Accelerated optimization of transparent, amorphous zinc-tin-oxide thin films for optoelectronic applications


1) Department of Physics, Applied Physics and Astronomy, Binghamton University, Binghamton, New York 13902, USA
2) Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, United Kingdom
3) Department Structure and Dynamics of Energy Materials, Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner-Platz 1, 14109 Berlin, Germany
4) Stephenson Institute for Renewable Energy, University of Liverpool, Liverpool, L69 7ZF, United Kingdom
5) University College London, Department of Chemistry, 20 Gordon Street, London, WC1H 0AJ, United Kingdom
6) Materials Science and Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, United States
7) Department of Materials, Imperial College London, Exhibition Road, London SW7 2AZ, United Kingdom
8) Materials Science & Engineering, Binghamton University, Binghamton, New York 13902, USA

Supplementary Figure 1a shows a photo of a 10 x 10 cm ZTO thin film on glass, cut into 25 pieces of 2 x 2 cm for experimental measurements. The film was grown using co-deposition of a SnO$_2$ and a ZnO target, with the SnO$_2$ target positioned towards the upper right-hand corner and the ZnO target near the lower left-hand corner. Supplementary Figure 1b shows a photo of a ZTO film grown using the same growth parameters, but cut into only 4 pieces for scanning XPS measurements. Variations in the optical band gap can be observed with the naked eye, with most of the film appearing completely transparent while the tin-poor, lower left-hand corner possess a slightly brown tint. This pattern of coloration agrees well with all of the experimentally determined band gap evolution across the film.

FIG. 1. Photograph of ZTO thin film. a, Photo of a 10 x 10 cm ZTO thin film on glass, cut into 25 pieces for most experimental measurements. b, Photo of a 10 x 10 cm ZTO thin film on glass, cut into 4 large pieces for scanning XPS and ellipsometry measurements.

Supplementary Figure 1a shows a photo of a 10 x 10 cm ZTO thin film on glass, cut into 25 pieces of 2 x 2 cm for experimental measurements. The film was grown using co-deposition of a SnO$_2$ and a ZnO target, with the SnO$_2$ target positioned towards the upper right-hand corner and the ZnO target near the lower left-hand corner. Supplementary Figure 1b shows a photo of a ZTO film grown using the same growth parameters, but cut into only 4 pieces for scanning XPS measurements. Variations in the optical band gap can be observed with the naked eye, with most of the film appearing completely transparent while the tin-poor, lower left-hand corner possess a slightly brown tint. This pattern of coloration agrees well with all of the experimentally determined band gap evolution across the film.

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Electronic mail: lpipe@binghamton.edu
FIG. 2. Compositional mapping comparison. a, The predicted Sn:Zn ratio based on ellipsometry of separate SnO$_2$ and ZnO depositions. b, The measured Sn:Zn ratio from scanning XPS measurements on the co-deposited film.

Supplementary Figure 2 shows the Sn:Zn ratio variation predicted by combining ellipsometry measurements taken on separate SnO$_2$ and ZnO reference films (Supp. Fig. 2a), and the Sn:Zn ratio variation measured using scanning XPS on the actual co-deposited ZTO film (Supp. Fig. 2b). The two plots show relatively good agreement in terms of the compositional evolution across the film.
Supplementary Figure 3 shows the ZTO film thickness variation predicted by combining ellipsometry measurements taken on separate SnO$_2$ and ZnO reference films (Supp. Fig. 3a), as well as the thickness variation measured using ellipsometry on the actual co-deposited ZTO film (Supp. Fig. 3b). The two plots show relatively good agreement in terms of the thickness evolution across the film, however the co-deposited film appears slightly thicker on average than was predicted.

FIG. 3. Thickness mapping comparison. a, The predicted film thickness based on ellipsometry of separate SnO$_2$ and ZnO depositions. b, The measured film thickness from ellipsometry measurements on the co-deposited film.
FIG. 4. Example analysis of optical transmittance and reflectance data. a, Transmittance and b, reflectance spectra for select points across the 10 x 10 cm deposition area, including SnO$_2$, ZnO, and glass substrate references. c, Optical absorption coefficients calculated using the transmittance and reflectance spectra. d, An example of the fitting performed on the transmittance spectra. e, The interference-free transmittance spectra and f, indices of refraction resulting from the fitting.

Supplementary Figure 4a shows some example transmittance spectra taken across the ZTO film, with very high optical transparency observed for all compositions. The spectra show that the optical band gap decreases as tin percentage decreases. It can be observed in Supplementary Figure 4b that the thick glass substrate (Glass ref.) has a non-negligible optical reflection and some absorption which must be considered during the optical analysis. To isolate the optical properties of the thin a-ZTO film, the raw optical transmittance spectra were divided by the substrate reference spectra to normalize the data, and then multiplied by 100 to convert the values back to percentages.

In addition to substrate effects, strong Fabry-Perot oscillations are observed in the spectra due to thin film interference effects. The period of these oscillations is dependent on the thickness and index of refraction of the thin film,
and the magnitude is dependent on film uniformity. To remove the effects of the Fabry-Perot oscillations from our optical data when creating Tauc plots, both reflectance and transmittance measurements were utilized. The absorption coefficients ($\alpha$) were calculated using the thin film approximation, $T \approx (1 - R)^2 e^{-\alpha d}$, where $T$ is the corrected transmittance, $R$ is the corrected reflectance, and $d$ is the film thickness. Due to imperfect calibration of the spectrometer, the relative scaling of reflectance and transmittance measurements resulted in an incomplete removal of the Fabry-Perot oscillations from the absorption coefficient spectra. As such, a scaling factor, $S$, was introduced into the calculations as follows: $T \approx (1 - SR)^2 e^{-\alpha d}$. This artificial scaling factor was adjusted until complete removal of the Fabry-Perot oscillations was achieved and the resulting absorption coefficients tended to zero at energies below their respective absorption onsets. These corrected spectra were then used to determine the average optical absorption at wavelengths 420, 490, 560, 630, and 700 nm, used when calculating the film’s Figure of Merit (FOM) values. The calculated absorption coefficients used to produce Tauc plots are then shown in Supplementary Figure 4c.

The film thicknesses used to create Tauc plots from the UV-Vis measurements were determined using ellipsometry. However, thicknesses for select points across the ZTO film were also determined from the UV-Vis measurements themselves and found to compare very well to the ellipsometry determined values. Fitting was performed to determine film thickness and index of refraction following the method described by Swanepoel. Supplementary Figure 4d shows an example of the fitting that was performed. The transmittance spectra were fit with the following function,

$$T = \frac{Ax}{B - Cx \cos(\phi) + Dx^2} \tag{1}$$

where

$$A = 16n^2s \tag{2a}$$
$$B = (n + 1)^3(n + s^2) \tag{2b}$$
$$C = 2(n^2 - 1)(n^2 - s^2) \tag{2c}$$
$$D = (n - 1)^3(n - s^2) \tag{2d}$$
$$\phi = \frac{4\pi nd}{\lambda} \tag{2e}$$
$$x = \exp(-\alpha d) \tag{2f}$$

For these fittings, the film index of refraction ($n$), substrate index of refraction ($s$), and absorption coefficient ($\alpha$) were all treated as functions of wavelength. $n(\lambda)$ was approximated as a double exponential, as this function was found to fit reference SnO$_2$ and ZnO index of refraction data reasonably well within the wavelength range of interest. $s(\lambda)$ was calculated from reference spectra taken on a clean piece of substrate glass. $\alpha(\lambda)$ was approximated as the addition of absorption coefficients relating to allowed and forbidden direct transitions, indirect transitions, and transitions between band tails with independent scaling factors provided for each coefficient.

Following this fitting, the envelope functions were calculated using the follow equations,

$$T_m(\lambda) = \frac{Ax}{B + Cx + Dx^2} \tag{3}$$
$$T_M(\lambda) = \frac{Ax}{B - Cx + Dx^2} \tag{4}$$

where $T_m$ and $T_M$ are the minimum and maximum envelope functions, respectively. These envelope functions were then used to calculate interference-free transmittance spectra, $T_\alpha(\lambda) = \sqrt{T_M T_m}$, shown in Supplementary Figure 4e.

The indices of refraction resulting from the fitting procedure are shown in Supplementary Figure 4f. The indices for the reference films agree well with literature references. These fitting results suggest that across the compositional range investigated herein, ZTO possesses an index of refraction closer to that of pure ZnO than that of SnO$_2$. 
Supplementary Figure 5 shows the variation in optical band gap across the ZTO film determined from Tauc plots when treating the film as a direct band gap material (Supp. Fig. 5a), and an indirect band gap material (Supp. Fig. 5b). Plotting the data in these two different ways can provide valuable information about the structure of the absorption edge for an amorphous material.

Treating a semiconductor as a direct band gap material scales the Tauc plot in such a way as to emphasize the strong absorption, while treating it as an indirect material will emphasize any weak absorption below the main absorption edge. Subgap states are likely to contribute only weakly to the optical absorption at energies below that of the main absorption edge. As such, a large difference between the "direct" and "indirect" band gap is an indicator of transparency reducing subgap states in an amorphous semiconductor. Therefore, these plots indicate that the tin-rich corner of the ZTO film is far more likely to possess transparency reducing subgap states.
FIG. 6. **Thickness mapping extrapolation.** a, The measured film thickness from ellipsometry measurements on the co-deposited film. b, The film thickness extrapolated out to the edges of the deposition area.

Supplementary Figure 6 shows the ZTO film thickness as measured (Supp. Fig. 6a) and extrapolated to the edges of the deposition area (Supp. Fig. 6b) for use in calculating resistivity values from the measured sheet resistance values. The extrapolation was performed assuming a continuous and smoothly varying film thickness, as is observed in the optical color banding due to thin film thickness variations in Supp. Fig. 1a and 1b. Resistivity was calculated using the following simple formula: $\rho = R_S \times T$, where $\rho$ is resistivity, $R_S$ is sheet resistance, and $T$ is film thickness.
FIG. 7. Resistivity and Hall measurement points. a, Contour map of the resistivity across the $10 \times 10$ cm deposition area measured using 4-point probe measurements, with the measurement points identified. b, Resistivity of select $1 \times 1$ cm sample pieces from Hall measurements.

Supplementary Figure 7a shows the resistivity variation across the ZTO film measured using a 4-point probe system. The actual points at which measurements were taken are identified. Points that were too resistive to measure with our probe system (out of range) were assigned the maximum measurable resistivity of $2000 \ \Omega \cdot \text{cm}$ for the purposes of creating the contour map.

Although the non-uniformity across the deposition area (both thickness and composition) combined with the amorphous nature of the films makes Hall measurement results unreliable, select areas of the film were cut into $1 \times 1$ cm sample pieces for Hall measurements. Au/Ti contacts were deposited on the corners of each square sample via electron beam deposition in order to perform Hall measurements using a Van der Pauw Ecopia HMS-3000 Hall Measurement System. As shown in Supplementary Figure 7b, the resistivity values obtained from these measurements agree fairly well with the values from the 4-point probe measurements, with the areas too resistive to be measured by 4-point probe also being too resistive for measurement by the Hall system.

The obtained bulk concentration and Hall mobility values have a large uncertainty, as expected due to issues caused by the marked non-uniformity of the film across sample areas. However, a clear trend can still be observed from the general magnitudes of the values. The tin-rich region is found to have a Hall mobility around $10 \ \text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ and a bulk concentration around $10^{17} \ \text{cm}^{-3}$, while the highly resistive tin-poor region possesses higher mobilities but also orders of magnitude lower bulk concentrations ($10^{14} - 10^{16}$). In contrast, despite the much lower resistivities/higher conductivities, the low resistivity tin-poor region possesses mobilities and carrier concentrations comparable that of the tin-rich region.

The full results of the Hall measurements are given in the following table.

<table>
<thead>
<tr>
<th>X (cm)</th>
<th>Y (cm)</th>
<th>Approx. Thickness (nm)</th>
<th>Sheet Resistance ($\Omega \cdot \text{sq}^{-1}$)</th>
<th>Resistivity ($\Omega \cdot \text{cm}$)</th>
<th>Conductivity ($\text{S} \cdot \text{cm}^{-1}$)</th>
<th>Bulk Concentration ($\text{cm}^{-3}$)</th>
<th>Mobility ($\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.5</td>
<td>7.5</td>
<td>520</td>
<td>$3.37(7) \times 10^9$</td>
<td>175(4)</td>
<td>$5.7(1) \times 10^{-4}$</td>
<td>$-0.5(10) \times 10^{17}$</td>
<td>9(4)</td>
</tr>
<tr>
<td>3.5</td>
<td>4.5</td>
<td>550</td>
<td>$1.024(5) \times 10^9$</td>
<td>563(3)</td>
<td>$1.775(9) \times 10^{-3}$</td>
<td>$-1.8(5) \times 10^{19}$</td>
<td>19(7)</td>
</tr>
<tr>
<td>3.5</td>
<td>3.5</td>
<td>565</td>
<td>$2.92(2) \times 10^9$</td>
<td>1652(1)</td>
<td>$6.05(5) \times 10^{-4}$</td>
<td>$-0.1(20) \times 10^{24}$</td>
<td>30(20)</td>
</tr>
<tr>
<td>1.5</td>
<td>3.5</td>
<td>590</td>
<td>$1.274(2) \times 10^9$</td>
<td>7.52(1)</td>
<td>$1.330(2) \times 10^{-4}$</td>
<td>$-0.6(10) \times 10^{18}$</td>
<td>0.8(4)</td>
</tr>
<tr>
<td>1.5</td>
<td>2.5</td>
<td>630</td>
<td>$4.477(4) \times 10^4$</td>
<td>2.821(3)</td>
<td>$3.545(3) \times 10^{-1}$</td>
<td>$-5.9(2) \times 10^{17}$</td>
<td>3.7(1)</td>
</tr>
</tbody>
</table>
Supplementary Figure 8 shows Tauc plots for select Sn:Zn ratios created using UV-Vis spectra compared to Tauc plots created using optical constants calculated from hybrid DFT results. The calculated optical properties, i.e., the imaginary part of the frequency dependent dielectric tensor, have been obtained by summing over empty states using Fermi’s Golden Rule and transition matrix elements. Hybrid DFT calculations incorporating a percentage of Hartree-Fock exchange were employed to ensure a quantitatively accurate description of the band gap. In order to ensure converged results, the number of empty bands in the calculations have been increased by a factor of three. The real part of the dielectric tensor has been obtained by the Kramers-Kronig transformation. For each energy value the resulting real and imaginary dielectric tensors have been diagonalized and the final results have been obtained by averaging over the main diagonal matrix elements.

The band gap of the a-ZTO film is observed to increase as the tin concentration increases, with the a-SnO\textsubscript{2} reference clearly having the largest optical band gap. Additionally, a broadening of the absorption edge is observed in the a-ZTO and a-SnO\textsubscript{2} spectra, which is mostly consistent with exponential Urbach tail absorption due to structural disorder. However, the more tin-rich a-ZTO and a-SnO\textsubscript{2} display some additional absorption below the main absorption edge (denoted by a red arrow) that is more likely due transparency reducing subgap states.

While experiment and theory compare well for the tin-rich ZTO, the plots for tin-poor ZTO display striking differences. This is due to strong subgap state absorption in the theoretical results, which does not seem to exist in the real samples. This is likely due to a large overestimation of the prevalence of subgap states in tin-poor ZTO, due to the small, repeating unit cells that must be utilized for DFT calculations. Without this additional subgap state absorption the band gap values would compare far more favorably between experiment and theory.
FIG. 9. X-ray photoelectron spectroscopy raw data comparison. Comparison between raw XPS valence band spectra of select ZTO films (top) and the same spectra after applying a low-pass filter to remove high frequency noise (bottom).

High resolution XPS was performed across the sample area to compare to the low resolution XPS and HAXPES spectra. Measurements were performed using a laboratory based monochromated Al Kα source with a hemispherical analyzer located in the ADL at Binghamton University, with a pass energy of 23.5 eV, corresponding to an instrumental resolution of 0.51 eV determined from analyzing the Fermi edge and Au 4f7/2 peak of gold foil references. Energy calibration of the high resolution XPS spectra was performed using external Au references in electrical contact with the samples. A low-pass filter was applied to the XPS valence band and near-valence core level spectra to remove high frequency noise, as shown in Supplementary Figure 9. The parameters of the filter were chosen to remove as much noise as possible without broadening the features of interest. As the actual spectral features of the raw data (top) are much lower frequency than the high frequency noise, the filtered spectra (bottom) do not display any noticeable broadening. The removal of the noise simply makes it easier to visually see the important peak shifts.
FIG. 10. X-ray photoelectron spectroscopy core levels. XPS core level spectra of select points from high to low tin composition.

Supplementary Figure 10 shows the high resolution XPS core level spectra for select points from high to low tin composition across the ZTO film, including c-ZnO and a-SnO$_2$ for reference. The cation peak positions agree well with the shifts observed in the valence band/near-valence core levels. Below $\sim 25\%$ tin, the Sn 3d - Zn 2p energetic separation is found to abruptly decrease by $\sim 0.3 - 0.5$ eV.

Film oxygen content is found to follow the expected trend from a more oxygen rich, SnO$_2$-like ratio on the top right to a more one-to-one, ZnO-like ratio on the bottom left. However, over-oxidation and carbon contamination on the surface from atmospheric exposure after growth makes it difficult if not impossible to assign precise compositions using surface-sensitive XPS.
Supplementary Figure 11 shows the HAXPES core level spectra for select points from high to low tin composition across the ZTO film, including a-SnO$_2$ for reference. The cation peak positions agree well with the shifts observed in the valence band/near-valence core levels. Below $\sim 25\%$ tin, the Sn 3d - Zn 2p energetic separation is found to abruptly decrease by $\sim 0.3 - 0.5$ eV.
FIG. 12. **Optical band gap comparison.** Optical band gap evolution with changing Sn:Zn ratio determined using a, UV-Vis and b, ellipsometry, including a-SnO$_2$ and c-ZnO endpoints. Band gap trends including (red line) and excluding (gray dashed line) subgap absorption are extrapolated to the a-SnO$_2$ endpoints determined by including (gray circle) and excluding (white circle) weak absorption tailing during Tauc analysis. The compositional region where crystallization begins is indicated (blue hatching).

Supplementary Figure 12 shows the optical band gap evolution as determined by both UV-Vis and ellipsometry measurements. Both measurement methods show the same general data trend, however the ellipsometry shows a far greater spread. This spread seems to correlate with the film thickness shown by the coloration of the data points, with the thinner film resulting in a lower band gap and the thicker points a higher band gap. In addition, this spread seems to better follow the expected trend without subgap formation. These differences are likely due to the different ways the band gap is calculated between the two experimental methods.

The optical band gaps were determined from the UV-Vis measurements using the Tauc plot method, in which a line is fit to the optical absorption edge of the measured spectra. As subgap state absorption broadens this edge, it will therefore directly lower the optical band gap values determined via this method if subgap states exist in the material. In contrast, the optical band gaps were determined from ellipsometry by first fitting the data using a theoretical model. The optical parameters are then determined by this fit. As the model used to perform the fit represents an idealized situation, it may not properly account for subgap state absorption.
The partial density of states (PDOS) from DFT calculations for amorphous and crystalline ZnO are shown in Supplementary Figure 13. The PDOS shows little change to the actual structure of the bands other than broadening in the amorphous case due to disorder. However, the separation between the conduction and valence band is found to decrease. This agrees with the band gap values determined from optical measurements, wherein the tin-poor, amorphous ZTO was found to possess a slightly smaller band gap than that of the polycrystalline ZnO.