X-ray absorption spectroscopy elucidates the impact of structural disorder on electron mobility in amorphous zinc-tin-oxide thin films

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We investigate the correlation between the atomic structures of amorphous zinc-tin-oxide (a-ZTO) thin films grown by atomic layer deposition (ALD) and their electronic transport properties. We perform synchrotron-based X-ray absorption spectroscopy at the K-edges of Zn and Sn with varying [Zn]/[Sn] compositions in a-ZTO thin films. In extended X-ray absorption fine structure (EXAFS) measurements, signal attenuation from higher-order shells confirms the amorphous structure of a-ZTO thin films. Both quantitative EXAFS modeling and X-ray absorption near edge spectroscopy (XANES) reveal that structural disorder around Zn atoms increases with increasing [Sn]. Field- and Hall-effect mobilities are observed to decrease with increasing structural disorder around Zn atoms, suggesting that the degradation in electron mobility may be correlated with structural changes. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4884115]

Amorphous metal-oxide semiconductors (AMOS) have attracted attention for transparent optoelectronic applications including liquid-crystal displays and transparent conducting oxides for organic light-emitting diodes. Zinc oxide and related oxide classes are investigated due to their high electron mobility compared to conventional amorphous oxides for organic light-emitting diodes. Nomura et al. demonstrated high-performance flexible transistors using amorphous indium-gallium-zinc-oxide (a-IGZO) with electron mobilities exceeding 10 cm²/V·s.1 The high mobility and amorphous structure of AMOS enable a faster operation of the devices and elimination of grain-boundary related defects, respectively.2,3 The high electron mobility in the amorphous state originates from the conduction band, which mainly consists of unoccupied Ns (N ≥ 5) orbitals of metal atoms such as In-5s in a-IGZO.2–6 The spherical symmetry of the s orbitals makes them less prone to form traps and scattering centers when the metal-oxygen-metal bonds are distorted by rotation of metal-oxygen polyhedrons.

Amorphous zinc-tin-oxide (a-ZTO) is recently highlighted as a promising candidate material for cost-effective applications, as it is free from toxic and expensive elements (e.g., indium and gallium).7–15 To synthesize high-quality a-ZTO thin films, various techniques have been used, including sol-gel,9 sputtering,13 pulsed laser deposition,15 and ALD.7,14 In particular, ALD provides a precise and conformal control of the atomic concentrations of Zn ([Zn]) and Sn ([Sn]) in the film. By controlling the [Zn]/[Sn] ratio, ALD a-ZTO channels in thin-film transistors have demonstrated a field-effect mobility up to 13 cm²/V·s with a large on-to-off ratio of drain current (>10⁶).7 Furthermore, controlling the [Zn]/[Sn] ratio allows tunability of conduction-band edge positions, which is also useful for photovoltaic applications by reducing interface recombination and improving device performance.12,16,17 The significant impact of the [Zn]/[Sn] ratio in a-ZTO thin films on device performance suggests a strong correlation between the atomic structure and electronic transport properties of the films. Because amorphous materials can exhibit a continuum of structures,18 a probe of local order is needed.

In this work, we investigate the effect of atomic structure in a-ZTO on electronic transport properties by using synchrotron-based X-ray absorption spectroscopy (XAS). We perform EXAFS at the Zn and Sn K-edges to probe the local chemical neighborhoods of Zn and Sn atoms in a-ZTO films, respectively. We find that the Debye-Waller factor, which gives a measure of structural disorder,19 at the Zn K-edge increases with increasing [Sn] in the films. The structural disorder is further investigated by XANES analysis, which indicates the amorphization around Zn atoms with increasing [Sn] in the films. Disorder as measured by EXAFS and XANES coincides with a decrease in measured electron mobility, suggesting that the degradation in electron mobility may be correlated with structural changes for Zn rich films ([Zn] > 0.5), whereas for Sn rich regions, larger ionic size of Sn dominates the electron mobility.

A set of a-ZTO thin films is grown on quartz substrates by ALD at a growth temperature of 120°C. Diethylzinc (DEZ) and a cyclic tin (II) amide ((1,3-bis(1,1-dimethylethyl)-4,5-dimethyl-(4R,5R)-1,3,2-diazastannolidin-2-ylidene)Sn(II))20 are used as the Zn and Sn precursors, respectively. Hydrogen peroxide (H₂O₂, 50 wt. %, Sigma Aldrich) is used as the common oxygen source. The compositions of a-ZTO films are

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controlled by varying the sub-cycle ratio of ZnO and SnO₂.
For example, a sub-cycle ratio of 3/1 involves depositing 3
consecutive cycles of ZnO followed by 1 cycle of SnO₂.
Pure ZnO and SnO₂ films are also deposited by ALD at 120°C on
quartz substrates, respectively. The thickness of all films is
~200 nm to minimize self-absorption issues in XAS measure-
ments. The atomic compositions of the resulting films are
measured by Rutherford backscattering spectroscopy (RBS),
summarized in Table 1.

XAS is performed at the MRCAT Sector 10-ID beam-
line of the Advanced Photon Source, Argonne National
Laboratory (IL, USA). The beamline uses a cryo-cooled
Si(111) double-crystal monochromator. In this study, we per-
f orm XAS at both the Zn and Sn K-edge transitions, which
occur at 9.66 and 29.2 keV, respectively. The thin film sam-
ple s are measured in fluorescence mode with an incident
beam of area 500 × 500 μm² and a 13-element Canberra ger-
manium solid-state detector with a liquid nitrogen coolant to
collect the fluorescence emission. To improve the signal-
to-noise ratio, multiple scans are averaged together to
achieve effective counts higher than 10⁶. The energy scale is
calibrated by using the absorption edge of reference metallic
Zn or Sn thin films measured simultaneously and the
XANES and EXAFS are isolated by normalizing the absorp-
tion spectrum and subtracting the smooth atomic background
signal from the measured absorption signal using
the AUTOBK algorithm in Athena with R_{bkg} = 1.0 Å⁻¹.²¹,²²

After the background removal, the processed data are trans-
formed from energy space to k-space using the relationship,
k² = 2m(E - E₀)/h², where k is the electron wavenumber,
m is the electron mass, E₀ is the K-edge absorption energy of
the respective elements, and h is Planck’s constant.
The entire spectrum is weighted by k² to compensate for amplit-
dude decay. For further analysis, the k²-weighted spectra data
are Fourier-transformed with a Hanning window as a band-
pass filter to enhance the signal-to-noise ratio defined by
k = 1.5 to 8.0 Å⁻¹.

Fig. 1 shows the resulting Fourier-transformed spectra plotted as the magnitude, |y(R)|, for both the Zn and Sn K-
edges. The first large peak in the spectrum is indicative of the scattering signal from the first nearest neighbor (1NN)
shell of atoms.²² It can also be noted that the amplitudes of
|y(R)| from higher-order shells (R > 2 Å) for all other spectra
are strongly attenuated, except for the spectrum collected at
Zn K-edge for sample Z1T0 (pure ZnO). This suggests that
the higher-order shells around the Zn atoms are well-ordered
in the pure ZnO sample, verifying its crystalline nature. For
all a-ZTO and SnO₂ films, the EXAFS spectra exhibit lim-
ited structure beyond 1NN, indicating a lack of long-range
order.

The lack of long-range order in the Z3T1, Z1T1, and
Z1T3 samples is consistent with the amorphous structure as
characterized by X-ray diffraction measurements we reported
elsewhere.¹² Previously, we reported that SnO₂ deposited by
ALD at 120°C is nano-crystalline (nc-SnO₂).²³ The nc-SnO₂
films are grown using a closed-valve mode, during which the
nitrogen flow into the reactor was stopped until a base pres-
sure (50 mTorr) was reached, and then a valve between the
ALD reactor and the pump was closed during the injection of
the Sn precursor.²¹ In contrast to these previous results, the
SnO₂ films in our study are found to be amorphous when
made by an open-valve ALD mode without either stopping
the nitrogen flow or pumping the reactor down to base pres-
sure between precursor pulses. Furthermore, the saturated
growth rate of ~1.2 Å/cycle in the open-valve mode is
observed as compared to the slightly increased growth rate of
~1.7 Å/cycle obtained for closed-valve mode growth. We
hypothesize that the discrepancy in both crystallinity and sat-
urated growth rate to be due to differences in growth kinetics
and highly dependent on precursor’s partial pressure during
growth. More frequent collisions of the precursor molecules
in the closed-valve mode leads to a higher growth rate and
makes the film nano-crystalline. Nevertheless, the pure ZnO

### Table 1. Atomic composition of a-ZTO films measured by RBS and
\( x = \frac{[Sn]}{[Zn] + [Sn]} \).

<table>
<thead>
<tr>
<th>Sample</th>
<th>ZnO/SnO₂ sub-cycle ratio</th>
<th>[O] (at. %)</th>
<th>[Zn] (at. %)</th>
<th>[Sn] (at. %)</th>
<th>x</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z1T0</td>
<td>1/0</td>
<td>51.8</td>
<td>48.2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Z3T1</td>
<td>3/1</td>
<td>57.6</td>
<td>33.4</td>
<td>9.0</td>
<td>0.21</td>
</tr>
<tr>
<td>Z1T1</td>
<td>1/1</td>
<td>61.7</td>
<td>24.2</td>
<td>14.1</td>
<td>0.37</td>
</tr>
<tr>
<td>Z1T3</td>
<td>1/3</td>
<td>65.8</td>
<td>12.2</td>
<td>22.0</td>
<td>0.64</td>
</tr>
<tr>
<td>Z0T1</td>
<td>0/1</td>
<td>67.9</td>
<td>0</td>
<td>32.1</td>
<td>1</td>
</tr>
</tbody>
</table>

FIG. 1. Fourier-transformed EXAFS spectra at Zn and Sn K-edges. Figures
(a) and (b) compare the peak intensity of the 1NN shell at the Zn and Sn K-
edges, respectively. The arrows illustrate the decreasing peak intensity with
increasing [Sn]. Figures (c) and (d) show the measured (symbols) and fitted
spectra (lines) at the Zn and Sn K-edges, respectively (offset for clarity).

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films grown with open-valve ALD mode are polycrystalline. These results are verified by XRD measurements (not shown). From Figs. 1(a) and 1(b), it can also be observed that the amplitude of the first shell peak decreases with increasing [Sn].

To gain quantitative structural information for the first shell, we isolate the 1NN peaks from all samples (1.0–2.0 Å for the Zn K-edge and 1.0–2.1 Å for the Sn K-edge) and fit the peaks using the EXAFS equation given by

$$\chi(k) = S_0^2 \sum_{j} N_j f_j(k) \frac{R_j^2}{k^2} e^{-2R_j/k} e^{-2\sigma_j/k} \sin(2kR_j + \delta_j(k)), \quad (1)$$

where $j$ indicates shells of like atoms, $S_0^2$ is the passive electron reduction factor, $N_j$ is the coordination number of atoms in the $j$th shell, $k$ is the photoelectron wavenumber, $R_j$ is the distance to the neighboring atoms, $\sigma_j^2$ is the Debye-Waller factor or the mean-squared disorder of neighbor distance, and $\lambda(k)$ is the electron mean free path. The scattering amplitude, $f_j(k)$, and the phase shift, $\delta_j(k)$, are dependent on the atomic number of the scattering atoms. Due to the similarity in the first-shell EXAFS spectra between a-ZTO samples and reference samples, we expect the local structures around the Zn and Sn atoms of the a-ZTO films to resemble those of crystalline ZnO and amorphous SnO$_2$, respectively. In this case, the 1NNs of Zn and Sn atoms contain only oxygen atoms, thus only the single-scattering paths Zn – O and Sn – O are considered. As starting inputs, the relevant EXAFS parameters for the Zn – O and Sn – O paths are estimated using the crystal structures of ZnO (wurtzite, space group P6$_3$mc) and SnO$_2$ (rutile, space group P4$_2$/mm) using the ATOMS and FEFF6 codes implemented in Artemis. To reduce the number of fitting parameters, $S_0^2$ for both Zn (0.84) and Sn (1.00) are obtained by fitting the EXAFS spectra of metallic Zn or Sn thin films collected simultaneously with each sample. Subsequently, non-linear least squares fitting is performed in Artemis to obtain structural parameters like $R_j$, $N_j$, and $\sigma_j^2$ as summarized in Table II. We obtained R-factors of < 0.01 for all fits.

It can be observed that the bond lengths of Zn – O and Sn – O of all a-ZTO samples have very small changes with respect to composition and are comparable with the reference ZnO and SnO$_2$. The fitted average bond-lengths, $R_{Zn-O} \sim 1.98$ Å and $R_{Sn-O} \sim 2.05$ Å, are also in close agreement with previously reported values for wurtzite ZnO and rutile SnO$_2$. In addition, our fitting results indicate that Zn and Sn atoms have tetrahedral and octahedral coordination, respectively, as predicted by theoretical calculations. This observation is consistent with the oxygen-rich atomic composition measured by RBS, which can be attributed to the use of H$_2$O$_2$ as the oxidizing agent.

While both $R$ and $N$ have very small changes with Sn content, higher [Sn] leads to an increase in the pseudo-Debye-Waller factor, $\sigma^2_{Zn}$ (the subscript is used to denote the respective metal atom) in Zn – O path. The increase in $\sigma^2_{Zn}$ can be attributed to an increase in the level of structural disorder surrounding the Zn atoms resulting in a larger spread in the Zn – O bond-length or distortion of the ZnO tetrahedron. Furthermore, structural disorder manifests itself as feature changes in the Zn XANES spectra as shown in Fig. 2(a). Such feature changes in the Zn XANES spectra from 9.66 to 9.67 keV are due to a lack of the distinct multiple scattering contributions and have been associated with the amorphization of the Zn chemical environment as observed by Cho et al. In addition, isosbestic points observed in Zn-edge XANES as shown in Fig. 2(a) suggest that the local environments of Zn atoms in the three a-ZTO films comprise of a two-phase mixture that is distinctly different from crystalline wurtzite ZnO structure. One plausible explanation of the presence of two phases can be attributed to a segregation of ZnO and SnO$_2$, which is likely to occur considering the distinct difference in 1NN coordinated oxygen atoms between Zn and Sn. One of the phases could be due to Zn atoms which lie along the interface between the ZnO$_4$ tetrahedron and SnO$_6$ octahedron and experience a different coordination environment whereas the second phase can be due to the Zn atoms located further away from the ZnO/SnO$_2$ interface. On the other hand, an almost constant $\sigma^2_{Sn}$ is consistent with almost identical Sn-edge XANES for all samples.

In Fig. 3, the Hall- and field-effect mobilities together with $\sigma^2$ of all samples are plotted as a function of cation composition. The field-effect mobilities of a-ZTO are measured by fabricating thin-film transistors with a-ZTO layers as n-channels and more details are reported elsewhere. The Hall mobilities are measured by using the van der Pauw configuration and a magnetic field of 0.75 T. The ZIT1 and ZIT3 samples exhibit too small Hall voltages to measure Hall mobility. In Zn-rich ([Sn]/([Sn] + [Zn]) < 0.5) a-ZTO samples, increasing $\sigma^2_{Zn}$ is well-correlated with a decrease in mobility, with respect to increasing [Sn]. The decreased mobility suggests that structural disorder around Zn atoms reduces the film’s mobility significantly. In the Sn-rich ([Sn]/([Sn] + [Zn]) = 0.64) a-ZTO sample, on the other...

### Table II. Summary of EXAFS fit parameters for Zn – O and Sn – O bonds. $x = [Sn]/([Sn] + [Zn]).$

<table>
<thead>
<tr>
<th>Sample</th>
<th>$x$</th>
<th>$R$ (Å)</th>
<th>$N$</th>
<th>$\sigma^2$ (Å$^2$)</th>
<th>$E_0$ (eV)</th>
<th>R-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZIT0</td>
<td>0</td>
<td>1.97(3)</td>
<td>3.8(2)</td>
<td>0.002(1)</td>
<td>6.0(8)</td>
<td>0.003</td>
</tr>
<tr>
<td>ZIT1</td>
<td>0.21</td>
<td>1.96(6)</td>
<td>3.7(6)</td>
<td>0.005(1)</td>
<td>4.7(1)</td>
<td>0.002</td>
</tr>
<tr>
<td>ZIT1</td>
<td>0.37</td>
<td>1.98(1)</td>
<td>3.7(7)</td>
<td>0.007(1)</td>
<td>4.4(3)</td>
<td>0.001</td>
</tr>
<tr>
<td>ZIT3</td>
<td>0.64</td>
<td>1.98(1)</td>
<td>3.8(9)</td>
<td>0.008(1)</td>
<td>4.0(5)</td>
<td>0.005</td>
</tr>
<tr>
<td>ZIT1</td>
<td>1</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>
hand, the mobility remains at $\sim 0.5$ cm$^2$/V·s with a subtle increase in $\sigma_{2p}$.

For AMOS with high ionicity, the conduction band edge typically comprises overlapping $Ns$ orbitals from the metal cations. The isotropic nature of these $Ns$ orbitals causes electron transport to be less sensitive to bonding geometries. However, prior results from other authors on similar material systems such as amorphous ZnO$^{30,31}$ (a-ZnO) and amorphous ZnSnO$_3$ $^{32}$ (a-ZnSnO$_3$) suggest that the conduction band of a-ZTO can comprise of a mixture of Zn-4s and Sn-5s orbitals that are hybridized with O-2p orbitals. In particular, Cho et al. have shown from O $K$-edge XANES that the hybridization strength between Zn-4s and O-2p orbitals in a-ZnO weakens due to structural disorder. $^{31}$ In Zn-rich a-ZTO films, the predominant conduction paths are between hybridized Zn-4s and O-2p orbitals. Thus, the reduced mobility by increased [Sn] can be attributed to the structural disorder between Zn and O atoms; reduced hybridization strength of Zn-4s and O-2p orbitals can limit electron conduction pathways. $^{30,31}$ On the other hand, Sn-rich a-ZTO films exhibit a very slight increase in the mobilities as [Sn] increases. The dependence of electron mobilities on the composition of the larger metal ion has similarly been observed in Al-Zn-Sn-O$^{33}$ and In-Ga-Zn-O$^5$ systems where the effect has been hypothesized to be due to species with larger ionic radii (Sn$^{4+}$ and In$^{3+}$ ions ($N \geq 5$), respectively) contributing towards conductance. These results suggest that for the Sn-rich a-ZTO film investigated in this work, Sn$^{4+}$ ions which have larger ionic radii thus larger $Ns$ orbital ($N \geq 5$), may begin to dominate electron conduction via Sn-5s – O-2p pathways, thereby increasing electron mobility closer to that of SnO$_2$.

In summary, we use synchrotron-based XAS to investigate the effect of atomic structure of a-ZTO thin films on their electron transport properties. The a-ZTO thin films exhibit higher degree of structural disorder as [Sn] increases in the films. Quantitative EXAFS analysis reveals a strong correlation between $\sigma_{2p}$ and electron mobility for Zn-rich films. XANES measurements provide further evidence of structural disorder near Zn atoms in Zn-rich a-ZTO films. The decrease in mobility is correlated with increasing local structural disorder surrounding Zn atoms. Literature reports suggest that the decrease in mobility may be due to reduced hybridization strength of Zn-4s and O-2p orbitals, which may limit electron conduction pathways. Lastly, we observe a slight increase in mobility for the Sn-rich a-ZTO films that can be due to the larger ionic radii ($N \geq 5$) of Sn$^{4+}$ ions.

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