Cation Size Effects on the Electronic and Structural Properties of Solution-Processed In–X–O Thin Films

Jeremy Smith, Li Zeng, Rabi Khanal, Katie Stallings, Antonio Facchetti, *, Julia E. Medvedeva, *, Michael J. Bedzyk, *, and Tobin J. Marks *

These include, but are by no means limited to, display backplanes, smart windows, solar cells, and radio-frequency identification tags. A combination of high carrier mobility, even in the amorphous state, excellent optical transparency, and the ability to process these thin-film materials from solution offers the potential of novel applications and a paradigm shift away from current technologies such as those based on amorphous silicon (a-Si). AMOs have recently achieved industrial prominence, with amorphous indium–gallium–zinc oxide (a-IGZO) for optical displays being a key example. [3] Typically, for both conducting and semiconducting electronic components, indium and/or zinc-based oxides are heavily doped with secondary cations such as Ga, [1a] Y, [4] Cd, [5] or Sn. [6] These transition and post-transition metal ions with large spherical ns-orbitals (n ≥ 4) provide the dispersive conduction band required for electron transport, even in the amorphous phase. [7] In general, the secondary metal cations also affect several important film properties such as the degree of crystallinity, the local lattice structure, the formation of defects, as well as the electronic structure. [8] Furthermore, such cations are almost always necessary to control the film charge carrier concentration and to disrupt the lattice crystallinity, thus generating the amorphous phase. Therefore, deeper understanding of the role of these cations will be necessary to design future oxide systems with tailored properties.

1. Introduction

In the past decade amorphous metal oxides (AMOs) have become attractive contenders as semiconducting and conducting materials for thin-film electronics. [1] There is a major driving force for applications based on optoelectronic device production using large-area, roll-to-roll processing methods enabled by mechanical flexibility and low-cost fabrication. [2]

The nature of charge transport and local structure are investigated in amorphous indium oxide-based thin films fabricated by spin-coating. The In–X–O series where X = Sc, Y, or La is investigated to understand the effects of varying both the X cation ionic radius (0.89–1.17 Å) and the film processing temperature (250–300 °C). Larger cations in particular are found to be very effective amorphosizers and enable the study of high mobility (up to 9.7 cm² V⁻¹ s⁻¹) amorphous oxide semiconductors without complex processing. Electron mobilities as a function of temperature and gate voltage are measured in thin-film transistors, while X-ray absorption spectroscopy and ab initio molecular dynamics simulations are used to probe local atomic structure. It is found that trap-limited conduction and percolation-type conduction mechanisms convincingly model transport for low- and high-temperature processed films, respectively. Increased cation size leads to increased broadening of the tail states (10–23 meV) and increased percolation barrier heights (24–55 meV) in the two cases. For the first time in the amorphous In–X–O system, such effects can be explained by local structural changes in the films, including decreased In–O and In–M (M = In, X) coordination numbers, increased bond length disorder, and changes in the MO₄ polyhedra interconnectivity.

Dr. J. Smith, L. Zeng, K. Stallings, Prof. A. Facchetti, Prof. T. J. Marks Department of Chemistry and Materials Research Center Northwestern University Evanston, IL 60208, USA E-mail: a-facchetti@northwestern.edu; t-marks@northwestern.edu

L. Zeng Graduate Program in Applied Physics Northwestern University Evanston, IL 60208, USA

R. Khanal, Prof. J. E. Medvedeva Department of Physics Missouri University of Science and Technology Rolla, MO 65409, USA E-mail: juliaem@mst.edu

DOI: 10.1002/aelm.201500146

Prof. A. Facchetti Polyera Corporation 8045 Lamon Avenue, Skokie, IL 60077, USA

Prof. M. J. Bedzyk Department of Materials Science and Engineering and Materials Research Center Northwestern University Evanston, IL 60208, USA E-mail: bedzyk@northwestern.edu
High-performance AMO films are typically grown by chemical vapor deposition,[9] physical vapor deposition such as sputtering and pulsed laser deposition,[10] or by atomic layer deposition.[10] In these cases, the resulting thin film transistors (TFTs) have electron mobilities exceeding 10 cm² V⁻¹ s⁻¹.[11] However, solution-based methods are attractive because of their roll-to-roll compatibility, reduced materials waste, and atmospheric pressure growth conditions. Additionally, it becomes possible to tune the oxide composition by simply changing the precursor solution composition in a straightforward and comprehensive fashion. Numerous oxide precursor routes have been developed, often based on sol–gel chemistry,[12] and generally high-temperature annealing steps (>400 °C) are required to remove impurities and achieve full oxide lattice condensation. Recently, several new methods have been reported that reduce processing temperatures.[13] Here we employ the “combustion” synthesis approach as developed in this laboratory,[13b] and previously applied to In₂O₃, In–Zn–O, In–Sn–O, In–Y–O, and In–X–Zn–O (X = Ga, Sc, Y, La) systems.[14] The precursor solution consists of an oxidizer in the form of the metal nitrate and a fuel (in this case acetylacetone), where, upon annealing at 250–300 °C, a rapid, highly exothermic and localized chemical reaction drives the formation of the metal oxide lattice/network, while not significantly increasing the film temperature. Combustion synthesis and other low-temperature routes allow complete conversion to the oxide in this temperature range but often result in device performance that varies with annealing temperature.[11]

The incorporation of secondary elements into the indium oxide lattice is expected to alter the local structure and lead to diminished long-range order. Furthermore, the composition dependence of the film crystallinity is predicted to differ for each added element due to the increased disorder induced by disparate cation sizes within the lattice. The chemical properties of Sc³⁺, Y³⁺, and La³⁺ are similar, namely a 3+ oxidation state, octahedral coordination of oxygen around the metal in M₂O₃, and comparable oxide lattice enthalpies; however, their ionic radii R₉⁺(X) range from 0.95 R₉⁺(In³⁺) to 1.25 R₉⁺(In³⁺).[15] The size of the cation, which is determined by its electron configuration, will therefore be the dominant variable in this particular system and is expected to result in changes to the oxide properties. Consequently, in this contribution, we focus on the In–X–O system, where X = Sc, Y, La, with X concentrations varied between 2.5 and 12.5 at%, which crosses the crystalline-to-amorphous transition while maintaining complete oxide solid solution. We employ two processing temperatures, 250 and 300 °C, which for the In–X–O system, represent a “lower-quality” and “higher-quality” oxide film respectively, and which have noticeable differences in their structural and electronic properties.

The amorphous compositions are of particular interest from both a fundamental perspective and a technological one. Long-range order is absent, necessitating multiple relatively sophisticated techniques to elucidate structure–function relationships compared to crystalline semiconductors. X-ray absorption spectroscopy (XAS) analysis is one important method used to probe AMO materials on the ~5 Å length scale and provides information on coordination number, average atomic separations, and atomic positional disorder of the different shells surrounding the central absorbing atom.[16] The XAS methods employed here are outlined in Sections 2.1 and 5. Computational modeling methods, specifically ab initio molecular dynamics (MD) simulations of the amorphous In–X–O lattices, are also employed, and it will be seen that they confirm the experimental trends. Since grain boundary defects are also largely suppressed in AMO materials, which is a significant factor influencing their electronic and mechanical properties, high electron mobilities can be achieved even by expeditious solution-processing methods. For example, this report demonstrates amorphous In–La–O (La: 5 at%) with μ_FET = 9.7 cm² V⁻¹ s⁻¹. Furthermore, electron transport in In–X–O TFTs is characterized as a function of temperature in the range 150–300 K. It will be seen that these films exhibit thermally activated transport, and this can be associated with either trap-limited conduction for more disordered films, or percolation conduction for more ordered films (details of these models are provided in Section 2.3). Activation energies as a function of the X cation size are used to extract tail state distributions as well as conduction band potential barriers, and therefore provide a direct link between the electrical properties and the structural disorder induced by the secondary cation.

2. Structural and Electronic Characterization

2.1. X-Ray Absorption Spectroscopy

Due to large oxygen electronegativity, the structure of an amorphous oxide can be described as a network of MO₃ polyhedra where distortions and the connectivity of the polyhedra govern the transport properties. Therefore, it is crucial to investigate these structural characteristics in detail. For amorphous samples, which lack long-range order, XAS is an ideal technique complement to X-ray diffraction (XRD). XAS can be divided into two parts: X-ray absorption near-edge structure (XANES) which is indicative of the chemical state and site symmetry, and extended X-ray absorption fine structure (EXAFS), which can be analyzed quantitatively to obtain local structural information. The normalized linear EXAFS absorption coefficient \( \chi(k) \) can be fitted by Equation (1)[16b]

\[
\chi(k) = S_0 \sum_i N_i f_i(k) \frac{k R_i}{R_i} \exp\left(\frac{2R_i}{\lambda(k)}\right) \exp\left(-2k^2 \sigma_i^2 \right) \sin(2kR_i + \delta_i(k))
\]

where \( S_0 \) is the intrinsic loss factor, \( \lambda(k) \) is the electron mean free path, \( N_i \) and \( R_i \) are the coordination number and bond distance of the ith shell of the absorbing atom, respectively, \( f_i(k) \) and \( \delta_i(k) \) are the backscattering amplitude and the phase shift, and \( \exp(-2k^2 \sigma_i^2) \) is the Debye–Waller factor—a measure of the structural disorder or the variation in \( R_i \). The Fourier transformation of \( \chi(k) \) generates a pseudo-radial distribution function (p-RDF) for the absorbing atom. For amorphous oxides we are interested in how the coordination number, bond distances, and the Debye–Waller factors change with processing temperature and choice of X cation.
2.2. Ab Initio Molecular Dynamics Simulation

The results of the EXAFS analysis can be compared to the local structure characteristics of amorphous oxides obtained from ab initio molecular dynamics (MD) simulations. The total, M–O, and M–M radial distribution functions are readily available from the MD models of amorphous oxide structures. Furthermore, an accurate comparison of the local (first-shell) structural characteristics in amorphous indium oxide (a-InO) and In–X–O materials can be made based on the average pair correlation function (Equation (2))[17]

$$R_n = \frac{\sum_i \exp \left(1 - (l_i / l_{\text{min}})^n \right)}{\sum_i \exp \left(1 - (l_i / l_{\text{min}})^n \right)}$$

(2)

where $l_i$ and $l_{\text{min}}$ are individual metal–oxygen bond lengths and minimum bond length in the polyhedron, respectively. Using the pair correlation function $R_n$, the effective coordination number $N_{\text{ECN}}$ can be calculated for each polyhedron according to Equation (3)

$$N_{\text{ECN}} = \sum_i \exp \left(1 - (l_i / R_n)^n \right)$$

(3)

We stress here that the above equations are used only to obtain the In–O and X–O first shell information; the wide distribution of the second-shell In–In and In–X distances makes the exponential fit in the $R_n$ and $N_{\text{ECN}}$ calculations inapplicable and a running coordination number $N_{\text{RCN}}$ is used instead. It is possible, however, to distinguish between the second and third shells using the optimized atomic coordinates of the MD simulated structures. For every In atom, the number of M (In or X) neighbors that share one, two, or three oxygen atoms with the central In can be determined, giving the average coordination number for corner, edge, or face-shared In–M, respectively. Then, the pair distribution functions, average distances, and statistical spreads can be found for edge- and corner-shared In–In pairs separately.[18]

Once a satisfactory agreement between the EXAFS and MD results for the structural properties as a function of cation size is obtained, the electronic structure of amorphous In–X–O materials is calculated. The ab initio nature of the MD simulations (density-functional equations are solved at every step during the MD quench) allows us to accurately describe the electronic states, defects, and the orbital character of all cations (5s0  for In vs (n − 1)s0p0n0 for Sc, Y, or La) even during the quench. As such, our ab initio MD approach differs from a classical MD simulation, commonly employed to obtain amorphous oxide structures: the classical approach cannot describe the electronic localization and defects.

To analyze the localized states in the band gap and near the band edges, the inverse participation ratio (IPR) of an orbital $\psi_n (\vec{r})$ can be found from ab initio density-functional calculations according to Equation (4), where $N$ is the number of volume elements in the cell and $i$ is the index of the volume element

$$\text{IPR} (\psi_n) = \frac{\sum_{i=1}^{N} |\psi_n (\vec{r}_i)|^4}{\sum_{i=1}^{N} |\psi_n (\vec{r})|^4}$$

(4)

2.3. Thin Film Transistor Charge Transport Models

Charge transport in AMO semiconductors has been widely studied, both by TFT and Hall effect measurements. In general, amorphous semiconductors possess tail states that extend into the band gap close to the conduction band edge as a result of energetic disorder, as well as lower energy states arising from a variety of defects.[16] For example, in metal oxides there is evidence for subgap states,[19] which can result in effects such as persistent photoconductivity[20] and bias instability.[21] The AMO density of tail states is usually much less than that of amorphous silicon due to the more isotropic nature of the s-orbital derived conduction band. Additionally, it has been found that carriers can percolate between potential barriers at the conduction band edge. Generally, there exists the possibility for charge transport by Mott variable range hopping (VRH) through localized states,[16] as well as transport by carriers in extended states above the mobility edge $E_m$, either by trap limited conduction (TLC) or percolation conduction (PC).[22] VRH gives rise to a characteristic $1/T^{1/4}$ mobility relationship while TLC models can be described by a simple Boltzmann expression ($1/T$). The Kamiya–Nomura[23] PC model based on work by Adler et al.[24] assumes a Gaussian distribution of potential barriers attributed to the secondary cation; in the present case X, for the In–X–O system. This model ignores VRH because there is no evidence for the Hall voltage sign anomaly in AMO semiconductors but reproduces the apparent $1/T^{1/4}$ behavior at low temperature. Note, however, that Germs et al. argue that this is in fact a result of a new state VRH combined with band transport rather than PC.[25]

For n-type TFT operation the Fermi level $E_F$ moves toward the conduction band edge as the gate voltage $V_G$ is increased to more positive values. The ratio of free ($n_f$) to trapped ($n_t$) charge carriers is, therefore, a function of $V_G$ as well as temperature and the density of tail states. For most amorphous semiconductors, a linearly increasing $V_T$ is observed with decreasing temperature as carriers are thermally generated from localized states, which in the case of a-IGZO has been shown to be ionization of oxygen vacancies.[26] It is also well known that as the gate field is increased, $E_F$ moves toward the mobility edge $E_m$ and reaches the tail states at around $V_G - V_T = 0$. The percolation voltage $V_p$ is then defined as the point at which carriers can begin to move through extended states ($E_F = E_m$); however, the exact transition from TLC to PC dominated conduction is not abrupt. At higher voltages still, band transport may be feasible and the mobility becomes temperature independent. In this study, the focus is on relatively high-temperature measurements ($300 \geq T \geq 150$ K) and effective mobilities $\mu_{\text{EFF}}$ are extracted in the linear regime ($V_D << V_G$) for $V_G > V_T$. Therefore, a combination of TLC and PC models can be applied while assuming negligible VRH in this regime. The mobilities in each of these limits are given by Equations (5) and (6), respectively.
\[
\mu_{\text{TLC}} = \mu_0 A \left[ \frac{C_i (V_C - V_T)}{qN_{\text{tr}}^0} \right]^{\frac{1}{\chi}} 
\]

\[
\mu_{\text{PC}} = \mu_0 \exp \left[ -\frac{q\phi_B}{kT} + \frac{2(\sigma B)^2}{kT} \right] B \left( V_C - V_T \right) \]

where \( \mu_0 \) is the band mobility, \( A^* \) and \( B^* \) are constants that depend on the density of conduction band states, \( C_i \) is the dielectric geometric capacitance, \( N_{\text{tr}}^0 \) is the areal density of tail states, \( kT_0 \) is the width of the tail state distribution, \( \phi_B \) is the percolation barrier height, \( \sigma B \) is the variation in \( \phi_B \) assuming a Gaussian distribution of barriers, and \( \alpha \) is related to the spatial coherence ratio of the barriers. The constant \( \alpha \) depends on the spatial barrier width \( W_B \) and separation \( D_B \) and is given by \( \alpha = 4(D_B - W_B)/D_B \). In both of these limiting cases, an activation energy \( E_a \) can be extracted from the slope of the Arrhenius plot and is given by Equation (7)

\[
E_a(V_C) = -k \frac{\partial \ln(\mu)}{\partial (1/T)} = \begin{cases} 
    kT_0 \ln \left( \frac{qN_{\text{tr}}^0}{C_i} \right) - kT_0 \ln(V_C - V_T) & \text{for TLC} \\
    q\phi_B - \frac{(\sigma B)^2}{kT} & \text{for PC}
\end{cases}
\]

As can be seen here, the activation energy will be independent of \( V_C \) for the PC case, and be inversely related for the TLC case. Therefore by analyzing \( E_a \) as a function of \( \ln(V_C - V_T) \) as well as \( \mu \) as a function of \( (V_C - V_T) \), the relative importance of TLC versus PC can be estimated, and the relevant physical parameters, \( N_{\text{tr}}^0 \), \( kT_0 \), and \( q\phi_B \) can be extracted.

### 3. Results and Discussion

The processing temperature \( T_C \) and the choice of X cation have a strong influence on the degree of crystallinity \( \chi_c \) of the final oxide film as shown in Figure 1. In the case of \( X = \text{Sc} \) at \( T_C = 300^\circ C \) all films are crystalline as estimated from the XRD peak areas (\( \chi_c \) > 0.90). Note that moving to larger cations drastically reduces the crystallinity with In–Y–O showing a transition to the amorphous phase between 5 and 7.5 at% Y and In–La–O between 2.5 and 5 at% La. At \( T_C = 250^\circ C \), most compositions are amorphous with the exception of 2.5 at% Sc which has a crystallinity of around \( \chi_c = 0.15 \). Some films, for both processing temperatures, exhibit partial crystallinity (\( \chi_c < 0.15 \)) in the vicinity of the transition composition. As a control sample, an In\textsubscript{2}O\textsubscript{3} film processed at \( T_C = 450^\circ C \) had a crystallinity of \( \chi_c > 0.98 \). Despite differences in crystallinity, there is no significant difference in r.m.s surface roughness between these films as measured by AFM, which is found to be on average 0.17 nm. This demonstrates that: (i) differences in back surface roughness will not affect our electrical measurements, and (ii) even when crystalline, these films do not exhibit large grains or prominent grain boundaries.

In accord with the observed reduction in crystallinity with the X ionic size, ab initio MD simulations of amorphous In–X–O reveal that the number of InO\textsubscript{6} polyhedra varies with X: it is largest for \( X = \text{Sc} \) and notably smaller for \( X = \text{Y} \) or \( \text{La} \) (Figure 2). Moreover, in In–Sc–O the InO\textsubscript{6} polyhedra are mostly connected via edge sharing, resulting in the formation of large InO\textsubscript{6} clusters. The appearance of such clusters signifies the nucleation of In\textsubscript{2}O\textsubscript{3} nanocrystallites, as was observed for a–InO. In marked contrast to In–Sc–O, the InO\textsubscript{6} polyhedra in amorphous In–Y–O and In–La–O are distributed uniformly throughout the cell with a few polyhedra connected via edge- or corner sharing. This highlights the effectiveness of the larger cations such as \( \text{Y} \) or \( \text{La} \) in achieving amorphous In-based oxide structures.

The TFT properties at room temperature for all compositions and processing temperatures are shown in Figure 3 and typical transfer and output curves are plotted in the Supporting Information. We will first distinguish between compositions that are measured to be amorphous by XRD (\( \chi_c = 0 \)) and those that are crystalline or partially crystalline (\( \chi_c > 0 \)). For \( \chi_c = 0 \), the maximum electron mobilities are measured to be 9.7 and 5.1 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1} for \( T_C = 300 \) and 250 °C, respectively, and are obtained in the In–La–O system. It is important to note that the use of \( X = \text{La} \) provides the highest performance amorphous films, since the large cation can be introduced into the system at relatively low concentrations, thus minimizing impurity scattering while still realizing the amorphous state. This approach, therefore, provides a useful strategy to readily introduce amorphous character into otherwise easily crystallizable materials. However, it should be noted that when considering all films, for a fixed X concentration, the general trend is that mobility decreases with increasing cation size similar to the previously
reported In–X–Zn–O system.\textsuperscript{[14]} The crystalline ($\chi_c > 0.7$) and partially crystalline (0 < $\chi_c < 0.15$) samples typically exhibit good TFT characteristics ($\mu = 1$–10 cm$^2$ V$^{-1}$ s$^{-1}$), however, tend to be slightly more inconsistent in their device parameters, often having negative (and less controllable) threshold voltages, and more variability between devices in subthreshold behavior, especially in cases of low X content. This result highlights the fact that although In–Y–O and In–Sc–O may have higher electron mobilities than In–La–O for a given X concentration, their increased propensity to crystallize can, especially in this case, be disadvantageous, and motivates the more detailed study of complex oxides such as a-IGZO. From the present data, it is, therefore, possible to extract both tail state distributions (Equation (7)). In all cases, there is no strong dependence of $E_A$ on temperature, suggesting that the barrier height distribution $\sigma_B$ is very small. This is reasonable considering that these films only have two distinct cations unlike more complex oxides such as a-IGZO. From the present data, it is, therefore, possible to extract both tail state distributions ($\sigma_B$) from the $T_a = 250 \degree C$ films, and the approximate percolation barrier heights ($\phi_B$) from the $T_a = 300 \degree C$ films; these parameters are summarized in Table 1. Note that $kT_B$ is comparable to $kT$ and therefore a purely TLC model is not appropriate. However, the advantage of the activation energy analysis is that the effects of TLC and PC can be separated by their $E_G$ dependence, and therefore an estimate of $kT_B$ can be made even for small values. For larger $R_{\text{on}}(x)$, increased structural disorder broadens the tail state distribution while the overall areal density of trap states at $E_{\text{in}}$ remains approximately constant. The DFT-calculated inverse participation ratios (IPR) for the MD-simulated nonstoichiometric amorphous In–X–O structures illustrate the existence of localized states within the band gap and near the band edges. These results support the broadening of the localized state distribution with the ionic size: a significant contribution from the localized states is found below, below and at, or below and above the Fermi level for X = Sc, Y, or La, respectively (full IPR data can be found in the Supporting Information).

**Figure 2.** Representative structures of a) In–Sc–O, b) In–Y–O, and c) In–La–O from ab initio MD simulation. In each case, 20% of the In atoms are replaced with the secondary cation, X. InO$_6$ polyhedra are indicated on the structures in purple with In represented as red spheres, X as yellow spheres, and O as blue spheres. The proportion of InO$_6$ polyhedra with $x = 4$, 5, and 6 are shown in d).

**Figure 3.** Thin film transistor data for measurements at room temperature taken in saturation to extract values of $\mu_{sat}$ and $V_T$. Regions corresponding to crystalline, semicrystalline, and amorphous films are indicated for films processed at a) $T_a = 250 \degree C$ and b) $T_a = 300 \degree C$. Optimal devices characteristics are around 5 and 10 at% doping for the low and high-temperature processed films, respectively.
In-Sc-O

Figure 4. Temperature-dependent field-effect electron mobility showing linear fits for the extraction of the activation energy, $E_A$. Effective linear mobility is plotted for values of $V_G-V_T$ for each film at and for processing temperatures of b) $T_s$ = 250 °C and c) $T_s$ = 300 °C. The extracted values of $E_A$ are plotted as a function of $\ln(V_G-V_T)$ for each film and at processing temperatures of b) $T_s$ = 250 °C and d) $T_s$ = 300 °C. Linear fits made to the $T_s$ = 250 °C data while the lines through the $T_s$ = 300 °C data are guides to the eye.

For the more structurally ordered films that show percolation behavior, $\phi_0$ also increases with increasing $R_{\text{atom}}(X)$. It has been suggested previously\cite{22b} that percolation can arise due to secondary cations perturbing the conduction band, which is primarily derived from the In s-states. Here, we are able to show, for the first time, a direct relationship between the measured potential barrier and the radius of the secondary cation, thus supporting this model. Details of the spatial coherence ratio for the potential barriers ($D_B-W_b)/D_B$ are also extracted from the $V_G$ dependence of the mobility (Figure 5a) and vary from 0.04 to 0.32, with the largest ratio observed in In–Y–O. Furthermore, a trend in the spatial distribution of $X_O$ polyhedra within the amorphous cell is clearly observed in the results of the MD simulations (Figure 5b). In the In–Sc–O series, the ScO$_x$ polyhedra are connected primarily via corner sharing; several ScO$_x$ polyhedra stand separate from each other, i.e., remain disconnected. In In–Y–O, the number of corner-shared YO$_x$ polyhedra increases substantially, leading to the formation of long chains spread over the cell—in agreement with the observed largest spatial coherence ratio. In In–La–O, the large ionic radius of La as well as its tendency for over-coordination leads to formation of clusters of LaO$_x$ polyhedra more than half of which are connected via edge- or even face-sharing. Such LaO$_x$ clustering may be connected with the observed large potential barrier in amorphous In–La–O and the resulting TFT mobility decrease for larger La contents. At the same time, the observed spatial coherence ratios have some dependence on temperature suggesting that a purely PC model is inadequate for these materials, which is consistent with the deviation of $E_B$ from a constant in Figure 4d. While alternatives to PC descriptions have been proposed,\cite{25} additional studies will be required before the current models for charge transport in amorphous metal oxide TFTs can be refined.

From the present TFT transport data, it is clear that two variables are especially important in these solution-processed In–X–O films: (i) the processing temperature, which strongly affects the charge transport mechanism; and (ii) the identity of the secondary cation, which influences both the tail state distribution and the percolation barriers. XAS is used here to further elucidate the nature of the structural disorder as seen in the electrical characterization.

Film XANES data at the In, Sc, Y, and La edges align well with their powder references (see the Supporting Information).

Table 1. Model fit parameters for the TFT measurements calculated from Equation (7).

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_s$ [°C]</th>
<th>$kT_0$ [meV]</th>
<th>$N_{\text{s}}^0$ [cm$^{-3}$]</th>
<th>$q\phi_0$ [meV]</th>
<th>Dominant mechanism$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>In–Sc–O</td>
<td>250</td>
<td>10</td>
<td>$4 \times 10^{13}$</td>
<td>–</td>
<td>TLC</td>
</tr>
<tr>
<td>In–Y–O</td>
<td>250</td>
<td>17</td>
<td>$5 \times 10^{13}$</td>
<td>–</td>
<td>TLC</td>
</tr>
<tr>
<td>In–La–O</td>
<td>250</td>
<td>23</td>
<td>$4 \times 10^{13}$</td>
<td>–</td>
<td>TLC</td>
</tr>
<tr>
<td>In–Sc–O</td>
<td>300</td>
<td>–</td>
<td>–</td>
<td>24</td>
<td>PC</td>
</tr>
<tr>
<td>In–Y–O</td>
<td>300</td>
<td>–</td>
<td>–</td>
<td>38</td>
<td>PC</td>
</tr>
<tr>
<td>In–La–O</td>
<td>300</td>
<td>–</td>
<td>–</td>
<td>55</td>
<td>PC</td>
</tr>
</tbody>
</table>

$^a$ Mechanisms: TLC = trap-limited conduction; PC = percolation conduction.
Combined with the XPS peak positions, all metal ions maintain the 3+ oxidation state in the films after the combustion process. A more quantitative analysis from the EXAFS region provides the coordination number $N_i$ and Debye–Waller coefficient $\sigma_i^2$ for the first In–O shell and the first In–M shell (M = In or X), as shown in Figure 6, and the fitting results presented in Table 2. For all films, the calculated radii $R_i$ are relatively constant at 2.16 Å for the In–O shell and 3.36 Å for the In–M shell, which are comparable to the radii for crystalline In$_2$O$_3$ reference powder samples. The reductions in peak intensities in the p-RDF, especially for shells beyond the first In–O, make the second In–O shell and the first In–M-shell ($M = $In or X) X cation normalized to the radius of In$^{3+}$.

Figure 6. Fitting parameters from the In–X–O EXAFS measurements and ab initio MD simulations plotted as a function of the ionic radius of the X cation normalized to the radius of In$^{3+}$. a) The change in coordination number, $N_i$ for both the In–O and In–M ($M =$In or X) shells. b) The same for the change in Debye–Waller factor coefficient, $\sigma_i^2$.

Table 2. EXAFS fitting parameters for the first In–O and In–M ($M =$In or X) shells calculated using Equation (1).

<table>
<thead>
<tr>
<th>$T_a$ [°C]</th>
<th>$N_i$</th>
<th>$R_i$ [Å]</th>
<th>$\sigma_i^2$ [10$^{-3}$ Å$^2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>In–O</td>
<td>In–M</td>
<td>In–O</td>
</tr>
<tr>
<td>In–Sc–O</td>
<td>250</td>
<td>5.62</td>
<td>3.04</td>
</tr>
<tr>
<td>In–Y–O</td>
<td>250</td>
<td>5.54</td>
<td>2.20</td>
</tr>
<tr>
<td>In–La–O</td>
<td>250</td>
<td>5.11</td>
<td>2.4$^4$</td>
</tr>
<tr>
<td>In–Sc–O</td>
<td>300</td>
<td>5.95</td>
<td>4.21</td>
</tr>
<tr>
<td>In–Y–O</td>
<td>300</td>
<td>5.75</td>
<td>3.62</td>
</tr>
<tr>
<td>In–La–O</td>
<td>300</td>
<td>5.56</td>
<td>3.32</td>
</tr>
</tbody>
</table>

$^4$Shells beyond the first have very low intensity (approaching EXAFS-free amorphous); therefore, the coordination number and Debye–Waller factor for the second shell cannot be uniquely fitted.

Table 3. Structural characteristics of the first In–O and X–O shell as obtained from the ab initio MD simulations. The average coordination $N_{ECN}$ and average distance $R_{av}$, parameters were calculated according to Equations (2) and (3).

<table>
<thead>
<tr>
<th>$T_a$ [°C]</th>
<th>$N_{ECN}$</th>
<th>$R_{av}$ [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>In–Sc–O</td>
<td>250</td>
<td>5.32</td>
</tr>
<tr>
<td>In–Y–O</td>
<td>250</td>
<td>5.06</td>
</tr>
<tr>
<td>In–La–O</td>
<td>250</td>
<td>5.02</td>
</tr>
</tbody>
</table>

The ab initio MD simulations for the In–X–O systems support the coordination number and bond length variations seen in the EXAFS experiments. For the first In–O or X–O shell, the calculated effective coordination numbers $N_{ECN}$ and bond lengths $R_{av}$ are summarized in Table 3. These values are in agreement with EXAFS showing: (i) a slight contraction in the In–O coordination number as the X cation size is increased and (ii) nearly invariant In–O bond lengths. For comparison, the average In–O distance and In–O coordination number in a-InO...
obtained from MD simulations are 2.16 Å and 5.0, respectively. Although the In–O local structure characteristics show little sensitivity to the X cation size, the $N_{ECN}$ and $R_{ECN}$ values for X–O vary significantly among X, as expected from the strong X–O bonds. The average X–O distances in amorphous In–X–O nearly match the corresponding natural X–O distances, i.e., those found in the respective crystalline X$_2$O$_3$ materials. The average effective coordination $N_{ECN}$ increases as the cation size increases, with Sc and La being under- and over-coordinated with O atoms, respectively, whereas the Y atoms retain the natural coordination number of 6.

As noted in Section 2.2, Equations (2) and (3) are not applicable for the second shell and beyond owing to broad In–M distances. Instead, the total In–M coordination or a running coordination number $N_{RCN}$ is calculated as a function of the radial distance $r$ from an In atom. The $N_{RCN}$ values for both In–O and In–M shells, Figure 7a,b, respectively, decrease with increasing cation size, but the effect is far more pronounced for the In–M shell. At $r = 3.35$ Å, which corresponds to the edge-shared In–In distance in crystalline In$_2$O$_3$, $N_{ECN}$(In–M) decreases from 3.82 to 3.16 to 2.05 for Sc to Y to La, respectively. In a-InO, the calculated $N_{RCN}$(In–In) is 2.69. Accordingly, the average distance between In and X connected by edge-sharing (second shell) increases with X ionic size: from 3.08 to 3.36 Å to 3.52 Å for In–Sc to In–Y to In–La, respectively. For comparison, the average edge-shared In–In distances are less affected, increasing from 3.26 to 3.31 Å for Sc and Y to La, respectively. Although it is impossible to directly compare these numbers to the experimental EXAFS data, which are derived from solution-processed films rather than a melt-and-quench simulation, it is evident that these numbers correlate well with those in Figure 6 and follow the same trend. The increased second shell (In–M) bond distances can contribute to a larger effective mass; however, the spatial distribution and interconnection of the InO$_x$ and XO$_x$ polyhedra are expected to play the key role in determining the electron mobility in these amorphous oxides.

In addition to local disorder, the strength and type of M–O bonding have been shown to be good indicators of electron transport properties since weakly bound oxygen or oxygen not fully coordinated by a metal ion can introduce trap states and reduce the mobility and bias-stress stability in TFTs. Previous work in this laboratory on oxygen “getter” effects in In–X–Zn–O materials suggests this may also be relevant to the In–X–O system. XPS measurements were therefore carried out, focusing on the O1s peak, deconvoluting it into a M–O–M peak, a M–O(H) peak, and a weakly bound M–O–R surface peak (Figure 8a,b). The ratio of M–O–M peak area to total peak area $\eta_{M-O-M}$ is shown in Figure 8c and represents the fraction of oxygen in the film that is completely incorporated into the metal oxide lattice. Additionally, using the ratio of O1s peaks to the In 3d, Sc 2p, Y 3d, or La 3d peaks allows estimation of the In–X–O film stoichiometry, which indicates that the oxide films preserve the precursor solution stoichiometry. All films, independent of the processing temperature or composition, are found to be close to stoichiometric (60 at% O). However, it is evident that $\eta_{M-O-M}$ is a function of the processing temperature. For the $T_p = 300$ °C case, the oxide is well formed and $\eta_{M-O-M}$ is relatively unaffected by the secondary cation since the thermal energy at this processing temperature allows good relaxation of the oxide lattice. However, $\eta_{M-O-M}$ is lower for all compositions processed at $T_p = 250$ °C, suggesting that the oxide film is more defective, leading to the change from charge transport being limited by percolation in the conduction band to trapping and detrapping from tail states. Additionally, the larger cations tend to reduce $\eta_{M-O-M}$ further, unlike in the high-temperature case, which is consistent with the broadening of the density of tail states at $T_p = 250$ °C when changing from Sc to Y to La.

### 4. Conclusions

The incorporation of the Group 3/4f cations Sc, Y, and La into indium oxide thin films by straightforward solution-processing techniques at low temperatures provides important information about the structural and electronic properties of amorphous oxide semiconductors. First and importantly, to facilitate the study of these systems, note that these elements can be introduced without the need for complex processing equipment and over a wide compositional range. It is found that large values of the X ionic radius $R_{ionic}(X)$ compared to indium, such as when X = La, can induce the amorphous state even at relatively low X concentrations, resulting in thin films with high electron mobilities. The effect of the cation size and processing temperature on the electron transport mechanism was also investigated here, and found to be dominated by trap-limited conduction...
ties (M–O–M). c) The ratio of M–O–M peak area to total area, (M–O(H)) and weakly bound oxygen at the surface or organic impurities correspond to fully bound oxygen (M–O–M), partially bound oxygen (M–O(H)) and weakly bound oxygen at the surface or organic impurities. The interconnectivity of the MO

5. Experimental Section

Oxide Precursor Solutions: Solutions were prepared by dissolving M(NO3)3 in 2-methoxyethanol (M = In, Sc, Y, or La, 0.05 mol L⁻¹, 10 mL) and adding acetylacetone (32 µL) and NH3(aq) (30 µL). Solutions were stirred for 16 h before mixing in the desired ratios. The solutions were then filtered through a 0.2 µm Teflon filter, spin-coated at 3500 s⁻¹ for 30 s and annealed at 250 or 300 °C (T_a) in air for 15 min yielding ≈5 nm thick oxide films. Repeated spin-coating and annealing was used to build up thicker films. This gave more dense oxide films than a single thick layer due to porosity caused by gas evolution during solution processing. The chosen thickness gave us optimal device performance. Hotplate surface temperatures were controlled to ±2 °C and only very small changes in substrate temperature were seen during film combustion. Changes in local temperature within the film during growth were extremely difficult to quantify accurately but were common to all solution-processing techniques. Generally in these films, heat energy generated from chemical reactions will either be consumed driving lattice/network formation or will be dissipated relatively rapidly due to the large surface area-to-volume ratio. T_a therefore defines the technologically relevant thermal budget for the process. Films for TFTs were fabricated on heavily doped silicon wafers with 300 nm of thermal oxide (four repeated layers of combustion oxide, film thickness ≈15 nm). Films for grazing incidence XRD studies were fabricated on silicon wafers (four layers), and films for XAS were fabricated on fused-quartz substrates (11 layers, X: 25 at%). A postanneal in clean dry air at T_a was carried out at <5% relative humidity on all films.

Thin-Film Transistors: TFTs were fabricated by patterning the In–X–O films with oxalic acid to reduce gate leakage, followed by evaporation of aluminum source-drain contacts through a shadow mask. Device dimensions were L = 50 µm, W = 1 mm. Electrical measurements were carried out either in air or a vacuum probe station (<5 × 10⁻⁴ mbar) with an Agilent B1500A parameter analyzer. Transfer characteristics were measured in both the linear and saturation regimes of the TFT. Samples for low-temperature measurements were mounted on an Advanced Research Systems liquid nitrogen cryostat controlled by a Lake Shore 331 temperature controller. Mobilities were extracted in the range of V_g=10 V between 5 and 25 V where leakage currents were always >>10× lower than the source-drain current. Effective mobility \( \mu_{EFF} \) was calculated in the linear regime (\( V_D = 5 \, V \)) using Equation (8) and choosing appropriate onset voltages \( V_ON \) estimated from the transfer characteristics. This method gave an average mobility for both trapped and untrapped electrons and correctly represented the gate voltage dependence of the mobility.[16]

\[
\mu_{EFF} = \frac{L}{W C_{ox}} \frac{I_D(V_D)}{V_D(V_D - V_{ON})}
\]  

X-Ray Absorption Spectroscopy: Experiments were conducted at sector 5BMD of the Advanced Photon Source of Argonne National Laboratory (ANL). A Si(111) double crystal monochromator was used to produce a 12 mm (horizontal) by 1 mm (vertical) beam. The incident beam energies were tuned to near the In, Sc, Y K-edge and La L-edge (27.940, 4.492, 17.038, 6.266 keV, respectively) to measure XAS spectra at the above four edges. Films were placed 45° from the incident direction, and data
were collected in fluorescence mode using a four-element silicon drift detector (SII NanoTechnology). The reference powders were uniformly spread on Scotch tape (3M Corp.) and measured in transmission mode using an ionization chamber (Oxford-Danfysik). EXAFS spectra were extracted and normalized using ATHENA software packages. The intrinsic loss factor ($S_0^2 = 1.106$) for fitting the indium K-edge was obtained by modeling of the reference powders for each absorbing atom, and kept fixed when fitting the film data. The bond distances, coordination numbers, and Debye–Waller factors were obtained by the FEFF simulations using a cluster of the bixbyte structure with a radius of 6 Å centered on the absorbing atom. All the normalized absorption coefficients $\chi(k)$ were Fourier transformed using a Hanning window over the specified k-range and fit in k-space with weight 3.

Ab Initio Molecular Dynamics Simulation: The amorphous In–O structures were generated using first-principles MD as implemented in the Vienna Ab initio Simulation package (vasp). The calculations were based on density functional theory within generalized gradient approximation (GGA) with the PBE functional. For the initial structure, a bixbyte In$_2$O$_3$ cell containing 130 atoms (In$_{52}$O$_{78}$) and a density of 7.116 g cm$^{-3}$ was used. For ternary structures, 20% of In atoms in crystalline In$_2$O$_3$ were replaced by metal X (Sc, Y, or La) resulting in nonstoichiometric In$_{44}$X$_{11}$O$_{77}$ structures were modeled by removing oxygen atoms in the initial structures, i.e., prior to liquid quench process. The amorphous In–O and In–X–O structures were then obtained using the liquid-quench approach as follows. First, to remove any crystalline memory, each initial structure was melted at 3000 K for 6 ps. The melt was then cooled to 1700 K at the rate of 100 K/1.2 ps, and then rapidly quenched to 100 K at the rate of 200 K/1.2 ps. In order to make the calculations computationally efficient, a cutoff of 260 eV was used and the k-point sampling was restricted to k-point only during melting and quenching processes. Finally, the structures were equilibrated at 300 K for 6 ps with a cut-off energy of 400 eV. All simulations were carried out within NVT ensemble with Nose–Hoover thermostat using integration time step of 2 fs.

Structural Characterization: Grazing incidence XRD was carried out on a Rigaku ATX-G workstation (Cu Kα, $\lambda = 1.541$ Å) with an incidence angle, $\alpha = 0.5^\circ$ compared to a critical angle for In$_2$O$_3$ of $\alpha_c = 0.37^\circ$. After background subtraction, the degree of crystallinity $\chi$ was estimated from the ratio of area under the crystalline peaks (after subtracting the amorphous peak) to total area under the X-ray diffraction pattern. Diffraction peaks were fitted with a pseudo-Voigt function (Gaussian–Lorentzian product). Atomic force microscopy (AFM) was carried out in tapping mode on a Bruker ICON system. XPS was carried out on a SPECS PHI-5000 ESCA system. XPS data were extracted and normalized using ATHENA software packages. EXAFS spectra were measured and analyzed using RIGON (3M Corp.) and EXAFS mode using an ionization chamber (Oxford-Danfysik). EXAFS spectra were extracted and normalized using ATHENA software packages. The intrinsic loss factor ($S_0^2 = 1.106$) for fitting the indium K-edge was obtained by modeling of the reference powders for each absorbing atom, and kept fixed when fitting the film data. The bond distances, coordination numbers, and Debye–Waller factors were obtained by the FEFF simulations using a cluster of the bixbyte structure with a radius of 6 Å centered on the absorbing atom. All the normalized absorption coefficients $\chi(k)$ were Fourier transformed using a Hanning window over the specified k-range and fit in k-space with weight 3.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements
The authors acknowledge support from the Office of Naval Research (MURI N00014-11-1-0690; J.S., K.S.) and the Materials Research Center of Northwestern University (NSF-MRSEC DMR-1121262; R.K., L.Z.). This work made use of the J. B. Cohen X-Ray Diffraction Facility supported by the NSF-MRSEC program (DMR-1121262) at the MRSEC Center of Northwestern University (NSF-MRSEC DMR-1121262; R.K., L.Z.). This work made use of the Keck II and NIFTI facilities at Northwestern University’s Atomic and Nanoscale Characterization Experimental Center (NUANCE) for XPS and AFM. NUANCE was supported by NSF-NSEC, NSF-MRSEC, Keck Foundation, the State of Illinois, and Northwestern University. The authors thank Prof. M. Grayson for insightful discussions. Computational resources were provided by the NSF-supported XSEDE program, Grant TG-DMR080007.


Received: April 28, 2015
Published online: June 5, 2015


