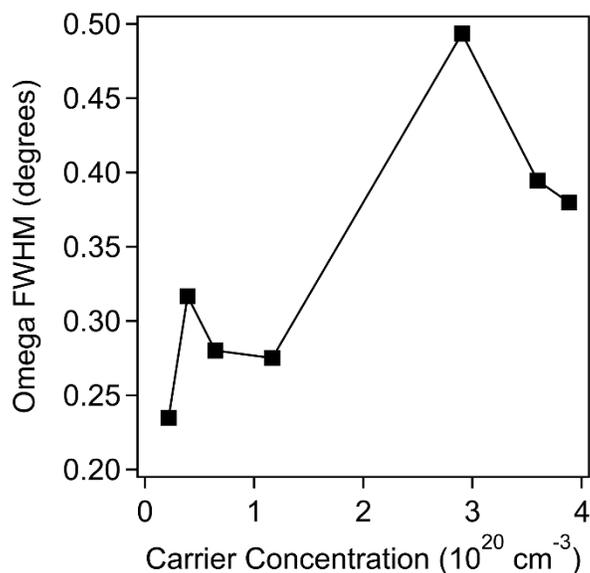


FIG. S1. FWHM (degrees) of XRD omega scans as a function of carrier concentration.

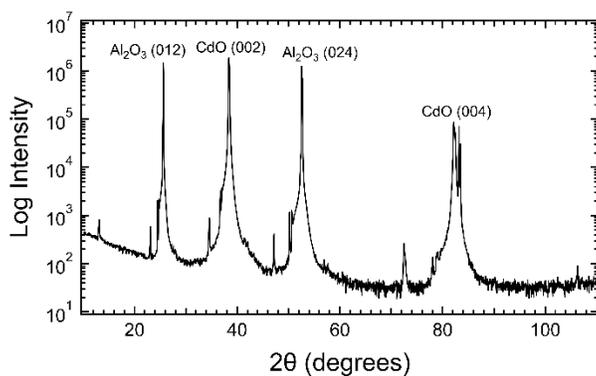


FIG S2. Wide angle  $\theta - 2\theta$  XRD scans for high-doped In: CdO ( $3.9 \times 10^{20} \text{ cm}^{-3}$ ) spanning 10 to 110 degrees, aligned to the film surface. Data represents entire doping series and confirms the absence of secondary phase formation.

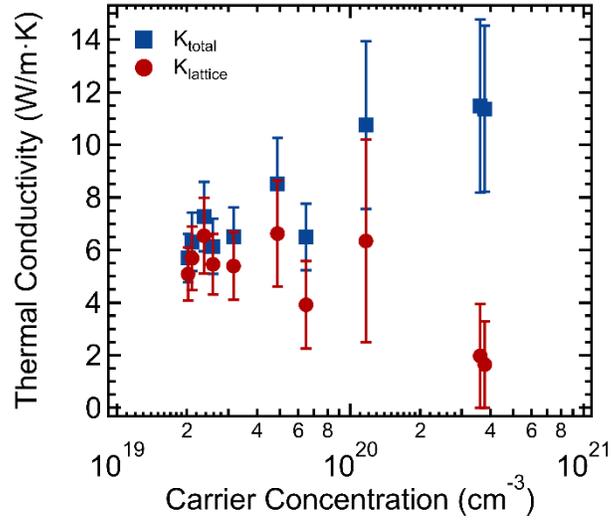


FIG. S3. Out-of-plane thermal conductivity ( $\kappa_{\text{total}}$ ), and lattice contribution of thermal conductivity ( $\kappa_{\text{lattice}}$ ), for the In:CdO dopant series.

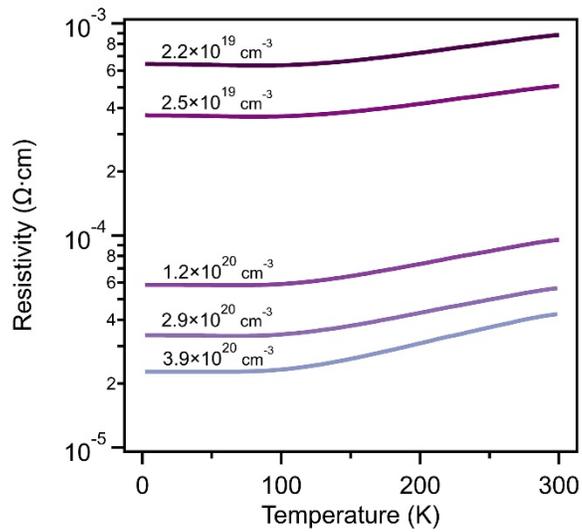


FIG. S4. Hall resistivity  $\rho_{xx}(B = 0)$  vs. temperature for the In:CdO series. The annotated carrier concentrations are measured at room temperature on an Ecopia Hall measurement system.

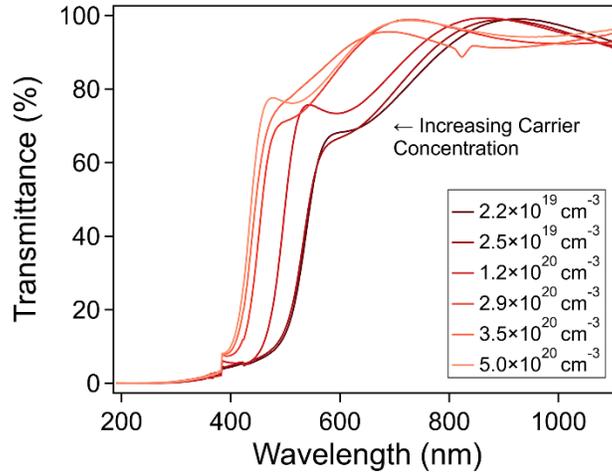


FIG. S5. UV-VIS transmittance spectra for In:CdO thin films showing a shift in the optical absorption threshold with increasing doping. The discontinuity present in all of the spectra at a wavelength of 380 nm (3.26 eV) is due to an automatic filter change in the spectrophotometer used to collect the data. The dip in the  $3.52 \times 10^{20} \text{ cm}^{-3}$  sample is likely due to an intrinsic absorption.

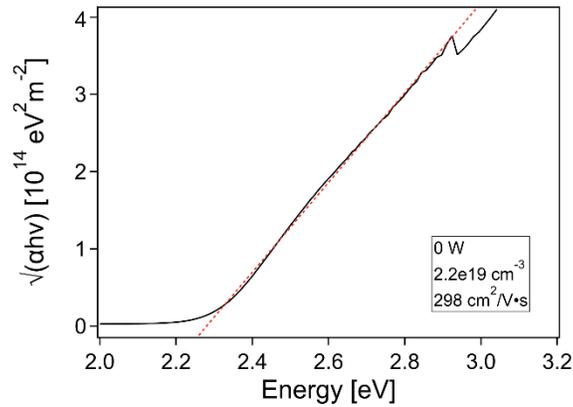


FIG. S6. Tauc plot for In:CdO with carrier concentration of  $2.17 \times 10^{19} \text{ cm}^{-3}$  with linear fit overlaid.

## Optical Bandgap Calculations

Optical bandgap,  $E_g^{opt}$  is determined through Tauc's Law[5],

$$\alpha hv \sim (hv - E_g^{opt})^r$$

where  $hv$  is the photon energy,  $r$  is set to 2 for direct allowed transitions,[6]–[8] and  $\alpha = \frac{A}{d}$  is the absorption coefficient ( $d$  is sample thickness and  $A$  is absorbance determined by the Bouguer-Lambert-Beer's Law  $A = 100 \log_{10} \frac{100}{T\%}$ ).  $E_g^{opt}$  is determined as the intercept on the abscissa of the line tangent to the  $(hv - E_g^{opt})^r$  curve as function  $\alpha hv$ .

## II. References

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