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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.
controlled by varying the sub-cycle ratio of ZnO and SnO$_2$. For example, a sub-cycle ratio of 3/1 involves depositing 3 consecutive cycles of ZnO followed by 1 cycle of SnO$_2$. Pure ZnO and SnO$_2$ films are also deposited by ALD at 120°C on quartz substrates, respectively. The thickness of all films is $\sim$200 nm to minimize self-absorption issues in XAS measurements. The atomic compositions of the resulting films are measured by Rutherford backscattering spectroscopy (RBS), summarized in Table I.

XAS is performed at the MRCAT Sector 10-ID beamline 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 perform XAS at both the Zn and Sn K-edge transitions, which occur at 9.66 and 29.2 keV, respectively. The thin film samples are measured in fluorescence mode with an incident beam of area 500 $\times$ 500 $\mu$m$^2$ and a 13-element Canberra germanium 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 $10^6$. 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 absorption spectrum and subtracting the smooth atomic background elsewhere.$^{12}$ Previously, we reported that SnO$_2$ deposited by ALD at 120°C is nano-crystalline (nc-SnO$_2$).$^{23}$ The nc-SnO$_2$ films are grown using a closed-valve mode, during which the nitrogen flow into the reactor was stopped until a base pressure (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 SnO$_2$ 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 pressure between precursor pulses. Furthermore, the saturated growth rate of $\sim$1.2 Å/cycle in the open-valve mode is observed as compared to the slightly increased growth rate of $\sim$1.7 Å/cycle obtained for closed-valve mode growth. We hypothesize that the discrepancy in both crystallinity and saturated growth rate to be due to differences in growth kinetics and highly dependent on precursor’s partial pressure during growth. More frequent collisions of the precursor molecules in the closed-valve mode leads to a higher growth rate and makes the film nano-crystalline. Nevertheless, the pure ZnO sample, verifying its crystalline nature. For all a-ZTO and SnO$_2$ films, the EXAFS spectra exhibit limited 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.$^{13}$ In contrast to these previous results, the SnO$_2$ 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 pressure between precursor pulses. Furthermore, the saturated growth rate of $\sim$1.2 Å/cycle in the open-valve mode is observed as compared to the slightly increased growth rate of $\sim$1.7 Å/cycle obtained for closed-valve mode growth.
fils 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

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

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 SnO2. 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 P63mc) and SnO2 (rutile, space group P42/mmm) using the ATOMS and FEFF6 codes implemented in Artemis.42 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 SnO2. The fitted average bond-lengths, $R_{Zn-O} \approx 1.98$ Å and $R_{Sn-O} \approx 2.05$ Å, are also in close agreement with previously reported values for wurtzite ZnO and rutile SnO2. 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 H2O2 as the oxidizing agent.12,23

While both $R$ and $N$ have very small changes with Sn content, higher [Sn] leads to an increase in the pseudo-Debye-Waller factor, $\sigma_{Zn}^2$ (the subscript is used to denote the respective metal atom) in Zn – O path. The increase in $\sigma_{Zn}^2$ 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 ZnO4 tetrahedra.19 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.30 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 SnO2, 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 ZnO4 tetrahedron and SnO2 octahedron and experience a different coordination environment whereas the second phase can be due to the Zn atoms located further away from the ZnO/SnO2 interface. On the other hand, an almost constant $\sigma_{Sn}^2$ 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.7 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.12 In Zn-rich ([Sn]/([Sn] + [Zn]) < 0.5) a-ZTO samples, increasing $\sigma_{Zn}^2$ 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>
<thead>
<tr>
<th>Sample</th>
<th>$x$</th>
<th>$R$ (Å)</th>
<th>$N$</th>
<th>$\sigma^2$ (Å²)</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>1.97(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>ZIT1</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>1.00</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>

**Table II. Summary of EXAFS fit parameters for Zn – O and Sn – O bonds. $x = [Sn]/([Sn] + [Zn])$.**
ZnSnO$_3$ typically comprises overlapping $Ns$ orbitals, the predominant conduction paths are between hybridized Zn-4$s$ and O-2$p$ orbitals. In particular, Cho et al. have shown from O K-edge XANES that the hybridization strength between Zn-4$s$ and O-2$p$ orbitals in a-ZnO weakens due to structural disorder. In Zn-rich a-ZTO films, the predominant conduction paths are between hybridized Zn-4$s$ and O-2$p$ orbitals. Thus, the reduced mobility by increased $[\text{Sn}]$ can be attributed to the structural disorder between Zn and O atoms; reduced hybridization strength of Zn-4$s$ and O-2$p$ orbitals can limit electron conduction pathways. On the other hand, Sn-rich a-ZTO films exhibit a very slight increase in the mobilities as $[\text{Sn}]$ increases. The dependence of electron mobilities on the composition of the larger metal ion has similarly been observed in Al-Zn-Sn-O$_3$ and In-Ga-Zn-O$_5$ systems where the effect has been hypothesized to be due to species with larger ionic radii ($\text{Sn}^{4+}$ and In$^{3+}$ ions ($N \geq 5$), respectively) contributing towards conduction. These results suggest that for the Sn-rich a-ZTO film investigated in this work, $\text{Sn}^{4+}$ ions which have larger ionic radii thus larger $Ns$ orbital ($N \geq 5$), may begin to dominate electron conduction via Sn-5$s$ – O-2$p$ 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 $[\text{Sn}]$ increases in the films. Quantitative EXAFS analysis reveals a strong correlation between $\sigma_{\text{Zn}}$ 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-4$s$ and O-2$p$ 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 $\text{Sn}^{4+}$ ions.

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