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Defect Cluster Aggregation and Nonreducibility in Tin-Doped Indium Oxide

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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 Sn_{In}. 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 Sn^{4+} 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-workers[1,2] have deduced from measured electrical properties (conductivity, carrier density, and mobility as a function of oxygen partial pressure (p_{O_2}), and tin content) the existence of associated neutral defects. At high p_{O_2} and medium tin-doping levels, they have postulated two types of defects: "reducible" and "nonreducible" clusters of composition $(2Sn_{In}{\cdot}O_i)^{\times}$, formed by two Sn^{4+} ions substituting for In^{3+} and one interstitial oxygen anion.[§,1] Of these, the loosely bound reducible cluster, with Sn_{In} in nonnearest coordination to O_i, disassociates following reduction.

$$(2Sn_{In}{\cdot}O_i)^{\times} \rightarrow 2Sn_{In}^{\bullet} + 2e' + \tfrac{1}{2}O_2 \quad (1)$$

$Sn_{In}^{\bullet}$ 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 p_{O_2}).[1] 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 Sn_{In} 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 p_{O_2} 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/CO_2, $p_{O_2} = 10^{-14}$ 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 (O_i) and up to three tin dopants in the first and second coordination shells. These calculations further confirmed the trend of Sn_{In} and O_i 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 Sn_{In} and O_i 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.

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[§]Frank and Köstlin[1] denote reducible and nonreducible clusters as $(Sn_2^{\bullet}O_i'')$ and $(Sn_2O_4)^{\times}$, 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 ($O_O^{\times}$ in Kröger–Vink notation) equally present in reducible and nonreducible clusters. Therefore, $(Sn_2^{\bullet}O_i'')$ and $(Sn_2O_4)^{\times}$ in Ref. 1 represent neutral defect clusters $(2Sn_{In}{\cdot}O_i)^{\times}$ 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_2O_3,[7] 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.[8,9] 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 energies are calculated using the Mott–Littleton[11] procedure, which involves explicit atomic relaxation within a preset distance (here, 12 Å) from a suitable center of the defect and an approximate representation of the response of the remainder of the crystal. This yields defect energies in the limit of infinite dilution. We generally renormalize the energies of defect clusters with respect to the constituent point defects. Referred to as "cluster formation energies," they represent the energy gain or loss of assembling the cluster from isolated point defects. For the purpose of discussion, we consider an Sn_{In} to be bound to an interstitial if it is located in its first or second coordination shell. In the energetic calculations, however, interactions to all distances are included. When relevant, we use a vertical bar (|) in our cluster nomenclature to distinguish Sn_{In} positioned in the first and second shell. For example, $(Sn(b)|Sn(d)\cdot O_i)^{\times}$ denotes a defect cluster with one Sn positioned at a d-site in the nearest-neighbor shell and one b-site Sn in the second cation shell.

III. Results and Discussion

(1) Microscopic Model

We formulate the reduction of a defect cluster as a two-step process: (i) detachment of the interstitial from the cluster to form a nonclustered oxygen interstitial and a cluster with one less interstitial;

$$(mO_i\cdot nSn_{In}) \rightarrow ((m-1)O_i\cdot nSn_{In}) + O_i'' \quad (2)$$

and (ii) the reduction of the isolated interstitial

$$O_i'' \rightarrow \tfrac{1}{2}O_2 + 2e' \quad (3)$$

characterized by a reaction energy that is independent of the type of defect cluster from which the interstitial originated.

For the purpose of discussion, this entirely formal partitioning of the reduction process has a twofold advantage: First, the nature of the defect cluster and its effect on the reducibility of the interstitial is entirely contained in the first step (Eq. (2)); and, second, it separates out as a constant, the second electronic step that is not really accessible to the atomistic model used in this work. Thus, Eq. (2) is the critical modifier to the reduction energy because of clustering, computable from the atomistic cluster formation energies of the species involved. We refer to this reaction energy in the following as the "interstitial detachment energy." With the cluster formation energy of the isolated interstitial defined as zero, the interstitial detachment energy is given by the difference of the cluster formation energy for the 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 $Sn_{In}^{\bullet}$ 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 $Sn_{In}:O_i = 2:1$, the interstitial detachment energy is ~2.4 eV for those clusters with nonnearest positioning of the two Sn_{In} sites. Further listed are two defect clusters with two Sn_{In} sites in relative nearest cation position. The product of reduction of these two clusters are nearest $(Sn_{In}\cdot Sn_{In})^{\bullet\bullet}$ 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_{In} 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 $Sn_{In}:O_i$ 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 I. Calculated Interstitial Detachment Energy for Various Defect Clusters

$Sn:O_i$ Ratio	Defect cluster	Sn_{In} relative position	Cluster formation energy (eV)	Cluster formation energy of reduced cluster (eV)†	Interstitial detachment energy (eV)‡
0:1	O_i''		0.00	0.00	0.00
1:1	$(Sn(d)\cdot O_i)'$		−1.29	0.00	+1.29
2:1	$(Sn(b)\|Sn(d)\cdot O_j)^{\times}$	Nonnearest	−2.09	+0.34	+2.43
	$(2Sn(b)\|O_i)^{\times}$	Nonnearest	−2.08	+0.39	+2.47
	$(Sn(d)\|Sn(d)\cdot O_i)^{\times}$	Nonnearest	−2.05	+0.31	+2.36
	$(Sn(b)\|Sn(d)\cdot O_j)^{\times}$	Nearest	−1.99	+0.62	+2.61
	$(2Sn(d)\cdot O_i)^{\times}$	Nearest	−1.91	+0.55	+2.46
3:1	$(3Sn(b)\|O_i)^{\cdot}$	Nonnearest	−2.55	+1.02	+3.57
	$(2Sn(b)\cdot Sn(d)\|O_i)^{\cdot}$	Nonnearest	−2.43	+1.00	+3.43
	$(Sn(b)\cdot 2Sn(d)\|O_i)^{\cdot}$	Nonnearest	−2.36	+0.96	+3.32
	$(2Sn(b)\|Sn(d)\cdot O_i)^{\cdot}$	Nearest	−2.35	+1.31	+3.66
4:1	$(2Sn(b)\cdot 2Sn(d)\|O_i)^{\cdot\cdot}$	Nonnearest	−2.34	+2.01	+4.35
	$(3Sn(b)\|Sn(d)\cdot O_i)^{\cdot\cdot}$	Nearest	−2.34	+2.50	+4.84

†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. ‡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[1] nonreducible cluster is of the same composition $(2Sn_{In}{\cdot}O_i)^{\times}$ 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 Sn_{In}.

If we associate nonreducibility with increased tin coordination around O_i, we must address how it comes about as a function of tin doping: Frank and Köstlin's work[1] shows that, in oxidized (i.e., not-yet-reduced) ITO at low tin doping, the large majority of Sn_{In} and O_i are bound in neutral 2:1 defect clusters $(2Sn_{In}{\cdot}O_i)^{\times}$. 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 Sn_{In} dopants become shared between clusters and bound to more than one O_i. This in turn increases the number of Sn_{In} 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 Sn_{In} is shared and binds to both interstitials. One interstitial in this aggregate is coordinated by two Sn_{In}; we expect this interstitial to be 2:1-like and to remain reducible. The other interstitial is coordinated by three Sn_{In}; 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 $(3Sn(b)|O_i)^{\cdot}$ and $(2Sn(b)|O_i)^{\times}$ clusters (see Part 1) arranged such that one 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 Sn_{In}, respectively. These energies clearly match the energies calculated for 2:1 and 3:1 clusters (Table I), illustrating how it is the number of Sn_{In} dopants in the vicinity of the interstitial that is the critical factor. The fact that the center Sn_{In} 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 Sn_{In} dopants. The more Sn_{In} 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 inconsequential 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[1] 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 of 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) Macroscopic Model

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 Sn_{In} are more tightly bound than those with only two Sn_{In}, irrespective of how many interstitials the Sn_{In} are bound. We postulate the former to be nonreducible, even under highly reducing conditions. An oxygen interstitial, normally coordinated by two Sn_{In} in the form of a 2:1 clusters can gain additional Sn_{In}, 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 Sn_{In} and O_i distributed randomly in the In_2O_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_i over available interstitial sites, with two Sn_{In} in the immediate vicinity.

The probability P_{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_{Sn} (in atomic percent (at.%)). With 32 cation sites and 16 interstitial sites in the In_2O_3 unit cell and one interstitial for every two tin dopants, the probability P_{O_i} for the occupation of a given oxygen interstitial site is

$$P_{O_i} = \frac{1}{2}\left(\frac{32}{16}\right)P_{Sn} = \frac{1}{100}\,c_{Sn}\ (\text{at.}\%) \tag{4}$$

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

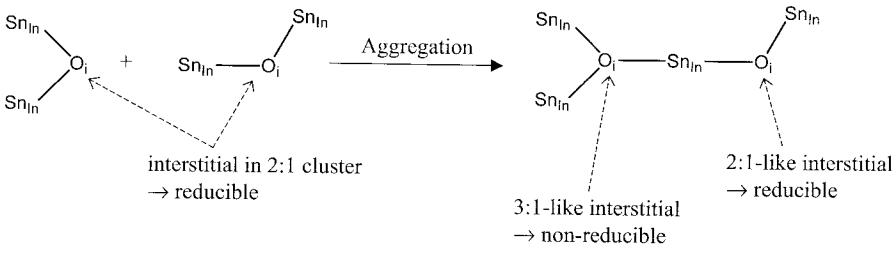

Fig. 1. Schematic illustration of an aggregation reaction of two reducible 2:1 clusters to form a 4:2 cluster. One of the interstitals in the aggregate gains an additional Sn_{In} in its coordination sphere. Interstitial local environment thus resembles a 3:1 cluster, and we expect it to be nonreducible. Other interstitial maintains a 2:1-like environment and, thus, remains reducible.

probability P_k that a given interstitial has exactly k of the N_{eff} sites in its vicinity occupied by other 2:1 clusters is given by the following expression:

$$P_k = \binom{N_{\text{eff}}}{k} P_{\text{O}_\text{i}}^k (1 - P_{\text{O}_\text{i}})^{N_{\text{eff}}-k} \tag{5}$$

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

$$P_0 = (1 - P_{\text{O}_\text{i}})^{N_{\text{eff}}} \tag{6a}$$

$$P_1 = N_{\text{eff}} P_{\text{O}_\text{i}} (1 - P_{\text{O}_\text{i}})^{N_{\text{eff}}-1} \tag{6b}$$

$$P_2 = \frac{1}{2} N_{\text{eff}} (N_{\text{eff}} - 1) P_{\text{O}_\text{i}}^2 (1 - P_{\text{O}_\text{i}})^{N_{\text{eff}}-2} \tag{6c}$$

These probabilities are tin-doping dependent through p_{O_i}.

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_{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_{In} and, thus, becomes nonreducible. The Sn_{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_{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.,

$$n_k = \left(\frac{1}{2}\right)^k \tag{7}$$

Combining the set of tin-doping level-dependent probabilities $P_k(c_{\text{Sn}})$ 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_2O_3, gives the maximum carrier concentration c_{n} after reduction as a function of doping level.

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

In Fig. 2, we have plotted the calculated carrier concentration versus doping level for various N_{eff} as an undetermined parameter together with the Frank and Köstlin[1] 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,[1] 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_{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.

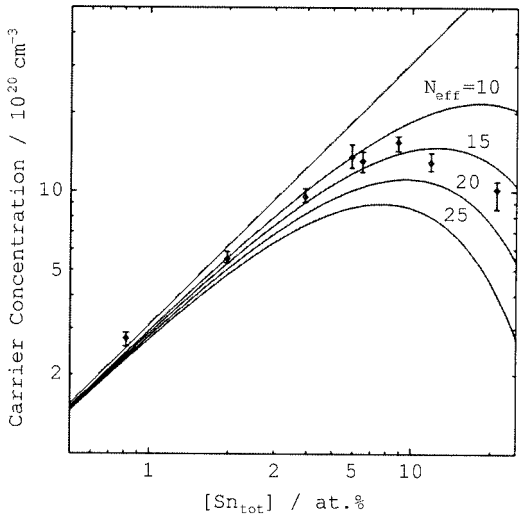

Fig. 2. Calculated and experimental carrier concentration n in reduced In_2O_3 as a function of tin doping. Experimental data were taken from Ref. 1. In the model (Eq. (8)), N_{eff} is the number of effective interstitial sites in the vicinity of a 2:1 cluster, that, if occupied by another 2:1 cluster, result in tin sharing between clusters.

The experimental data[1] 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_{eff} to be ~ 15 (± 3) nearby interstitial sites. Via the In_2O_3 crystal structure, we can translate the number of active sites N_{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 interstitial sites 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_{In} typically clusters around O_i'' (see Part 1). The fact that the N_{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,[1] we attribute reducible oxygen interstitials to neutral defect clusters $(2\text{Sn}_{\text{In}}{\cdot}\text{O}_\text{i})^\times$, in which the interstitial is paired with two Sn_{In}.

(2) We find only a weak correlation of interstitial binding energy with the relative positioning of two Sn_{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.[1]

(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_{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.

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