Structural and Physical Property Studies of Amorphous Zn–In–Sn–O Thin Films

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The structures in amorphous (α-) Zn, Sn co-doped In₂O₃ (ZITO) thin films grown by pulsed laser deposition on glass under varying oxygen pressure or with varying Sn:Zn ratios were determined using X-ray absorption spectroscopy and anomalous X-ray scattering. Typical structures around cations in α-ZITO films are described and compared with crystalline (c-) ZITO films. The results show that the Zn cations are four-fold coordinated with Sn–O bond lengths of 1.98 ± 0.02 Å, which is close to that in bulk ZnO. As a consequence, the second coordination shells around Zn contract. At longer distances away from Zn, the structure is commensurate with the averaged structure. The unit volume around In also contracts slightly compared to bulk In₂O₃, whereas the Sn–O bond length is similar to the one in bulk SnO₂. These unique structural characteristics may account for the films’ superior thermal stability over amorphous Sn-doped In₂O₃, and suggest that Zn and Sn act as network-forming cations. Like in c-ZITO, coordination numbers (N) around Sn, In, and Zn follow the order NSn > Nin > NZn. Unlike in c-ZITO, where electrical properties change significantly with a slight variation in the Sn:Zn ratio, this variation does not markedly alter the electrical properties, or the local structures, of α-ZITO films. Dramatic changes in the electrical properties occur for films grown under various oxygen pressures, which point to oxygen “defects” as the source of charge carriers.

I. Introduction

TRANSPARENT conducting oxides (TCOs) combine high electrical conductivity with optical transparency in the visible region, making them essential in transparent electrode applications. Due to the volatile nature of In₂O₃, it is industrially grown by sputtering of In–Sn targets. This growth method introduces structural disorder due to the electron mean free path, λ(k), and results in a spread of interatomic distances. Rᵢ. The EXAFS spectrum is analyzed via the equation

\[ \chi(k) = \sum_i \frac{N_i}{kR_i^2} \sin \left[ 2R_i k + \phi(k) + \frac{4}{3} C_3 k^3 \right] \times e^{-2R_i k/\lambda(k)} \]

where S₀, the intrinsic loss factor, and e⁻²Rᵢ/λ(k), the attenuation factor due to the electron mean free path, λ(k), are determined using a suitable reference material, and where e⁻²Rᵢk² is the Debye–Waller factor. fᵢ(k) and ϕ(k) are the backscattering amplitude and phase shift of traveling photo-electrons. Note that the angular dependence of Nᵢ is negligible in amorphous materials. The EXAFS third cumulant, C₃, can be used to account for the effect of an anharmonic potential on the measured interatomic distances. In practice, this parameter (or any other additional parameter) is only included if the quality of the fit is significantly increased by its use, which in this case indicates an asymmetric distribution at that atomic site. A Fourier transform of χ(k)
produces the pseudo-radial distribution function (p-RDF) around the absorbing atom.

Due to the limited length of $\lambda(k)$, often only the first coordination shell structure is measured by EXAFS in amorphous materials. Also, the phase complication caused by disorder renders it difficult to reliably determine coordination numbers. The anomalous X-ray scattering technique has proven to be unique, as well as complementary, to the EXAFS technique.\textsuperscript{17–19} It directly probes the electron density around a specific element and provides both short and medium range structural information without phase complication. For an X-ray scatter (i.e., a given atomic species), the scattering intensity is proportional to $f^2$, where $f$ is the scattering factor and is equal to $f_0 + f^\prime + if^\prime\prime$. The $f_0$ term is the normal atomic form factor (also known as the Thomson scattering factor), the $f^\prime$ term is associated with absorption, and the $f^\prime\prime$ term is the resonance of $f^\prime$, which is related optically by the Kramers–Kronig inversion. As a result, $f$ varies strongly around the absorption edge of an atomic species. This variation provides enough contrast between the scattering intensities measured near the absorption edge and, normally, at one or a few hundred electron volts below the absorption edge that the difference of these two measurements allows one to obtain a differential structure factor (DSF). The Fourier transform of the DSF produces a unique, as well as complementary, to the EXAFS technique.\textsuperscript{17} The anomalous X-ray scattering technique has proven to be useful and has been applied to many materials.\textsuperscript{18} Also, the phase complication caused by disorder appears to be independent of the cation composition. The coordination number around indium lies in the range of 5–6.\textsuperscript{32} Rosen et al.\textsuperscript{32} modeled various quasi-amorphous structures of In$_2$O$_3$ and ITO using molecular dynamics and saw that an increase in disorder resulted in a decrease in the average coordination number due to the appearance of 4- and 5-coordinated In and 3-coordinated oxygen. The Zn–O bond length in a-TCOs is also somewhat consistent at 1.95–1.97 Å, except for the same a-IGZO study\textsuperscript{30} (the Zn–O bond length was split at 1.91 and 2.10–2.12 Å) and one a-IZO study\textsuperscript{25} (the bond length was 2.02–2.03 Å). The Zn–O bond length is quite short versus the bond lengths in the crystalline counterparts, but matches well with the bond length in c-ZnO (1.96 Å). However, in ZnO, Zn is 4-coordinated. It should be noted that in most a-TCOs studied to date, with the two exceptions mentioned above (a-IGZO, a-IZO), Zn was found to be 4-coordinated. These studies provide a basis of comparison for the results of the present work.

### III. Experimental Procedure

#### (1) Thin Film Preparation

Amorphous ZITO thin films were grown by pulsed laser deposition (PLD) on -10 mm × 10 mm glass substrates at room temperature. A 248 nm KrF excimer-laser was operated at 2 Hz with 25-ns pulse duration and pulse energy of 200 mJ/pulse. The beam was focused to a 1 mm × 2 mm spot. To prevent local heating, the target was rotated at 5 rpm and the laser beam was rastered. The target-substrate separation was fixed at 10 cm. A dense, hot-pressed, ceramic ZITO target with a metallic composition of 70.3 at.% In, 13.4 at.% Sn and 16.3 at.% Zn was used. A series of three films were grown under varying deposition oxygen pressure (0.5, 7.5, and 15 mTorr) for measurement by XAS. Two more films were grown at 7.5 mTorr with the use of a second target (dense SnO$_2$) to slightly increase Sn concentration. The metallic compositions of the ZITO target and films were measured via electron dispersive X-ray analysis (EDX) in a scanning electron microscope (Hitachi S4500; Tokyo, Japan). Multiple measurements of the ZITO target gave a compositional standard deviation of 1 at.% Sheet resistance, carrier type, area carrier concentration, and carrier mobility of the films were measured via a Hall measurement system (Bio-Rad Microscience LTD HL5000) in the Van der Pauw configuration with a 0.320 Tesla field. The carrier density and resistivity were obtained by dividing the area carrier concentration and the sheet resistance by the film thickness, respectively. Film thicknesses were measured using a spectrometer reflectometer (Filmetrics F20; San Diego, CA) and were shown to range from 260–290 nm for thin films measured by EXAFS. X-ray diffraction (XRD) measurements (Rigaku ATX-G Workstation; Tokyo, Japan) were used to verify a lack of long-range order in the films.

#### (2) Composition and Electrical Property Characterization

The metallic compositions of the ZITO target and films were measured using energy dispersive X-ray analysis (EDX) in a scanning electron microscope (Hitachi S4500; Tokyo, Japan). Multiple measurements of the ZITO target gave a compositional standard deviation of 1 at.% Sheet resistance, carrier type, area carrier concentration, and carrier mobility of the films were measured via a Hall measurement system (Bio-Rad Microscience LTD HL5000) in the Van der Pauw configuration with a 0.320 Tesla field. The carrier density and resistivity were obtained by dividing the area carrier concentration and the sheet resistance by the film thickness, respectively. Film thicknesses were measured using a spectrometer reflectometer (Filmetrics F20; San Diego, CA) and were shown to range from 260–290 nm for thin films measured by EXAFS. X-ray diffraction (XRD) measurements (Rigaku ATX-G Workstation; Tokyo, Japan) were used to verify a lack of long-range order in the films.

The parent compound of the ZITO solid solution is In$_2$O$_3$, which has the bcc bixbyite structure (space group Ia$3$, number 206).\textsuperscript{20} Bixbyte is a fluoride-derivative structure with one quarter of the anions missing, resulting in a periodic structure with “structural vacancies” (oxygen interstitial positions). The unit cell has 80 atoms, 32 of which are indium cations. The cations are split between the b-sites (8 atoms, 25%) and the d-sites (24 atoms, 75%). All indium cations are surrounded by six oxygen atoms and two structural vacancy (interstitial) positions. At the b-sites, the structural interstitial positions sit at body diagonal positions such that six oxygen atoms are equidistant at 2.18 Å. At the d-sites, the structural interstitial positions sit at face diagonal positions such that two oxygen atoms sit at each of three distances (2.13, 2.19, 2.23 Å). The coordination numbers of the first three shells are $N_1 = N_2 = N_3 = 6$ and the lattice constant is 10.117 Å.

In Sn-doped In$_2$O$_3$, Sn substitutes on In sites and acts as an electron donor.\textsuperscript{21–23} However, many of these donors form neutral associates with oxygen interstitials, (2Sn$\text{O}^\cdot$)/$2^\cdot$, in so-called Frank–Köstlin (F–K) clusters. These donors must be activated by reducing the material to remove oxygen from the interstitial positions. F–K clusters indicate that the first shell around Sn in this structure can be easily over coordinatized. The same clusters occur in c-ZITO.\textsuperscript{24}

Previous studies show that Zn and Sn are substitutional dopants (on In sites) for both bulk c-ZITO (In$_{2-x}$Sn$_x$Zn$_3$O$_3$, $x = 0.0, 0.2, 0.3, 0.4$)\textsuperscript{25} and thin film c-ZITO.\textsuperscript{30} However, due to the smaller ionic radii of Zn and Sn, they have smaller cation-oxygen bond lengths. In both bulk and film, the In–O bond length was 2.16 Å, which is very close to that of In$_2$O$_3$. In contrast, the Zn–O bond distance in bulk was 2.08 Å and in the thin film, ranged from 2.04–2.18 Å. In both materials, the disorder around Zn was high. In bulk, the Sn–O bond length was 2.08 Å and in the thin film there were two distances, at 2.08 and 2.25 Å. The disorder around Sn was similar to that around indium. In addition to these basic structures, a structural rearrangement was proposed in the thin film ZITO30 case, in which oxygen shifts from a site around Zn to a structural interstitial position around Sn. It also appears that in the thin film, Sn is likely over coordinatized by oxygen when not compensated by Zn, forming F–K-like clusters.

The local structures of other amorphous materials, such as In$_2$O$_3$,\textsuperscript{26} In–Zn–O (IZO)\textsuperscript{27–28} In–Ga–Zn–O (IGZO)\textsuperscript{29,30} and ZITO\textsuperscript{31} have been investigated by EXAFS and X-ray scattering combined with computational methods such as molecular dynamics, reverse Monte Carlo, and density functional theory. The In–O bond length is fairly consistent across these materials at 2.11–2.14 Å, the only exception being one a-IGZO study\textsuperscript{30} (the In–O bond length was 2.24–2.30 Å). In general, the bond length is consistently shorter than in the crystalline case and appears to be independent of the cation composition. The coordination number around indium lies in the range of 5–6.
(3) Synchrotron X-Ray Absorption Spectroscopy and Anomalous X-Ray Scattering

Synchrotron X-ray absorption and anomalous scattering measurements were made at the 5-BMD beamline of DND-CAT at the Advanced Photon Source (APS) of Argonne National Laboratory (Argonne, IL). The XAS data were collected by measuring the Zn-Kα, In-Kα, and Sn-Kα fluorescence emissions from a-ZITO thin films using a Canberra 13-element Ge solid state detector with an incident X-ray angle θ = 45° with respect to the sample surface. A S(111) double crystal monochromator was used. Two of the a-ZITO thin films were also measured at low temperatures in a modified Advanced Research System dispex. Powder ZnO, In₂O₃, and SnO₂ were used as reference materials, for which the XAS data were collected in transmission mode. Reference powders were uniformly spread over Scotch tape and an appropriate number of tape layers were stacked to achieve statistically sound absorption. For the ZnO layers, caution was taken with regard to sample uniformity, since fewer layers were used due to low X-ray energies. The small-beam X-ray survey over the layered sample shows negligible variation in the transmitted intensities. Ion chambers (Oxford-Danlyksi; Taastrup, Denmark) were used to monitor both the incident and transmitted X-ray intensities (I₀ and Iₗ), and were filled with gases in proportions of Ar:Ne=16:540 Torr for I₀ and 36:1360 Torr for Iₗ, respectively.

The XAS data were analyzed with the ATHENA software packages. The S₀ values for Zn, In, and Sn were obtained using reference powders: S₀ ≈ 0.9 for wurtzite ZnO and S₀ ≈ 1.0 for rutile SnO₂ and bixbyite In₂O₃. These values all match well with those previously reported. The S₀ values were then fixed in the data fitting. The structural model used to fit the a-ZITO films was a cluster of the bixbyite structure with a radius of 6 Å centered on the absorbing atom (In, Sn, or Zn). A Hanning window function was used in the Fourier transforms and data fitting. The stability of the fitting results was tested by varying the data range, which aided in error estimation as well. The results presented here were obtained using the EXAFS data in the k ranges from 3.268 to 11.091 Å⁻¹ for the In K-edge, 3.511 to 11.555 Å⁻¹ for the Sn K-edge, and 2.463 to 11.080 Å⁻¹ for the Zn K edge. Fittings were carried out in R space from 1.0 to 2.1 Å for the In K-edge and from 1.0 to 2.12 Å for both the Sn and Zn K-edges.

The Zn K-edge XANES calculations were carried out using the FDMNES code in dipolar approximation. This code includes two approaches: the full-multiple-scattering (FMS) and the finite difference method (FDM). They differ in the cluster potential constructions. The FMS approach utilizes the spherical muffin-tin (MT) approximation, whereas the FDM approach utilizes a non-muffin-tin (NMT) numerical potential set on an equally spaced 3D-grid with a period of 0.25 Å. The FDM approach is sensitive to the geometrical details and can be carried out in a reasonable time for a small cluster, whereas the FMS computing is more rapid. The results from the FDM calculations are presented here. Electronic configurations of neutral Zn and In atoms were used in all the calculations; the Sn atoms were approximated by In ones. Except for the Fermi energy, which is determined self-consistently, the default parameters were used.

Anomalous X-ray scattering from the thicker a-ZITO film was measured around the Zn K-edge using a 4-element Si-drift detector (SII) mounted on the two theta (2θ) arm of a four-circle Huber diffractometer (Rimsting, Germany). The film was placed with the longer side along the X-ray beam. The measurements were carried out in glancing angle geometry with the X-ray incidence angle set near the critical angle so that no scattering from the substrate was seen. A vertically focused X-ray beam was employed for scattering experiments. The beam size was further defined by two pairs of Huber slits to height × width = 0.1 mm × 8 mm. The X-ray pulses were analyzed using the XMAP X-ray digital processing electronics (X-ray Instrument Associates; Hayward, CA). The peaking time was set at 1 μs, which is sufficiently fast for weak scattering from amorphous films. Therefore, no dead-time correction was needed. The four Si elements are squarely arranged, for which a double slit system was designed to separate the detectors into two pairs, each of which had a defined scattering angle (2θ). The angular offset between these two pairs of detectors was measured and applied to the collected data before merging them. For the measurements near the absorption edge, the Zn-Kα emissions were collected simultaneously in a separately defined range of interest (ROI). The ratio of Kβ/Kα was also measured using the photons 1 keV above the absorption edge, and was used to eliminate the Kβ content in the scattering intensities measured near the edge. For scattering measurements, the ROI was set large enough to include all the Compton scattering through the 20 span (2–154°).

Anomalous X-ray scattering data were processed using the Igor-Pro commercial software and the Rad-Grk+ package. The scattering factors and Compton scattering factors were obtained from tabulated values. The resonance terms f' and f″ were calculated from the XAS data measured on the film, and, for the Kramers–Kronig inversion, Sasaki's tabulated values were used to expand the data range to minimize the truncation effect. The relevant X-ray energies were 9558.6 and 9658.6 eV (2.5 eV below the Zn K-edge) with respective calculated f' values of –4.27 and –8.91 and calculated f″ values of 0.49 and 1.18. The details regarding the data processing can be found in Petkov.43

IV. Results

(1) Electrical Properties of a-ZITO Films

As described above, films were grown under varying oxygen pressures (pO₂) and with varying Sn:Zn ratios at room temperature. Tables I and II summarize pertinent film growth conditions or metallic composition and the resulting electrical properties. Varying oxygen pressure during growth has a strong effect on the electrical properties, as seen in previous work and in Table I: low pO₂ (0.5 mTorr) results in very low charge carrier concentration and mobility, midrange pO₂ (7.5 mTorr) maximizes both charge carrier concentration and mobility, and high pO₂ (15 mTorr) results in low charge carrier concentration, but maintains high mobility. Conversely, varying the donor-to-acceptor ratio (Sn:Zn) has a negligible effect on the electrical properties, unlike in c-ZITO, as seen in Table II. These properties will be discussed within the context of local structure below.

(2) Local Structures of a-ZITO

The XANES spectra for ZnO, the c-ZITO thin film, and the 12:14 a-ZITO thin film are shown in Fig. 1. These spectra are representative of all a-ZITO films. The Zn K absorption edges of a-ZITO, c-ZITO, and ZnO are well aligned, indicating that Zn cations have a charge state of 2+. The same is true for In and Sn K-edge XANES, suggesting that In is 3+ and Sn is 4+. The In and Sn K-edge XANES spectra contain no discernible features that would highlight the

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>0.5 mTorr</th>
<th>12:14 mTorr</th>
<th>p15 mTorr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>mTorr</td>
<td>0.5</td>
<td>7.5</td>
<td>15</td>
</tr>
<tr>
<td>σ</td>
<td>S/cm²</td>
<td>7</td>
<td>1457</td>
<td>342</td>
</tr>
<tr>
<td>Hall mobility</td>
<td>cm²/V s</td>
<td>1.4</td>
<td>49.5</td>
<td>53.0</td>
</tr>
<tr>
<td>n</td>
<td>1/cm³</td>
<td>2.9 × 10¹⁹</td>
<td>1.8 × 10²⁰</td>
<td>3.7 × 10¹⁹</td>
</tr>
</tbody>
</table>
difference between \textit{a-}ZITO and \textit{c-}ZITO. This is due in part to the core-hole broadening in In and Sn and instrumental broadening \([\Delta E/E = 1.33 \times 10^{-4}\) for Si(111)]\), which overshadow broadening caused by disorder. The Zn K-edge XANES features of \textit{a-}ZITO are markedly different, likely due to structural disorder. Modeling of this XANES spectrum will be presented later.

Figure 2 compares the phase-uncorrected \(p\)-RDFs of the 12:14 \textit{a-}ZITO film (left) and the \textit{c-}ZITO film\(^{15}\) (right) for all three K-edges. The dashed lines are the EXAFS modeling results. In comparison to \textit{c-}ZITO, only the first coordination shells were measured in \textit{a-}ZITO due to disorder. Therefore, modeling was focused on the first coordination shells using the phases and amplitudes generated by the FEFF code based on a bixbyte \textit{In}_2\textit{O}_3 cluster centered at Zn, Sn, or In, respectively. The bond lengths, coordination numbers, and \(\sigma^2\) values of all films except the \(p\)0.5 film are presented in Table III along with those of bulk oxides. The bond lengths, coordination numbers, and \(\sigma^2\) values of all films except the \(p\)0.5 film are presented in Table III along with those of bulk oxides. The bond lengths, coordination numbers, and \(\sigma^2\) values of all films except the \(p\)0.5 film are presented in Table III along with those of bulk oxides.

\begin{table}[h]
\centering
\caption{Electrical Properties of Films with Varying Sn:Zn Ratios Grown at 7.5 mTorr Oxygen Pressure}
\begin{tabular}{|l|c|c|c|}
\hline
Property & Units & 12:14 & 16:14 & 18:13 \\
\hline
In & at.\% & 74.6 & 70.9 & 69.1 \\
Sn & & 11.9 & 15.5 & 17.8 \\
Zn & & 13.5 & 13.6 & 13.3 \\
\(\sigma\) & S/cm & 1457 & 1226 & 1431 \\
Hall & cm\(^2\)/V-s & 49.5 & 48.4 & 46.7 \\
\hline
\end{tabular}
\end{table}

\[n = 1/cm^3 \times 1.8 \times 10^{20} \times 1.6 \times 10^{20} \times 1.9 \times 10^{20} \]

Given the strong correlation between \(N\) and \(\sigma^2\) \([\chi(k) \propto N \exp(-2\sigma^2k^2) = N(1-2\sigma^2k^2), \sigma^2k^2 \ll 1]\), a similar variation may occur in the \(\sigma^2\) values. Although the \(N\) values are generally smaller than those found in \textit{c-}ZITO,\(^{15}\) the relation of \(N_{\text{Sn}} > N_{\text{In}} > N_{\text{Zn}}\) is preserved for each sample, except for the \(p\)0.5 \textit{a-}ZITO film, which will be discussed later.

The bond lengths in \textit{a-}ZITO are generally shorter than those in \textit{c-}ZITO\(^{15}\) although the error bars overlap for the In-O bond. However, the consistency of the In-O bond length (2.14 \(\pm\) 0.02 Å) across samples and the agreement with values previously reported for amorphous In/O containing TCOs\(^{26,29}\) suggest the bond length is slightly shorter than that in \textit{c-}ZITO (2.17 \(\pm\) 0.03 Å). The \(\sigma^2\) value of the In–O bond is slightly larger in \textit{a-}ZITO (0.0069–0.0092) than in \textit{c-}ZITO (0.005–0.007). In addition, \(N\) around In is smaller in \textit{a-}ZITO (5.0 \(\pm\) 0.4) than in \textit{c-}ZITO (6–), which is also consistent with previously reported values.\(^{28,29}\) The Sn–O bond length (2.07 \(\pm\) 0.03 Å) matches well with that in bulk SnO\(_2\) (2.06 Å), both of which are similar to the shorter of the two bond lengths in \textit{c-}ZITO (2.06 Å). Achieving an acceptable fit of the Sn K-edge data required the use of a \(C_1\) parameter\(^{16}\) due to significant peak asymmetry. The use of this parameter affects the calculated bond length, so these effects are included in the reported bond lengths and error bars. The \(\sigma^2\) value around Sn is smaller than those around In and Zn in \textit{a-}ZITO.

The structure around Zn in \textit{a-}ZITO is different from that in \textit{c-}ZITO.\(^{15}\) The first coordination shell can be described satisfactorily by a single Gaussian distribution function centered at 1.98 \(\pm\) 0.01 Å, which is significantly shorter than the bond length in \textit{c-}ZITO (2.12 \(\pm\) 0.06 Å),\(^{15}\) but is very close to that in bulk SnO\(_2\) (1.96 Å). Moreover, the coordination number around Zn (3.3 \(\pm\) 0.2) appears to be significantly smaller than in \textit{c-}ZITO (4.7 \(\pm\) 0.6). These changes indicate a change to four-fold coordination around Zn cations in \textit{a-}ZITO as opposed to the five-fold-coordinated Zn, on average, that sits on an octahedral site in \textit{c-}ZITO.

Given the difficulties that EXAFS often presents in determining coordination numbers and the seemingly small coordination number around Zn obtained by EXAFS modeling, anomalous X-ray scattering was performed on the specially prepared (thicker) film similar in composition to the 12:14 film. Figure 3 compares the averaged PDF versus the \(d\)-PDF around a Zn atom. The Fourier transform was performed using scattering data up to \(q = 4\pi\sin(\theta)/\lambda = 9\) Å\(^{-1}\). Because there are no phase effects in PDFs, atomic distances can be obtained directly from the peak positions. However, due to the limited \(q\) range, the uncertainty is large. The Zn–O bond length (1.9 \(\pm\) 0.1 Å) is clearly shorter than the average metal (M)–O bond length in \textit{a-}ZITO (2.08 \(\pm\) 0.05 Å), thus supporting the EXAFS findings. In addition to the first coordination
shell, the higher coordination shell distances are clearly seen. The second shell distance around Zn (Zn–M or –O) is also shorter than the averaged one. At longer distances away from Zn, the structure becomes more commensurate with the averaged structure, which indicates no phase segregation of ZnO in the a-ZITO film. The radial distribution function (RDF) can be obtained from $G(R)$ using $4\pi R^2 P = 4\pi R^2 P_0 + R G(R)$, where $P$ is the density and $P_0$ is the average density. The peak areas in the RDF measure the electron densities and, thus, the coordination numbers. For a multi-element system, the integrated area of a RDF peak is approximately equal to the weighted sum of the coordination numbers. Using the scattering factors at $q = 0$, such a weighted sum in a-ZITO is estimated to be 9 if all cations are 6-coordinated (by oxygen anions) and all oxygen anions are 4-coordinated (by all cations), like in In$_2$O$_3$. If Zn is 4-coordinated, the weighted sum is 8. In contrast, the weighted sum of the coordination numbers is 10 if it is 6-coordinated. Therefore, the smaller first peak in the d-PDF compared to the PDF suggests $N < 6$ around Zn, which qualitatively supports the EXAFS results. More elaborate data simulation is necessary to quantify the Zn K-edge data.

EXAFS and anomalous scattering revealed the local structures in a-ZITO, but the local geometry, in particular around Zn, is not clear. Since XANES is sensitive to electronic structure and local geometry, detailed analysis of the Zn K-edge XANES of the a-ZITO film provides a better understanding of the structure. Figure 4 compares the results of the XANES calculations using the FDM approach (A, B, C) with the experimental XANES spectrum (dotted line) of 12:14 a-ZITO. Since the XAS data are dominated by the bond lengths measured by EXAFS. The removal of two oxygen atoms was also necessary to obtain a reasonable match to the magnitude of the features, which again is consistent with the small coordination number determined by EXAFS. Comparing the calculated versus measured XANES spectra, it appears that a combination of planar and tetrahedral local geometries would best match the experimental data, although other geometries could exist.

### Table III. Average Local Structures in All a-ZITO Films, Except p0.5, Compared to In$_2$O$_3$, SnO$_2$, and ZnO

<table>
<thead>
<tr>
<th>Bonds</th>
<th>Bulk oxide $\dagger$</th>
<th>a-ZITO</th>
<th>Bulk oxide $\dagger$</th>
<th>a-ZITO $\breve{N}(\text{SSD, range})$</th>
<th>Bulk oxide $\dagger$</th>
<th>a-ZITO</th>
</tr>
</thead>
<tbody>
<tr>
<td>In–O</td>
<td>2.18</td>
<td>2.14</td>
<td>(±0.02)</td>
<td>8.00</td>
<td>5.0 ± (±0.4, –0.5 to 0.5)</td>
<td>0.0059</td>
</tr>
<tr>
<td>Sn–O</td>
<td>2.06</td>
<td>2.07</td>
<td>(±0.03)</td>
<td>8.00</td>
<td>5.9 ± (±0.3, –0.4 to 0.6)</td>
<td>0.0030</td>
</tr>
<tr>
<td>Zn–O</td>
<td>1.96</td>
<td>1.98</td>
<td>(±0.01)</td>
<td>8.00</td>
<td>3.3 ± (±0.2, –0.2 to 0.3)</td>
<td>0.0043</td>
</tr>
</tbody>
</table>

$\dagger$Error bars for distance ranges include C$_{1}$ effects.

$\breve{N}$Bond lengths and coordination numbers are averaged over compositions and temperatures.

$\breve{N}$Bulk oxides: In$_2$O$_3$, SnO$_2$, and ZnO.

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Fig. 3. Top: The pair distribution function (PDF) of the average a-ZITO structure. Bottom: The difference pair distribution function (d-PDF) of the structure around Zn in a-ZITO.

Fig. 4. Top: First shell FDM calculations (A, B, C) for different local geometries around Zn in a-ZITO using the simplified (disordered) d-site in bixbyte (bottom) compared to the experimental XANES measurement (dotted line). Bottom: The oxygen atoms are labeled according to bond length such that Zn–O$_{1a,1b} =$ 2.19 Å, Zn–O$_{2a,2b} =$ 2.12 Å, and Zn–O$_{3a,3b} =$ 2.21 Å. The calculation A removed O$_{3a}$ and O$_{3b}$ to form a tetrahedral local structure, the calculation B removed O$_{1a}$ and O$_{1b}$ to form a planar structure, and the calculation C removed O$_{2a}$ and O$_{2b}$ to form a pyramidal structure.
Although the local structures presented in Table III represent all but one of the films, the thermal responses of the local structures do show an interesting compositional dependence, as revealed by temperature–dependent XAS measurements. Figure 5 overlays, for each absorption edge, the first shell EXAFS oscillations of the Sn/Zn = 12:14 and 16:14 a-ZITO films obtained by back Fourier transforms of the first shell peaks (with $R = 1$–2 Å) at all three temperatures (78, 165, and 300 K). The Sn environment in the Zn-rich film (12:14) changes only slightly with temperature, although changes are quite noticeable in the In and Sn environments. The opposite is true in the Sn-rich film (16:14). The FEFF fits of these data indicate that these structural changes can be accounted for mostly by changes in the Debye–Waller factor $e^{-2n[k]}$, indicating their thermal nature. Figure 6 plots $\sigma^2/N$ vs $T$ for the 12:14 and 16:14 a-ZITO films. Given the high correlation between $N$ and $\sigma^2$, $\sigma^2/N$ should minimize the effect of this correlation on the analysis. The error bars in Fig. 6 were obtained as follows

$$\pm \frac{\sigma^2 + \Delta \sigma^2_{SSD}}{N - \Delta N_{SSD}},$$

where SSD is the sample standard deviation ($= \sqrt{\sum((x_i - \bar{x})^2)/(n - 1))}$. These results show again that despite essentially indistinguishable (by EXAFS) local structures across compositions, compositional changes do result in different thermal responses. Unlike in crystalline materials where atoms act coherently, the rigidity of the local structure in an amorphous material could vary depending on the geometrical details of the overall structure. However, the overall structural rigidity may be reflected in the thermal responses of the In–O bonds since In is the majority cation in the films.

As mentioned above, the p0.5 a-ZITO film has a slightly different structure than the other films, specifically in its coordination number around Sn. $N$ is 4.1 ± 0.3 as compared to 5.9 ± 0.3 in the other a-ZITO films. This coordination number matches more closely to SnO (and the presence of Sn$^2$) than SnO$_2$, which aligns well with the relatively reducing deposition conditions of this film (as compared to the others). The other structural parameters fall within the ranges noted in Table III.

V. Discussion

The XAS and anomalous X-ray scattering results reveal details about the local structures of a-ZITO, and how they differ from those in c-ZITO. In a-ZITO, the In–O bond length is likely slightly smaller than that in c-ZITO, whereas the Sn–O bond length is similar to the shorter length in c-ZITO. $N_{\text{Sn}}$ is significantly smaller than $N_{\text{In}}$ (see Table III). Given the similarity in the a-ZITO and c-ZITO XANES around In and Sn (despite broadening), we speculate that their first shell structures likely maintain a similar geometry.

The first shell structure around Zn has a bond length of 1.98 Å. This indicates a significant volume contraction of ~25% compared to a cubic site in the bixbyte structure, which results in a lower coordination around Zn. Also as a consequence, the second shell structure contracts toward Zn, as found using anomalous X-ray scattering. However, the structure at longer distances becomes commensurate with the average structure. The smaller, four-fold coordinated Zn may be important in stabilizing the structural framework of a-ZITO. These films have a much higher crystallization temperature ($T_c$ - from our recent work, 300°C–345°C) than that of α-In$_2$O$_3$ (165°C–210°C)$^{39}$ and a-ITO (185°C–230°C).$^{39}$

Both the medium range order and higher $T_c$ of a-ZITO are consistent with a homogeneous amorphous phase in the films.

Linking the local structures to the electrical properties in a-ZITO is a significant challenge. In c-ZITO, it has been proposed that Sn donors compensated by Zn acceptors participate in a structural rearrangement in which Sn gains an oxygen atom at the expense of a Zn cation.$^{13}$ This rearrangement maintains charge balance and stoichiometry, while satisfying the preference of Zn to have a lower coordination. It is also consistent with the tendency of Sn donors to stabilize extra oxygen, as seen in the F-K clusters formed by excess Sn donors.$^{13,24}$ As a result, the coordination number trend in c-ZITO is $N_{\text{Sn}} > N_{\text{In}} > N_{\text{Zn}}$.

Interestingly, despite generally smaller $N$ values, this trend persists in a-ZITO. Sn tends to be over coordinated, whereas

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**Fig. 5.** Overlays of the first shell back Fourier transforms of the In, Sn, and Zn K-edges for the Sn:Zn = 12:14 (left) and 16:14 (right) a-ZITO films measured at 78 K (blue solid line), 165 K (green dotted line), and 300 K (red dash-dot line).
Zn tends to be under coordinated when compared to In. However, in α-ZITO, changes in the Sn:Zn (donor:acceptor) ratio do not result in significant changes in the electrical properties (Table II). This suggests that Sn and Zn function as network-forming cations (along with In) rather than as “dopants” (donor/acceptor).

In contrast, electrical properties change significantly with changes in oxygen pressure during deposition. However, EXAFS measurements show no significant difference between the local structures of the films deposited at 7.5 and 15 mTorr, despite the large difference in their carrier concentrations (see Table I). This is not surprising, since the oxygen “defect” donor (e.g., “vacancies”) population would be on the order of the carrier concentration (10^{19}-10^{20} cm^{-3}), which is relatively small compared to the overall oxygen concentration in α-ZITO (~10^{20} cm^{-3}). The results in Tables I and II suggest that oxygen “defects” play a dominant role in charge carrier creation.

The only α-ZITO film with a unique local structure compared to the others was that deposited at the most reducing conditions (0.5 mTorr). Although the bond lengths, σ^2 values, and coordination numbers around In and Zn match those listed in Table III, the coordination number around Sn dropped from 5.9 ± 0.3 to 4.1 ± 0.3. This local structure change is accompanied by large drops in mobility and charge carrier concentration (Table I), as well as a drop in optical transmittance. These factors suggest the presence of Sn^{2+} cations. Thus, under highly reducing conditions, Sn^{2+} will form leading to the detriment of the electrical and optical properties, which should be avoided.

VI. Conclusions

The local structures in α-ZITO thin films made by PLD were investigated using EXAFS and anomalous X-ray scattering and compared to those in c-ZITO thin films. The bond lengths and coordination numbers around In and Sn are slightly smaller than those in c-ZITO, which in the case of In is consistent with other studies reported in the literature. However, the structure around Sn is unique. In α-ZITO, the Zn-O bond length is 1.98 Å and the four-fold first shell coordination environment consists of a mix of tetrahedral, planar and other disordered geometries. As a result, the second coordination shell contracts toward Zn. Despite these differences in local structure, the structural framework in α-ZITO does not depart drastically from that in c-ZITO. In fact, coordination numbers (N) around Sn, In, and Zn follow the same order as in c-ZITO, N_{Sn} > N_{In} > N_{Zn}, but are generally smaller. However, the unique structure around Zn may account for the increased crystallization temperature of α-ZITO compared to α-In_{2}O_{3} and α-ITO. Also, unlike in c-ZITO, variations in the Sn:Zn ratio do not markedly change the electrical properties of α-ZITO. This suggests that Zn and Sn can be viewed as network-forming cations in the overall amorphous structure. On the other hand, variations in oxygen pressure during deposition dramatically change the electrical properties of α-ZITO, pointing to oxygen “defects” as the dominant donor species in α-ZITO.

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References


Fig. 6. $\sigma^2/N$ vs $T$ for the α-ZITO films with Sn:Zn = 12:14 (circles - left) and 16:14 (squares - right) deposited at 7.5 mTorr. Solid black markers indicate Zn-O bonds, open blue markers indicate In-O bonds, and crossed red markers indicate Sn-O bonds.


