Defect Cluster Aggregation and Nonreducibility in Tin-Doped Indium Oxide

Oliver Warschkow,† Donald E. Ellis,*‡ Gabriela B. González,*‡ and Thomas O. Mason,*‡

Department of Physics and Astronomy and Institute of Environmental Catalysis, and Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208

The conductivity of tin-doped indium oxide (ITO), a transparent conductor, is critically dependent on the amount of tin doping and oxygen partial pressure during preparation and annealing. Frank and Köstlin (Appl. Phys. A, 27, 197–206 (1982)) have rationalized the observed carrier concentration dependence by postulating the formation of two types of neutral defect clusters at medium tin-doping levels: "reducible" and "nonreducible" defect clusters, so named to indicate their ability to create carriers under reduction. According to Frank and Köstlin, both clusters are composed of one oxygen interstitial and two tin atoms substituting for indium, positioned in nonnearest and nearest coordination, respectively. This work, seeking to distinguish reducible and nonreducible clusters by means of an atomistic model, finds only a weak correlation of oxygen interstitial binding energies with the relative positioning of tin dopants. Instead, the number of tin dopants in the vicinity of the interstitial has a much larger effect on how strongly it is bound, a simple consequence of Coulomb interactions. We postulate that oxygen interstitials become nonreducible when clustered with three or more SnIn.

This occurs at higher doping levels as reducible clusters aggregate and share tin atoms. A simple probabilistic model, estimating the average number of clusters so aggregated, yields a qualitatively correct description of the carrier density in reduced ITO as a function of tin-doping level.

I. Introduction

The electronic and optical properties of the transparent conductor tin-doped indium oxide (ITO) are critically dependent on the presence and distribution of the Sn4+ electron donors, the local chemistry, and charge balance of the related defect sites. An understanding of atomic-scale defect properties is needed to maximize conductivity and transparency of this and related metal-doped oxides, which are now diversifying into ternary compounds, such as zinc indium tin oxide (ZITO). For ITO thin films, Köstlin and co-workers1,2 have deduced from measured electrical properties (conductivity, carrier density, and mobility as a function of oxygen partial pressure pO2, and tin content) the existence of associated neutral defects. At high pO2 and medium tin-doping levels, they have postulated two types of defects: "reducible" and "nonreducible" clusters of composition (2SnIn2O2)n, formed by two Sn4+ ions substituting for In3+ and one interstitial oxygen anion.3 Of these, the loosely bound reducible cluster, with SnIn in nonnearest coordination to O2, dissociates following reduction.

\[
(2\text{SnIn}2\text{O})_n \rightarrow 2\text{SnIn} + 2e' + \frac{1}{2} \text{O}_2
\]  

SnIn+ are freed and charge compensated by electrons, resulting in an increased conductivity in reduced ITO materials. Under strongly reducing conditions and the balance of Eq. (1) very much on the right hand side, a linear relationship between the number of charge carriers and the total tin concentration follows. This is indeed observed for tin levels up to a few percent (<3%, depending on the pO2).4 For higher tin-doping levels, the carrier density increases at a lower rate, which is rationalized by the presence of the more tightly bound, nonreducible cluster, with SnIn in nearest coordination. According to Frank and Köstlin,1 this cluster remains nonionized, even in highly reducing conditions. The decay of produced carriers at even higher doping levels is explained in terms of an aggregate of a reducible and a nonreducible cluster.1

Nadaud et al.3 and González et al.4 used Rietveld refinement on powder neutron diffraction data to obtain structural information about ITO materials as a function of pO2 and tin doping. The latter work found, for an oxidized 4.5-at.%-Sn ITO specimen, the ratio of tin to interstitial oxygen to be 2:2, consistent with the existence of the two neutral defect complexes. When the sample was annealed under reducing conditions (CO/CO2, pO2 = 10−14 atm), the tin:oxygen interstitial ratio increased to 6:2 because of the removal of some, but not all, the oxygen interstitials.4 A direct observation of charge carrier generation on release of oxygen in ITO was reported by Omata and co-workers.5,6

Complementing the experimental research, Warschkow et al.7 using atomistic-modeling techniques, performed an extensive survey of defect clusters, identifying low-energy structures of defect clusters involving a single oxygen interstitial (O2) and up to three tin dopants in the first and second coordination shells. These calculations further confirmed the trend of SnIn and O2 to form energetically stable clusters and provided insights into the structural aspects of defect clustering, such as substitution site preferences.

This work is a follow-up, using the same computational model to identify at an atomic level what precisely distinguishes reducible and nonreducible interstitials. We have computed the binding energy of oxygen interstitials for defect complexes of varying SnIn and O2 composition and relative positioning. Based on the qualitative picture that emerges from these results, a simple stochastic model is presented that rationalizes the observed macroscopic carrier concentration as a function of tin-doping level.

†Department of Materials Science and Engineering.
‡Department of Physics and Astronomy and Institute of Environmental Catalysis.
*Member, American Ceramic Society.
\footnote{Frank and Köstlin\cite{1} denote reducible and nonreducible clusters as (Sn3+O2) and (Sn4+O2)−, respectively. We find this notation problematic, because it may suggest that the nonreducible cluster contains an additional three oxygen atoms. Close inspection of Ref. 1, however, reveals these three oxygen atoms to be structural oxygen atoms (O2 in Kroger–Vink notation) equally present in reducible and nonreducible clusters. Therefore, (Sn3+O2) and (Sn4+O2)− in Ref. 1 represent neutral defect clusters (2SnIn2O2)n composed of one oxygen interstitial and two tin atoms substituting for indium.}
II. Models and Methodology

The atomistic model used in this work, including all parameterizations, is exactly as in our previous article on Sn-doped In$_2$O$_3$, referred to hereafter as Part 1. Briefly, all structural, lattice, and defect energies reported in this work have been calculated using the atomistic Born model of polar solids, as implemented by the GULP package.4,9 Lattice ions are represented as point ions, and all interactions between ions are assumed to be pairwise. Oxide ions are allowed to polarize by means of the shell model.10 Defect interactions between ions are assumed to be pairwise. Oxide ions and (ii) the reduction of the isolated interstitial Sn In positioned in the first and second shell. For example, we use a vertical bar (|) to distinguish Sn In from unoxidized Sn In, and Sn In from Sn In-O. In the energetic calculations, interactions to all distances are included. When relevant, its first or second coordination shell. In the energetic calculations, we formulate the reduction of a defect cluster as a two-step process: (i) detachment of the interstitial from the cluster to form an oxidized and reduced cluster. Differences in the reducibility of interstitials because of differences in the clusters in which they are bound should manifest themselves in this energy. Specifically, if, as stipulated by Frank and Köstlin,1 reducible and nonreducible defect clusters are composed of two Sn$_{ni}$ and one O$_{i}$ but with different relative positioning of the participating defects, then we should expect to identify these among clusters of 2:1 stoichiometry by a marked difference in the computed detachment energy.

In Table I, we have summarized for various defect clusters the calculated detachment energies together with the cluster formation energies of oxidized and reduced clusters. Only the lowest-energy structures of the respective stoichiometry groups (see Part 1) are considered, because we regard other structures not likely to be formed in the first place. Because a survey of 4:1 clusters was not undertaken in Part 1, the two 4:1 examples in Table I may not be the lowest-energy structures for this stoichiometry group.

In the group of defect clusters of composition Sn$_{ni}$O$_{i}$ = 2:1, the interstitial detachment energy is ~2.4 eV for those clusters with nonnearest positioning of the two Sn$_{ni}$ sites. Further listed are two defect clusters with two Sn$_{ni}$ sites in relative nearest cation position. The product of reduction of these two clusters are nearest (Sn$_{ni}$)~2~ clusters with formation energies of +0.62 and +0.55 eV, respectively. This is somewhat higher than for the nonnearest clusters in the group (approximately +0.3 eV); however, the nonreduced clusters are also less stable than their nonnearest counterparts, and the net effect is that the interstitial detachment energy of nearest and nonnearest clusters is very similar indeed (2.61 and 2.46 eV versus 2.4 eV, respectively). Clearly, competing effects occur; thus, within the 2:1 stoichiometry group, we find it difficult to distinguish any difference between a reducible and a nonreducible defect cluster.

On the other hand, stoichiometry, that is, the number of Sn$_{ni}$ around an interstitial, appears to be a much stronger modifier: Table I clearly illustrates that interstitial detachment energies increase dramatically and almost linearly with the Sn$_{ni}$O$_{i}$ ratio while exhibiting comparatively little variation between structures within a given ratio.

This suggests that the reducibility of a defect cluster is less associated with the relative positioning of dopants and interstitials

### Table 1. Calculated Interstitial Detachment Energy for Various Defect Clusters

<table>
<thead>
<tr>
<th>Sn$<em>{ni}$O$</em>{i}$ Ratio</th>
<th>Defect cluster</th>
<th>Sn$_{ni}$ relative position</th>
<th>Cluster formation energy (eV)</th>
<th>Cluster formation energy of reduced cluster (eV)$^1$</th>
<th>Interstitial detachment energy (eV)$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0:1</td>
<td>O$_{i}^+$</td>
<td></td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>1:1</td>
<td>(Sn(d)</td>
<td>O)$_{i}^+$</td>
<td></td>
<td>-1.29</td>
<td>0.00</td>
</tr>
<tr>
<td>2:1</td>
<td>(Sn(b)</td>
<td>Sn(d)</td>
<td>O)$_{i}^&lt;$</td>
<td>Nonnearest</td>
<td>-2.09</td>
</tr>
<tr>
<td></td>
<td>(Sn(b)</td>
<td>O)$_{i}^&lt;$</td>
<td>Nonnearest</td>
<td>-2.08</td>
<td>+0.39</td>
</tr>
<tr>
<td></td>
<td>(Sn(d)</td>
<td>O)$_{i}^&lt;$</td>
<td>Nonnearest</td>
<td>-2.05</td>
<td>+0.31</td>
</tr>
<tr>
<td></td>
<td>(Sn(b)</td>
<td>Sn(d)</td>
<td>O)$_{i}^&lt;$</td>
<td>Nearest</td>
<td>-1.99</td>
</tr>
<tr>
<td></td>
<td>(Sn(d)</td>
<td>O)$_{i}^&lt;$</td>
<td>Nearest</td>
<td>-1.91</td>
<td>+0.55</td>
</tr>
<tr>
<td>3:1</td>
<td>(3Sn(b)</td>
<td>O)$_{i}^&lt;$</td>
<td>Nonnearest</td>
<td>-2.55</td>
<td>+1.02</td>
</tr>
<tr>
<td></td>
<td>(2Sn(b)</td>
<td>Sn(d)</td>
<td>O)$_{i}^&lt;$</td>
<td>Nonnearest</td>
<td>-2.43</td>
</tr>
<tr>
<td></td>
<td>(Sn(b)</td>
<td>2Sn(d)</td>
<td>O)$_{i}^&lt;$</td>
<td>Nonnearest</td>
<td>-2.36</td>
</tr>
<tr>
<td></td>
<td>(2Sn(b)</td>
<td>Sn(d)</td>
<td>O)$_{i}^&lt;$</td>
<td>Nearest</td>
<td>-2.35</td>
</tr>
<tr>
<td>4:1</td>
<td>(2Sn(b)</td>
<td>2Sn(d)</td>
<td>O)$_{i}^&lt;$</td>
<td>Nonnearest</td>
<td>-2.34</td>
</tr>
<tr>
<td></td>
<td>(3Sn(b)</td>
<td>Sn(d)</td>
<td>O)$_{i}^&lt;$</td>
<td>Nearest</td>
<td>-2.34</td>
</tr>
</tbody>
</table>

$^1$Cluster formation energy of the reduced cluster with the interstitial oxygen atom removed. Positive energies indicate that the reduced clusters are metastable with respect to dissociation into nonclustered point defects. $^2$Reaction energy of Eq. (2).
within a stoichiometry group but is rather a consequence of differences in the local stoichiometry. Specifically, these results make it very unlikely that Frank and Köstlin's nonreducible cluster is of the same composition \(2\text{Sn}_n\text{O}_3\) and, thus, a mere structural variant of its reducible counterpart. As an alternative, we postulate that oxygen interstitials become nonreducible when coordinated by three or more \(\text{Sn}_n\).

If we associate nonreducibility with increased tin coordination around \(O\), we must address how it comes about as a function of tin doping: Frank and Köstlin's work shows that, in oxidized (i.e., non-reduced) ITO at low tin doping, the majority of \(\text{Sn}_n\) and \(O\) are bound in neutral 2:1 defect clusters \(2\text{Sn}_n\text{O}_3\). In our understanding, increased nonreducibility at higher tin-doping levels results from the increased probability that two (or more) 2:1 clusters are positioned close enough together such that cluster aggregation can occur. In such aggregated clusters, some \(\text{Sn}_n\) dopants become shared between clusters and bound to more than one \(O\). This in turn increases the number of \(\text{Sn}_n\) sites around some (but not all) of the interstitials to more than two, which renders them locally similar to an interstitial in a 3:1 or 4:1 cluster, etc., and, thus, nonreducible according to our proposal. We illustrate this mechanism schematically in Fig. 1 for the simplest case: an aggregation of two 2:1 clusters. In the aggregation product, a 4:2 cluster, a single \(\text{Sn}_n\) is shared and binds to both interstitials. One interstitial in this aggregate is coordinated by two \(\text{Sn}_n\); we expect this interstitial to be 2:1-like and to remain reducible. The other interstitial is coordinated by three \(\text{Sn}_n\); its local environment is that of a 3:1 cluster, and we expect this interstitial to be nonreducible.

Using the atomistic model, we calculate the interstitial detachment energies for an example of a 4:2 aggregate of the type illustrated in Fig. 1. Of the many possible structural variations, the relative positioning of dopants adopted in this example is a composite of the low-energy \((3\text{Sn}(b)\text{O})\) and \((2\text{Sn}(b)\text{O})^\times\) clusters (see Part 1) arranged such that one \(\text{Sn}(b)\) is common between the two subunits while maintaining a maximum distance between the interstitials.

For this particular aggregate, the detachment energy is calculated to be 2.32 and 3.13 eV for the interstitial coordinated by two and three \(\text{Sn}_n\) respectively. These energies closely match the energies calculated for 2:1 and 3:1 clusters (Table I), illustrating how it is the number of \(\text{Sn}_n\) dopants in the vicinity of the interstitial that is the critical factor. The fact that the center \(\text{Sn}_n\) is bound to two interstitials has a comparatively small effect.

Intuitively, it is, perhaps, not all that surprising that interstitial binding (and thus reducibility) is strongly correlated with the number of nearby \(\text{Sn}_n\) dopants. The more \(\text{Sn}_n\) are located in the vicinity of an interstitial, the more its presence is required in the lattice as a counterion to achieve some sort of local charge neutrality; in a sense, the interstitial behaves increasingly similar to a structural oxygen. Put differently, each positively charged tin dopant creates around itself an electrostatic well by which any nearby oxygen interstitial is held in place. Because electrostatics are additive, a number of tin dopants can cooperatively increase the binding on an interstitial by overlapping their respective wells. Mutual repulsion between tin dopants puts a limit on this number; however, this repulsion should be fairly inconsiderable on the interstitial detachment energy, because, in first approximation, it is equally present before and after reductive removal of the interstitial.

As an aside, we note that Frank and Köstlin propose aggregation of two 2:1 clusters (one reducible, one nonreducible) into an essentially nonreducible 4:2 cluster to account for the decay of carrier density at high doping levels. We believe our model improves on this interpretation in three important aspects: (i) We understand nonreducibility to be a consequence of aggregation, and, thus, we do not need to make a distinction between 2:1 clusters into a reducible and nonreducible variety; (ii) some of the interstitials in an aggregated cluster remain reducible; and (iii), as shown below, our model naturally extends to situations in which a cluster is aggregated with more than one other cluster.

(2) Macromodel

Before extending our model to the macroscopic domain, we recap the relevant atomic-scale or microscopic results and assumptions of our model. Our calculations show that interstitials neighbored by more than two \(\text{Sn}_n\) are more tightly bound than those with only two \(\text{Sn}_n\) irrespective of how many interstitials the \(\text{Sn}_n\) are bound. We postulate the former to be nonreducible, even under highly reducing conditions. An oxygen interstitial, normally coordinated by two \(\text{Sn}_n\) in the form of a 2:1 clusters can gain additional \(\text{Sn}_n\) when its 2:1 cluster aggregates with other clusters.

Based on this model, we can estimate the percentage of reducible interstitials and, thus, the maximum carrier concentration of reduced ITO as a function of tin-doping level, using the following probabilistic argument.

We assume \(\text{Sn}_n\) and \(O\) distributed randomly in the \(\text{In}_2\text{O}_3\) lattice in the form of 2:1 clusters. Considering the interstitial to be the center of a 2:1 cluster, the distribution of clusters is thus given by the random distribution of \(O\) over available interstitial sites, with two \(\text{Sn}_n\) in the immediate vicinity.

The probability \(P_{\text{Sn}}\) (in percent) of a given cation site to be occupied by a tin dopant atom is equal to the macroscopic tin dopant concentration \(c_{\text{Sn}}\) (in atomic percent (at.%)). With 32 cation sites and 16 interstitial sites in the \(\text{In}_2\text{O}_3\) unit cell and one interstitial for every two tin dopants, the probability \(P_{\text{O}}\) for the occupation of a given oxygen interstitial site is

\[
P_{\text{O}} = \frac{1}{2} \left( \frac{32}{16} \right) P_{\text{Sn}} = \frac{1}{100} c_{\text{Sn}} \text{(at.%)}
\]

(4)

Considering interstitials to be the center of a 2:1 cluster, we are now interested in the probabilities \(P_{\text{O}}\) that a given interstitial has \(k\) other 2:1 clusters within an effective radius \(R_{\text{eff}}\), which we understand to be the distance between two interstitials at which tin sharing between two clusters can occur. \(R_{\text{eff}}\) defines a sphere within which there are \(N_{\text{eff}}\) other interstitial sites; occupation of any one of these would result in an aggregated cluster. The

![Fig. 1. Schematic illustration of an aggregation reaction of two reducible 2:1 clusters to form a 4:2 cluster. One of the interstitials in the aggregate gains an additional \(\text{Sn}_n\) in its coordination sphere. Interstitial local environment thus resembles a 3:1 cluster, and we expect it to be nonreducible. Other interstitial maintains a 2:1-like environment and, thus, remains reducible.](image)
probability $P_k$ that a given interstitial has exactly $k$ of the $N_{\text{eff}}$ sites in its vicinity occupied by other 2:1 clusters is given by the following expression:

$$P_k = \left( \frac{N_{\text{eff}}}{k} \right) P_0^k (1 - P_0)^{N_{\text{eff}} - k}$$

(5)

Specifically, for zero, one, and two nearby 2:1 clusters, we have

$$P_0 = (1 - P_0)^{N_{\text{eff}}}$$

(6a)

$$P_1 = N_{\text{eff}} P_0 (1 - P_0)^{N_{\text{eff}} - 1}$$

(6b)

$$P_2 = \frac{1}{2} N_{\text{eff}} (N_{\text{eff}} - 1) P_0^2 (1 - P_0)^{N_{\text{eff}} - 2}$$

(6c)

These probabilities are tin-doping dependent through $P_0$.

Aggregation of a 2:1 cluster with other clusters does not necessarily make the interstitial at its center nonreducible, and we need to take this into account. It is instructive to observe in the example of a single pairing illustrated in Fig. 1 that the shared Sn$_{\text{In}}$ atom originates from one of the two participating 2:1 clusters. We distinguish here between tin-donating and tin-accepting 2:1 clusters, noting that the interstitial of the tin-accepting cluster gains an additional Sn$_{\text{In}}$ and, thus, becomes nonreducible. The Sn$_{\text{In}}$ count around the interstitial of the tin-donating cluster does not change; it remains reducible.

In a simple generalization, we assume that, in all cluster pairings, one cluster is tin-accepting and the other is tin-donating; thus, the probability of a given cluster being a tin donor in a single pairing is $\frac{1}{2}$. The probability of a $k$-fold aggregated cluster remaining reducible by being an Sn$_{\text{In}}$ donor to all the $k$ clusters it is paired with is $(\frac{1}{2})^k$. This probability is equal to the average number of carriers per tin atom $n_k$ freed by such a cluster on reduction; i.e.,

$$n_k = \left( \frac{1}{2} \right)^k$$

(7)

Combining the set of tin-doping level-dependent probabilities $P_0(c_{\text{Sn}})$ for $k$-fold aggregated 2:1 clusters (Eq. (5)) with the respective average number of carriers produced $n_k$ (Eq. (7)) yields a relation between the average number of carriers per tin atom as a function of tin-doping level. This, further multiplied with the total tin concentration in In$_2$O$_3$, gives the maximum carrier concentration $c_\text{x}$ after reduction as a function of doping level.

$$c_\text{x} = c_{\text{Sn}} \left( P_0(c_{\text{Sn}}) + \frac{1}{2} P_1(c_{\text{Sn}}) + \frac{1}{4} P_2(c_{\text{Sn}}) + \frac{1}{8} P_3(c_{\text{Sn}}) + \ldots \right)$$

(8)

In Fig. 2, we have plotted the calculated carrier concentration versus doping level for various $N_{\text{eff}}$ as an undetermined parameter together with the Frank and Köstlin’s measured concentrations for their most reduced sample.

At low doping levels, the probability for nearby positioned 2:1 clusters is small; thus, most clusters have reducible interstitials at their core, and, thus, on reduction, the carrier density is proportional to the doping level. At higher doping levels, however, the probability for 2:1 clusters being positioned close together increases, and the number of carriers shows a lesser increase. Ultimately, at even higher doping levels, because most clusters have two or more other clusters nearby and increasing aggregation occurs, the carrier concentration decreases with further doping. In particular, the primary cause for the decrease of carrier concentration at high doping is not, as in the Frank and Köstlin model, a single nonreducible aggregate but, instead, the gradual shift to higher degrees of aggregation and, thus, an increasingly smaller probability (Eq. (7)) of an interstitial maintaining an environment out of which it can be reduced. The parameter $N_{\text{eff}}$ acts as a modulator; the larger the number of active sites that can influence a given 2:1 clusters ability to create carriers, the earlier the onset of below-proportional carrier density.

The experimental data in Fig. 2 exhibits the same qualitative behavior with the highest carrier concentration after reduction in the doping range of 6–10 at.%. From Fig. 2, we can estimate $N_{\text{eff}}$ to be ~15 (±3) nearby intersite sites. Via the In$_2$O$_3$ crystal structure, we can translate the number of active sites $N_{\text{eff}}$ into an effective radius. Taking the interstitial site to be at (0.113, 0.113, 0.113) in fractional lattice units (see Part 1), we find, for example, 11 and 17 other intersite intersites within radii of 5.6 and 5.8 Å, respectively. These effective radii are remarkably consistent with our proposed tin-sharing mechanism, because this range is between 1 and 2 times the distance (3.9–4.2 Å) of the second cation shell around an interstitial, the shell in which Sn$_{\text{In}}$ typically clusters around O$^-$ (see Part 1). The fact that the $N_{\text{eff}}$ parameter—the only parameter in an otherwise very simple stochastic model—adopts a value that is physically very plausible attests to the merit of the underlying assumptions, especially, increased tin coordination of interstitials through cluster aggregation as the source of nonreducibility in ITO.

IV. Conclusions

Based on calculated binding energies of interstitial oxygen in defect clusters of varying structure and composition using and atomistic scheme, we conclude the following.

(1) In agreement with the Frank and Köstlin model, we attribute reducible oxygen interstitials to neutral defect clusters (2Sn$_{\text{In}}$O$_3$)$^-$, in which the interstitial is paired with two Sn$_{\text{In}}$.

(2) We find only a weak correlation of interstitial binding energy with the relative positioning of two Sn$_{\text{In}}$ around the interstitial; thus, we do not believe that the nonreducible defect cluster is structural variant of a neutral 2:1 defect, as proposed by Frank and Köstlin.

(3) Instead, we propose that oxygen interstitials in ITO become nonreducible when bound to more than two tin dopants; this occurs when two or more 2:1 clusters are positioned close enough so that some Sn$_{\text{In}}$ bind to more than one interstitial. This becomes more likely with increasing tin-doping level as the concentration of 2:1 clusters in ITO increases.

(4) Assuming a random distribution of 2:1 clusters at preparation, a simple probabilistic argument yields a qualitatively correct description of the proportion of reducible oxygen and, thus, the maximum carrier concentration in ITO as a function of tin-doping level.
References


