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# Metallic Networks and Hydrogen Compensation in Highly Non-Stoichiometric Amorphous $\text{In}_2\text{O}_{3-x}$

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The unique response of amorphous ionic oxides to changes in oxygen stoichiometry is investigated using computationally-intensive *ab-initio* molecular dynamics simulations, comprehensive structural analysis, and hybrid density-functional calculations for the oxygen defect formation energy and electronic properties of amorphous  $\text{In}_2\text{O}_{3-x}$  with  $x=0-0.185$ . In marked contrast to non-stoichiometric crystalline nanocomposites with clusters of metallic inclusions inside an insulating matrix, the lack of oxygen in amorphous indium oxide is distributed between a large fraction of under-coordinated In atoms, leading to an extended shallow state for  $x<0.037$ , a variety of weakly and strongly localized states for  $0.074<x<0.148$ , and a percolation-like network of single-atom chains of metallic In-In bonds for  $x>0.185$ . The calculated carrier concentration increases from  $3.3\times 10^{20} \text{ cm}^{-3}$  at  $x=0.037$  to  $6.6\times 10^{20} \text{ cm}^{-3}$  at  $x=0.074$  and decreases only slightly at lower oxygen content. At the same time, the density of deep defects located between 1 eV and 2.5 eV below the Fermi level increases from  $0.4\times 10^{21} \text{ cm}^{-3}$  at  $x=0.074$  to  $2.2\times 10^{21} \text{ cm}^{-3}$  at  $x=0.185$ . The wide range of localized gap states associated with various spacial distribution and individual structural characteristics of under-coordinated In, are passivated by hydrogen that helps enhance electron velocity from  $7.6\times 10^4 \text{ m/s}$  to  $9.7\times 10^4 \text{ m/s}$  and restore optical transparency within the visible range, and also is expected to improve the material's stability under thermal and bias stress.

## I. INTRODUCTION

Stoichiometry in metal oxides serves as a primary tool to manipulate the optical and electrical properties of these versatile materials. In post-transition metal oxides, commonly known as transparent conducting oxides, oxygen deficiency is  $10^{18}-10^{19} \text{ cm}^{-3}$  even under equilibrium deposition conditions in ambient environment owing to a weak metal-oxygen bonding, ionic in nature. As a result, these materials have relatively low enthalpy of formation making it easy to manipulate the oxygen to metal ratio during deposition process and/or with a post-deposition treatment and hence to optimize their properties for a wide range of optoelectronic applications [1–10]. A thorough understanding of the structural and electronic properties of the defects induced by oxygen sub-stoichiometry [11–18] is key to achieving optimal material's performance.

Highly non-stoichiometric indium oxide grown in argon atmosphere was shown to have metallic nanoclusters embedded in crystalline oxide matrix, increasing both carrier concentration (to as high as  $8 \times 10^{20} \text{ cm}^{-3}$ ) and carrier mobility of the material [19]. Formation of metallic nanoclusters was also observed in highly non-stoichiometric In-Sn-O that showed metallic (In and Sn) conductivity via percolation with a superconducting transition at 6 K [20]. These nanocomposite films were shown to exhibit phase separation between the stoichiometric crystalline oxide with insulating properties and the embedded metallic nano-inclusions [21–23].

Amorphous oxides of post-transition metals [24–26] may offer a way to combine high carrier concentration and good mobility while maintaining a uniform morphology. It has been shown that the disordered indium oxide exhibits crystalline-like electron mobility and two orders of magnitude higher carrier concentration as compared to the crystalline oxide grown under the same oxygen partial pressure [27–29]. This sets the ionic amorphous oxides apart from covalent amorphous materials, *e.g.*, Si-based semiconductors, where disorder leads to a strong electron localization suppressing both the carrier mobility and density [25, 26, 30], and opens up new prospects in

their technological utilization [31–38].

The unique electrical properties of the wide-bandgap amorphous oxide semiconductors have been shown to arise from ionic metal-oxygen bonding [24–26]. Unlike amorphous Si or Ge,  $\text{SiO}_2$  glasses, or amorphous chalcogenides, all of which have covalent bonding between the nearest neighbors, weaker metal-oxygen interactions in wide-bandgap oxides of post-transition metals lead to strong distortions in the M-O polyhedra, broad distributions of the M-O coordination numbers, as well as fully-suppressed structural features in the radial distribution beyond the next-nearest neighbor shell in amorphous phase [27, 28, 39–41]. Owing to the strong distortions in the metal-oxygen polyhedra associated with weak ionic In-O bonding, a direct overlap of the In 5s-orbitals becomes possible in disordered oxides. The metal-metal bonding has been observed earlier in other amorphous post-transition metal oxides such as In-Ga-Zn-O, Zn-Sn-O, etc [28, 42–50]. The metal-metal pairs resulting in the so-called sub-gap defects, have been proposed for sub-stoichiometric disordered oxides as an alternative to an oxygen vacancy concept that belongs exclusively to crystalline oxides [29]. Despite the aforementioned theoretical reports on the subject, the interplay between the structural and electronic characteristics of the metallic inclusions is far from being understood. A quantitative analysis of key structural features that enable the formation of metal-metal pairs, determine their distribution within the amorphous oxide matrix, and promote growth into metallic nanoclusters and/or metallic networks as the oxygen stoichiometry is gradually decreases, has been lacking.

In this work, the structural and electronic properties of amorphous indium oxide are systematically studied as a function of oxygen non-stoichiometry using *ab-initio* molecular dynamics simulations and accurate electronic structure calculations with a hybrid functional. The work combines computationally-intensive simulations that offer statistically-reliable results with comprehensive structural analysis that allows one to thoroughly investigate the coordination, interatomic distances and distortion in individual metal-oxygen

polyhedron as well as the polyhedra sharing of metal atoms in amorphous structures with respect to diverse structural environments created by oxygen sub-stoichiometry. Specifically, one of the goals of this work is to establish a connection between individual metal coordination and/or polyhedra distortion and the resulting defect binding energies as well as the degree of electron localization caused by the defect. For the latter, the work employs Bader charge calculations for individual metal atoms that account for non-uniform charge density distribution within a Voronoi volume near the highly-distorted under-coordinated and under-shared metal atoms. This approach departs from the widespread reliance on the traditional calculations of the density of states or atomic orbital contributions that are based on a fixed cut-off radius near the atoms, hence, may misinterpret the nature of the defect and its localization. This is especially important in ionic oxides with interstitial charge density distribution [51] and becomes crucial in disordered oxides with large fractions of under-coordinated atoms or highly-distorted Metal-Oxygen polyhedra and in structures with low density.

In addition, this work considers defect compensation in highly-nonstoichiometric amorphous indium oxide with hydrogen, identifying the H defect types (donor In-OH vs acceptor In-H-In) and their role in the structural reconfiguration, and determining the resulting electronic properties of hydrogenated amorphous transparent conductors.

## II. COMPUTATIONAL METHODS

The amorphous  $\text{In}_2\text{O}_{3-x}$  structures were obtained using *ab-initio* molecular dynamics (MD) liquid-quench approach as implemented in the Vienna Ab Initio Simulation Package (VASP) [52–55]. The calculations are based on density functional theory (DFT) with periodic boundary conditions [56, 57] and employ Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [58, 59] within the projector augmented-wave method [60, 61]. A stoichiometric cell that consisted of 135 atoms,  $\text{In}_{54}\text{O}_{81}$ , was used as initial structure which was melted at 3,000 K to eliminate any crystalline structure memory. In this work we used density of  $7.1 \text{ g/cm}^3$  for all amorphous indium oxide structures; this optimal density value was previously found from calculated energy-volume curves for amorphous  $\text{In}_{54}\text{O}_{80}$  [29]. Density-dependent structural changes in amorphous indium oxide have been studied by directly comparing the calculated and experimentally measured extended X-ray absorption fine structure (EXAFS) spectra and an excellent agreement for the first and second EXAFS peaks was found, as reported in [62].

To model non-stoichiometric structures with lower oxygen content, oxygen atom(s) were randomly removed from the initial cell. Specifically, in addition to perfectly stoichiometric case,  $\text{In}_{54}\text{O}_{81} = \text{In}_2\text{O}_{3.000}$ , we studied  $\text{In}_{54}\text{O}_{80} = \text{In}_2\text{O}_{2.963}$ ,  $\text{In}_{54}\text{O}_{79} = \text{In}_2\text{O}_{2.926}$ ,  $\text{In}_{54}\text{O}_{78} = \text{In}_2\text{O}_{2.889}$ ,  $\text{In}_{54}\text{O}_{77} = \text{In}_2\text{O}_{2.852}$ , and  $\text{In}_{54}\text{O}_{76} = \text{In}_2\text{O}_{2.815}$ . The above under-stoichiometric cells correspond to oxygen defect concentration of 5.7, 11.5, 17.2, 23.0 and  $28.8 \times 10^{20} \text{ cm}^{-3}$ , respectively. We stress here that the sub-stoichiometric structures of amorphous  $\text{In}_2\text{O}_{3-x}$  (with

$x=0, 0.037, 0.074, 0.111, 0.148,$  and  $0.185,$  respectively) were simulated using so-called non-stoichiometric quench, i.e., when the oxygen stoichiometry is set at the melting stage of MD, prior to cooling. This approach was shown [29] to provide lower-energy solutions as compared to a static-DFT calculation where an oxygen “vacancy” is created in an already quenched amorphous structure. The non-stoichiometric quench also yields a better statistical representation of the overall structural morphology in the disordered material as compared to the vacancy calculations in a single amorphous structure. As a result, the non-stoichiometric quench was shown to capture the formation of both shallow defects that produce carriers and localized deep defects that limit carrier mobility via electron trapping or scattering [29].

After the stoichiometry and density adjustments, all structures were subsequently melted at 3,000 K for at least 10 ps in order to randomize the specific-volume or sub-stoichiometric configuration and to stabilize the total energy. Next, liquid quench simulations were performed as follows. Each structure was cooled to 2,500 K at the MD rate of 100 K/ps and then rapidly quenched to 100 K at 200 K/ps rate. The initial slower cooling rate helps to avoid the formation of  $\text{O}_2$  defects; at 2,500 K, the second peak in the distribution function (responsible for the medium range structure) begins to develop, hence, the quench rate is increased for temperatures below 2,500 K. An energy cut-off of 260 eV and a single  $\Gamma$ -point method were used during melting and quenching processes. Finally, each structure was equilibrated at 300 K for 6 ps with a cut-off energy of 400 eV. All MD simulations for non-stoichiometric amorphous oxides were carried out in the NVT ensemble with the Nose-Hoover thermostat using an integration time step of 2 fs. For H-containing structures, the integration time step is 0.5 fs.

To obtain adequate statistical distributions in the structural and, consequently, the electronic properties, 10 separate MD liquid-quench realizations with the same conditions (initial temperature, quench rate, equilibration) were performed for each oxygen stoichiometry, resulting in 60 independent MD quenches. **First, we calculate the enthalpy of formation per atom and plot it as a function of MD steps at room temperature for each realization in order to illustrate that the solutions are stable with no energy drift, Figure 1. The thermal fluctuations in the energy, i.e., the average changes in the energy squared, are 6-15 times smaller as compared to the  $kT^2 c_v$ , where  $c_v$  is the heat capacity for  $\text{In}_2\text{O}_3$  at room temperature, suggesting that configurations are indeed in equilibrium. We note that the energies for 10 realizations are intermixed for the structures with high oxygen content ( $\text{In}_{54}\text{O}_{81}$  and  $\text{In}_{54}\text{O}_{80}$ ), so that the configuration ensemble represents an amorphous state with a normal distribution of possible energy values. This is consistent with the delocalized nature of the electronic conduction states  $\text{In}_{54}\text{O}_{81}$  and  $\text{In}_{54}\text{O}_{80}$ , reported in this work and in Ref. [29]. In contrast, the structures with lower oxygen content ( $\text{In}_{54}\text{O}_{79}$ ,  $\text{In}_{54}\text{O}_{78}$ ,  $\text{In}_{54}\text{O}_{77}$ , and  $\text{In}_{54}\text{O}_{76}$ ) exhibit either bi-modal or multi-modal energy distributions, Figure 1. Importantly, the largest energy difference between the modes is about 40 meV/atom which implies that all such configurations are likely to occur in an amorphous state at the specified sto-**

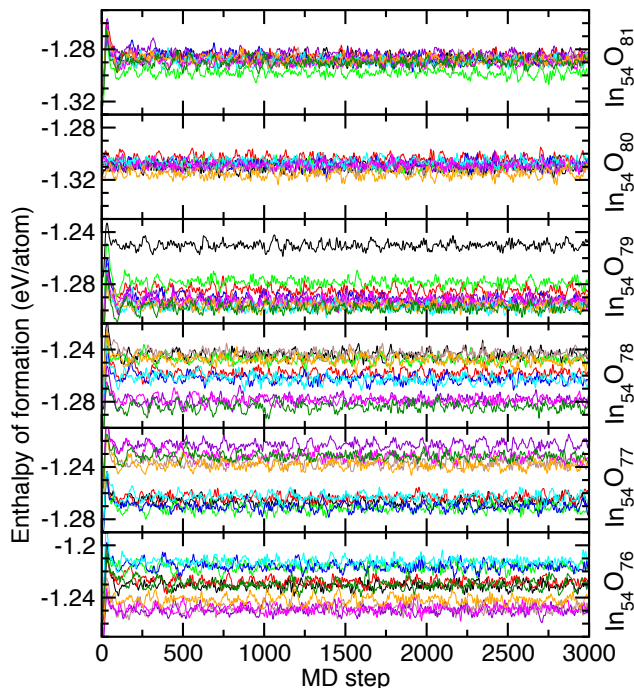


FIG. 1. Enthalpy of formation as a function of MD steps during the equilibration step at 300 K for all amorphous oxides considered in this work.

ichiometry. The energy difference between the modes represents specific coordination morphology (as will be discussed in detail in this work) with a "frozen" localized state which is stable at room temperature, at least within several ps time frame. Indeed, it will be shown later in this work, that deep electron traps are formed 2-3 eV below the Fermi level, hence, are stable against thermal fluctuations. It must be pointed out that an even larger statistical ensembles are required to predict the density for specific mode(s) or to perform principle component analysis in order to study the underlying mechanisms behind the structural transformations found in this work.

For accurate structural analysis of the crystalline and amorphous oxides, the room-temperature configurations obtained from the MD simulations at 300 K (3,000 MD steps resulting in 3,000 atomic configurations for each structure) were used. Specifically, the average first-shell In-O distance for each In-O polyhedron (or for O-In distance in each O-In polyhedron) is calculated according to [63, 64]:

$$l_{av} = \frac{\sum_i l_i \exp \left[ 1 - \left( \frac{l_i}{l_{min}} \right)^6 \right]}{\sum_i \exp \left[ 1 - \left( \frac{l_i}{l_{min}} \right)^6 \right]}, \quad (1)$$

where the summation runs over all oxygen neighbors of a particular metal atom and  $l_{min}$  is the shortest In-O distance in the given In-O polyhedron (or the shortest O-In distance in the given O-In polyhedron). The effective coordination number (ECN) for metal atom in the In-O polyhedron (or for oxygen

atom in the O-In polyhedron) is then defined as:

$$ECN = \sum_i \exp \left[ 1 - \left( \frac{l_i}{l_{av}} \right)^6 \right]. \quad (2)$$

The contribution to the ECN from a given In-O bond is greater if the In-O bond length ( $l_i$ ) is shorter than the average In-O distance ( $l_{av}$ ) in the given In-O polyhedron, and *vice versa*. For example, in crystalline  $In_2O_3$  with bixbyite structure, the largest contribution to the ECN from an In-O bond is 1.46 (shortest bond), while the smallest is 0.15 (longest bond). Summation of the contributions from all bonds for a given In atom will result in a non-integer ECN value unless all In-O bonds in a polyhedron are identical. In addition, we evaluate the distortion of each In-O polyhedron characterized by the standard deviation of the individual In-O bond length ( $l_i$ ), from the average In-O bond length ( $l_{av}$ ) for the given polyhedron. For an ideal polyhedron (*i.e.*, all In-O distances are identical) this parameter equals to zero. Similarly, the distortion of each O-In polyhedron was calculated. In this work, the average bond length, average effective coordination number, and average distortion were calculated according to the above equations for each atom in each MD configuration and then averaged over the 3,000 steps (6 ps) and over the number of MD realizations for each stoichiometry and, in specific cases, over the number of In or O atoms in the cell.

Furthermore, sharing between In-O polyhedra is calculated based on the results of Eqs. 1 and 2. The sharing type, namely, face, edge, or corner-sharing that corresponds to three, two, or one oxygen shared between any given pair of In atoms, respectively, is determined for each In-In pair in the cell (within 6 Å In-In distance). To establish bonding between an oxygen atom and its two In neighbors, and hence, to determine whether the oxygen is shared between the two In atoms, the contribution to the exponential term of the Eq. 2 is evaluated for each In-O bond. To account for possible weak bonds and strong polyhedral distortions caused by disorder in amorphous oxides, the minimum contribution from an In-O bond for the bond to be considered in sharing calculations is set to 0.05 which is three times smaller than the minimum contribution to the ECN from the longest In-O bond in crystalline  $In_2O_3$  with bixbyite structure, 0.15. As an example, the smallest contribution to ECN from an In-O bond to be accounted for in a corner-shared connection in amorphous  $In_{54}O_{76}$  with smallest oxygen content is found to be 0.06 that corresponds to the In-O distance of 2.70 Å, given that the minimum and average In-O distances are 2.14 Å and 2.16 Å, respectively, and the resulting ECN value is 3.14 for this In atom. Of course, both  $l_{min}$  and  $l_{av}$  are unique for each In atom in amorphous cells.

Next, each of the 60 atomic configurations obtained from the *ab-initio* MD liquid quench simulations was optimized within DFT using the PBE functional. For the optimization, the cut-off energy of 500 eV and the 4x4x4  $\Gamma$ -centered  $k$ -point mesh were used; the atomic positions were relaxed until the Hellmann-Feynman force on each atom was below 0.01 eV/Å. Finally, the electronic and optical properties of the PBE-optimized amorphous  $In_2O_{3-x}$  structures were calculated using the hybrid Heyd-Scuseria-Ernzerhof (HSE06) approach

[65, 66] with a mixing parameter of 0.25 and a screening parameter  $\alpha$  of  $0.2 \text{ \AA}^{-1}$ . Note that only the electronic self-consistent calculations were performed in HSE06, whereas the atomic positions were not relaxed further in HSE06. For each of the 60 realizations, total energy, density of states, electronic band structure, and charge density distributions were obtained. To quantify the localization of the electronic states, the inverse participation ratio (IPR) of an orbital  $\Psi_n(\vec{r}_i)$  can be found from *ab-initio* density-functional calculations according to following equation:

$$\text{IPR}(\Psi_n) = N \frac{\sum_{i=1}^N |\Psi_n(\vec{r}_i)|^4}{\left[ \sum_{i=1}^N |\Psi_n(\vec{r}_i)|^2 \right]^2}, \quad (3)$$

where  $N$  is the number of volume elements in the cell and  $i$  is the index of the volume element. IPR calculations help quantify the electron localization as it represents how many states each atomic orbital is distributed over. The higher the IPR value, the stronger the localization is, while a delocalized state with equal contributions from all atoms in the system corresponds to an IPR value of 1.

In addition, Bader charge analysis for each atom [67] was performed for valence and conduction states. We argue that such calculations provide a significantly more accurate description of the electron localization in disordered materials—especially near highly-distorted under-coordinated under-shared metal atoms where the charge distribution is likely to be non-uniform—as compared to the traditional electronic structure tools such as density of states calculations or atomic orbital contributions that rely on a fixed cut-off radius around atoms. We believe that this drawback of the DOS calculations is one of the major reasons that has hampered the progress in theoretical understanding of the amorphous oxide semiconductors.

Here we stress that HSE approach provides a significant improvement in the description of the electronic properties of metal oxides not only for the accurate band gap values and optical properties but also for the electron localization at the defect states. Specifically, charge trapping in amorphous metal oxides have been associated with low-coordinated ions and elongated metal-oxygen bonds in the amorphous oxide network, and theoretical models of electron polarons and bipolarons have been proposed for several oxides [68]. Therefore, structural relaxation is important in the description of the structure-electronic property relationships. While further atomic relaxation with HSE method for the 60 disordered 130-138-atom supercells (that are fully relaxed in PBE) is not computationally feasible, we believe that the results of this work are reliable given that (i) a diverse electronic behavior is found in  $\text{a-In}_2\text{O}_{3-x}$ —from shallow, to weakly localized, to deep trap states, each of which is carefully described by specific In-In distances and In-O coordination near the defect; and (ii) excellent agreement between our theoretically calculated carrier and defect concentrations with those observed experimentally.

Finally, optical absorption was derived from the frequency-

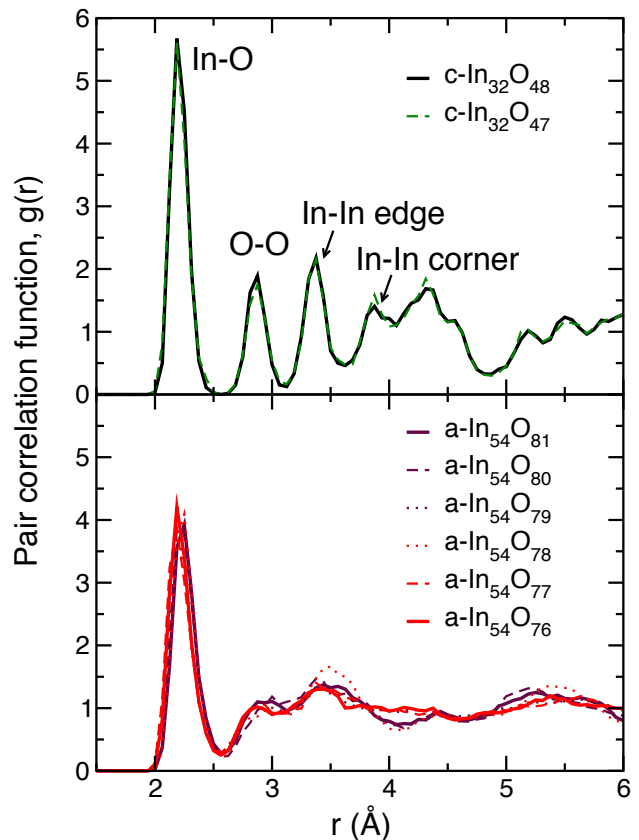


FIG. 2. Pair correlation function in crystalline and amorphous  $\text{In}_2\text{O}_{3-x}$  as calculated from the last 200 MD steps obtained at 300 K for each MD realization. For bixbyite oxide, the first four peaks are labeled. For disordered oxide, each line represents an average of 10 separate MD realizations for the given oxygen stoichiometry.

dependent dielectric function,  $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ , calculated within independent particle approximation as implemented in VASP. The imaginary part,  $\epsilon_2(\omega)$ , is related to the optical absorption at a given frequency  $\omega$ , and is determined based on the electronic transitions of the hybrid functional solution. The real part of the complex dielectric function is obtained using Kramers-Kronig relations.

The optimized atomic structures and charge densities were plotted using VESTA software [69].

### III. AVERAGE STRUCTURAL CHARACTERISTICS AND DEFECT FORMATION

Figure 2 shows the calculated pair correlation functions for crystalline (bixbyite) and amorphous indium oxides with different sub-stoichiometries. As already mentioned in the Introduction, disorder suppresses not only the structural features beyond the third In shell but also the O-O peak for which  $g(r)$  is nearly 1, as has been reported earlier [27, 28, 39–41]. The first peak in the distribution that corresponds to In-O distance is well developed and separated by a pseudo-gap implying that amorphous structure has developed in all  $\text{In}_2\text{O}_{3-x}$ . As the oxy-

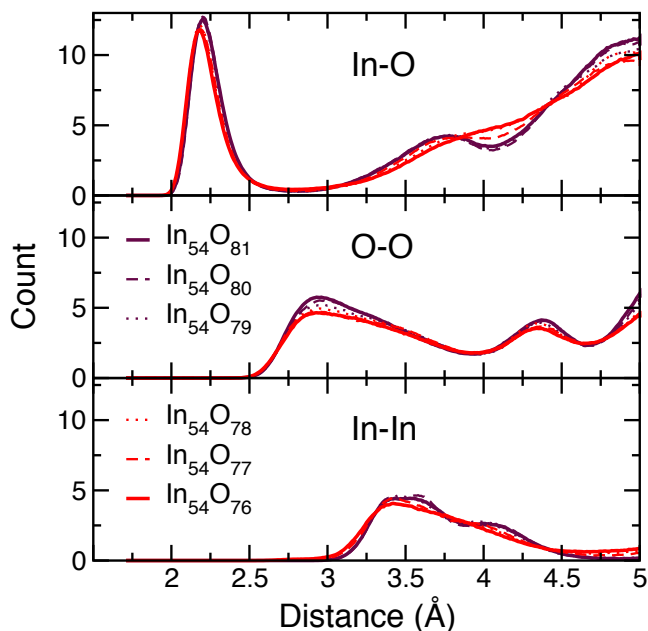


FIG. 3. Distance distributions for In-O, O-O, and In-In pairs in amorphous  $\text{In}_2\text{O}_{3-x}$  calculated using 10 separate MD realizations for each oxygen stoichiometry. The results combine 3,000 MD configurations (6 ps) obtained at 300 K for each MD realization, resulting in 30,000 atomic configurations analyzed for each stoichiometry. The results are normalized by the number of MD steps and by the number of realizations, but not by the number of atoms.

gen sub-stoichiometry increases, the first peak slightly shifts toward the shorter distances, whereas the medium and long-range features continue to decrease, signifying that disorder increases for lower O content. The changes in the total distribution function are minimal, hence, may not be captured experimentally. To the best of our knowledge, measurements of radial distribution function for amorphous  $\text{In}_2\text{O}_x$  as a function of oxygen content are not available in literature, whereas published works on the structure of amorphous indium oxide often do not report density and/or stoichiometry, making a comparison with theory challenging.

The In-O, In-In, and O-O distance distributions for amorphous  $\text{In}_2\text{O}_{3-x}$  obtained from MD simulations at 300 K are shown in Figure 3. Reduction in oxygen stoichiometry slightly shifts the first-shell In-O peak toward shorter distances and also suppresses the features at the longer distances suggesting an increase in disorder. In the O-O distance distribution, Figure 3, the main changes are found for the O-O distances from 2.8 Å to 3.2 Å, suggesting that oxygen reduction suppresses the number of the O-O pairs near the middle of the soft peak, *i.e.*, the highest-occurring O-O distances, while maintaining the width in the distribution. Since the O-O distances represent the edges in the In-O polyhedra, the results imply stronger deviations from the regular (*e.g.*, octahedral) In-O polyhedra and that the local disorder increases as the oxygen content decreases. The suppressed O-O peak is characteristic for the post-transition metal oxides with weak metal-oxygen bonding, ionic in nature [28], where the spherical s-

orbitals of the In atoms are indifferent to the distortions in the In-O polyhedra [70]. In contrast to the O-O distances, the In-In distribution shifts toward shorter In-In distances with oxygen reduction, Figure 3. The In-In distance distribution represents the medium-range structure, *i.e.*, how the neighboring In-O polyhedra are shared with each other. While the edge- or corner-sharing correspond to specific In-In distance in crystalline  $\text{In}_2\text{O}_3$ , namely, 3.4 Å or 3.8 Å, respectively, oxygen reduction broadens the distribution and completely erases the distinction between the edge- and corner-sharing peaks, Figure 3. Moreover, the presence of short In-In distances, *e.g.*, comparable to 3.26 Å found in elemental In with tetragonal  $I4/mmm$  structure, are likely to correspond to a metallic bond formation if a lack of oxygen between the two In atoms allows for direct In-In bonding.

The average In-O bond length, effective coordination number (ECN), and polyhedra distortion  $\sigma^2$  were calculated next. The statistical averages of these three characteristics are given in Table I for both In and O atoms. Among them, only the coordination numbers show a clear trend with oxygen stoichiometry, with most pronounced changes found for the In-O coordination which decreases by almost 7% from the stoichiometric case, a- $\text{In}_{54}\text{O}_{81}$ , to a- $\text{In}_{54}\text{O}_{76}$ . Figure 4(a) shows the average ECN(In) for each of the 10 realizations at different oxygen stoichiometry. The differences between the realizations are largest for a- $\text{In}_{54}\text{O}_{77}$  and a- $\text{In}_{54}\text{O}_{78}$ , suggesting a diverse coordination morphology is at play for this range of oxygen content. While the decrease in the In-O coordination with oxygen reduction is expected, we find that it is not accompanied by a commensurate change in the average In-O distance. More intriguingly, the polyhedra distortion ( $\sigma^2$ ) that measures the deviation of individual In-O distances from the average value in a given polyhedra, decreases when the oxygen content is slightly reduced from the perfect stoichiometric case, Table I. It has been argued that the reduction of the average polyhedra distortion in a- $\text{In}_{54}\text{O}_{80}$  is likely to signify that the small sub-stoichiometry helps alleviate the internal strain in the amorphous oxide [29]. Here we find that further reduction in oxygen stoichiometry recovers the strong distortion values for both In and O polyhedra, Table I. While  $\sigma^2$  for In and O become highest in a- $\text{In}_{54}\text{O}_{76}$ , *i.e.*, in the structure with largest non-stoichiometry, the calculated average distortion for all other  $\text{In}_2\text{O}_{3-x}$  considered in this work is comparable to that in the perfectly stoichiometric case, Table I. The results show that the amorphous indium oxide structures tend to maintain the average local distortion even when the oxygen defect concentration reaches as high as  $2.3 \times 10^{21} \text{ cm}^{-3}$  (that corresponds to the oxygen non-stoichiometry of  $\text{In}_{54}\text{O}_{77} = \text{In}_2\text{O}_{2.852}$ ). This implies that changes in the medium-range structure, *i.e.*, in the way how the In-O polyhedra are connected with each other to form the network, must occur in response to the oxygen reduction.

The lowest average polyhedra distortion in a- $\text{In}_{54}\text{O}_{80}$  correlates with the lowest defect formation energy calculated from DFT-HSE approximation for the sub-stoichiometric cases with respect to the average energy of the structure with higher stoichiometry by one oxygen atom per cell:

$$\Delta E_{\text{defect},i}(\mu) = E_i(\text{In}_{54}\text{O}_{n-1}) - E_{\text{ave}}(\text{In}_{54}\text{O}_n) + \mu \quad (4)$$

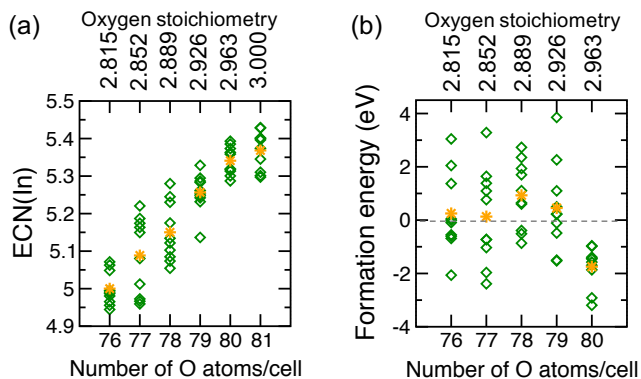


FIG. 4. (a) The effective coordination number (ECN) for the first-shell (In-O) in amorphous  $\text{In}_2\text{O}_{3-x}$  as calculated from *ab-initio* MD simulations at 300 K. Each value is an average over 3,000 MD steps (6 ps) at 300 K and the number of In atoms in the cell; (diamonds) represent the average for each of the 10 MD realizations for each stoichiometry, while (stars) represent the average over the 10 MD realizations. (b) Defect formation energy in amorphous  $\text{In}_2\text{O}_{3-x}$  calculated from DFT-HSE approach according to Eq. 4 with O-poor conditions. For each oxygen stoichiometry, the calculations are performed for the structures obtained from 10 MD realizations followed by the structural relaxation in DFT-PBE (diamonds). (Stars) represent the average over the 10 MD realizations at a given stoichiometry.

where  $\mu$  is the oxygen chemical potential,  $n$  stands for the number of oxygen atoms in the cell, and index  $i$  represents different MD configurations. Figure 4(b) shows the defect formation energy for all sub-stoichiometric cases, while Table I lists the same energy values averaged over 10 MD realizations. Using oxygen-poor conditions, we find that  $\Delta E_{defect}$  is negative in all 10 realizations for a- $\text{In}_{54}\text{O}_{80}$  and, on average, the defect formation energy is  $-1.75$  eV for this case, suggesting that the formation of oxygen defects in slightly sub-stoichiometric amorphous indium oxide is highly favorable. Although on average the formation of oxygen defects becomes less favorable for higher oxygen non-stoichiometries, many configurations have negative  $\Delta E_{defect}$  at each stoichiometry considered in this work, Figure 4(b). Therefore, the amorphous indium oxide structure is capable to accommodate large defect concentrations by adjusting its local structure and morphology. Both are discussed in great details in the next sections.

#### IV. IN-O COORDINATION DISTRIBUTIONS AND LOCAL CHARACTERISTICS OF IN-O POLYHEDRA

To determine the cause of the decreasing average ECN of In atoms with oxygen reduction, the effective coordination number histograms are plotted for all MD realizations for each  $\text{In}_2\text{O}_{3-x}$ , Figure 5. The results reveal that, on average, the number of fully-coordinated In atoms ( $\text{ECN} > 5.5$ ) decreases only slightly in a- $\text{In}_{54}\text{O}_{80}$  (48.6%) and a- $\text{In}_{54}\text{O}_{79}$  (45.1%) as compared to the stoichiometric case, a- $\text{In}_{54}\text{O}_{81}$  (50.5%). This implies that the amorphous indium oxide struc-

TABLE I. The local (first-shell) structural characteristics in amorphous  $\text{In}_2\text{O}_{3-x}$  as calculated from *ab-initio* MD simulations at 300 K. The average distance  $l_{av}$ , effective coordination number (ECN), and polyhedra distortion  $\sigma^2$  are calculated for both In and O atoms. Each value is an average over 3,000 MD steps (6 ps) at 300 K, In(O) atoms in the cell, and over 10 MD realizations for each stoichiometry. The average defect formation energy calculated according to Eq. 4 based on DFT-HSE results is given as an average over 10 realizations for each stoichiometry.

	In-O			O-In		Defect formation energy, eV
	$l_{av}$ , Å	ECN	$\sigma^2$ , Å <sup>2</sup>	ECN	$\sigma^2$ , Å <sup>2</sup>	
a- $\text{In}_{54}\text{O}_{81}$	2.20	5.37	0.0135	3.60	0.0137	—
a- $\text{In}_{54}\text{O}_{80}$	2.20	5.34	0.0128	3.62	0.0132	-1.75
a- $\text{In}_{54}\text{O}_{79}$	2.20	5.25	0.0131	3.61	0.0131	+0.45
a- $\text{In}_{54}\text{O}_{78}$	2.19	5.15	0.0139	3.59	0.0135	+0.93
a- $\text{In}_{54}\text{O}_{77}$	2.19	5.09	0.0134	3.59	0.0133	+0.13
a- $\text{In}_{54}\text{O}_{76}$	2.19	5.00	0.0144	3.56	0.0140	+0.25

ture is capable to accommodate oxygen defect concentrations of up to  $11.5 \times 10^{20}$  (that corresponds to the oxygen stoichiometry of  $\text{In}_2\text{O}_{2.926} = \text{In}_{54}\text{O}_{79}$ ) while maintaining the number of fully-coordinated In atoms. In a- $\text{In}_{54}\text{O}_{80}$ , the second peak in the coordination distribution ( $\text{ECN} < 5.0$ ) begins to develop, whereas a- $\text{In}_{54}\text{O}_{79}$  features a notable fraction of severely under-coordinated In atoms with ECN 3.0 in a few MD realizations, Figure 5. It has been shown that even a small fraction of under-coordinated In atoms may affect the carrier generation and transport properties of the oxides due to formation of highly-localized deep trap states [29]. The binding energy and the degree of electron localization associated with the defects are determined by the spacial distribution of the under-coordinated In atoms, *e.g.*, their proximity with each other. For a- $\text{In}_{54}\text{O}_{79}$ , the probability of the In atoms with severe under-coordination is low, and only a few MD realizations result in clustering of such In atoms [29].

Further reduction of oxygen content leads to significant decrease of the number of fully coordinated In atoms with  $\text{ECN} > 5.5$ , specifically, to 38.5% in a- $\text{In}_{54}\text{O}_{78}$ , 37.5% in a- $\text{In}_{54}\text{O}_{77}$ , and 34.0% in a- $\text{In}_{54}\text{O}_{76}$ . Therefore, the under-coordinated In atoms become the majority species, with the heights of the peaks in the distribution function at ECN 4.9, 4.0, and 3.0 steadily increasing as the oxygen content decreases. Our results predict a transition for oxygen defect concentrations between  $11.5 \times 10^{20} \text{cm}^{-3}$  and  $17.2 \times 10^{20} \text{cm}^{-3}$ , *i.e.*, from around  $\text{In}_2\text{O}_{2.926}$  to  $\text{In}_2\text{O}_{2.889}$ . Within this range of oxygen stoichiometries, the In coordination morphology is expected to change dramatically, having an effect on the carrier mobility [71, 72], as discussed in the sections below. It must be noted here that individual MD realizations have different ECN distributions for all considered values of oxygen stoichiometry, Figure 5. This is in accord with the largest differences in the average ECN(In) values for each realization in a- $\text{In}_{54}\text{O}_{78}$  and a- $\text{In}_{54}\text{O}_{77}$ , Figure 4(a). The realization differences point out that a diverse coordination morphology is possible when the under-coordinated In atoms prevail. This is also supported by the wide distribution in the formation energy in highly-non-stoichiometric oxides, Figure 4, and signi-

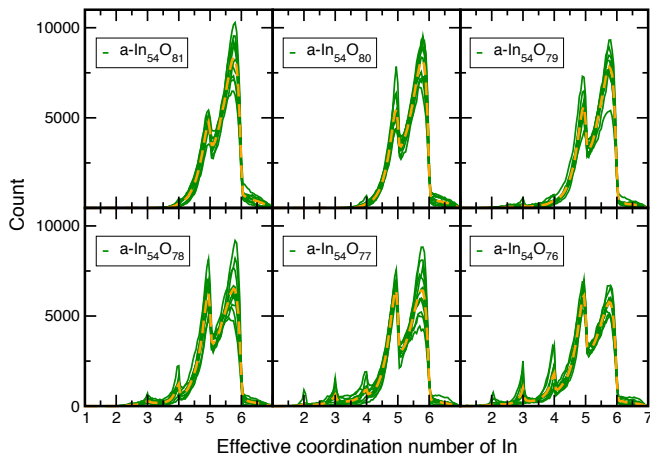


FIG. 5. Distribution of effective coordination numbers (ECN) of In atoms with oxygen for 10 MD realizations in each amorphous  $\text{In}_2\text{O}_{3-x}$ . The results are based on 3,000 MD configurations (6 ps) obtained at 300 K during equilibration step. The dashed orange lines are an average of the 10 MD simulations for each oxygen stoichiometry.

finds that a single MD calculation may yield misleading conclusions, highlighting the importance of statistical validation of the results as it is done in this work.

Next, we analyze how the changes in the effective coordination numbers of In correlate with the In-O distances and distortions in the In-O polyhedra. For this, the time-average ECN for every In atom in the cell is calculated as a function of the time-average distortion of that In atom, Figure 6(a), or as a function of the time-average In-O distance of that In atom, Figure 6(b). Each point in the plots represent a time average obtained from MD simulations at 300 K for 3,000 steps (6 ps) by calculating the corresponding values for each individual In atom in every configuration and then averaging over the 3,000 MD configurations. Comparing a- $\text{In}_{54}\text{O}_{81}$  and a- $\text{In}_{54}\text{O}_{80}$ , the differences in the ECN and  $\sigma^2$  distributions are almost negligible, with the exception for a reduced number of the fully-coordinated In (ECN>5.5) that have large distortions ( $\sigma^2>0.02$ ) in the non-stoichiometric case. Independent of the In coordination values, the overall fraction of highly-distorted polyhedra ( $\sigma^2>0.02$ ) decreases from 10.6% in a- $\text{In}_{54}\text{O}_{81}$  to 8.3% in a- $\text{In}_{54}\text{O}_{80}$ . This substantiates the smaller average distortion in the latter case, Table I, where a small reduction in oxygen content helps suppress the number of strongly-distorted In polyhedra leading to a more uniform amorphous structure.

At larger oxygen sub-stoichiometries, *i.e.*, for a- $\text{In}_{54}\text{O}_{79}$ , a- $\text{In}_{54}\text{O}_{78}$ , a- $\text{In}_{54}\text{O}_{77}$ , and a- $\text{In}_{54}\text{O}_{76}$ , the number of fully-coordinated In atoms continues to decrease, Figure 6. At the same time, the number of under-coordinated In atoms (ECN<4.0) steadily increases with oxygen reduction. On average, the distortion of In-O polyhedra increases, Table I, and the fraction of highly-distorted polyhedra ( $\sigma^2>0.02$ ) for all In atoms (independent of their coordination) increases to as much as 18.5% in a- $\text{In}_{54}\text{O}_{76}$ . Interestingly, the distor-

tion distribution for the severely under-coordinated In atoms (ECN<4.0) covers the entire range of values, with nearly equal fractions of weakly ( $\sigma^2<0.02$ ) and strongly ( $\sigma^2>0.02$ ) distorted In-O polyhedra, Figure 6. The wide distribution of both the In coordination numbers and the In-O distortions, Figure 6, is a result of weak ionic In-O bonding as well as the spherical symmetry of the In  $4s^0$  state—both make In atoms indifferent to the exact positions of the oxygen neighbors.

In the ionic materials, a reduction in metal coordination numbers is usually accompanied by a shorter M-O bond length. Indeed, the majority of In atoms follow a well-defined dependence of ECN on the In-O distance with the same characteristic slope, Figure 6(b). However, a notable fraction of low-coordinated In atoms (ECN<5.0) does not follow the trend, having longer In-O distances than those for In with higher coordination. It has been shown for stoichiometric a- $\text{In}_{54}\text{O}_{81}$  that longer In-O distances than those that are expected based on the coordination number of a specific In atom lead to charge density accumulation at the In atom and, consequently, larger electronic contributions from the In atom to the conduction states as compared to other In atoms with close-to-average In-O distances [29]. When the concentration of the In atoms with longer-than-expected In-O distances increases, the spacial distribution of such In atoms, *i.e.*, their clustering or chain formation *vs* random distribution within the cell, will govern the energy location and the degree of the electron localization of the associated states and hence will determine the resulting transport properties.

We would like to stress here that capturing the structural characteristics of individual In atoms is key to understanding the unique electronic and transport properties of the amorphous indium oxide. The presence, concentration, and spacial distribution of the In atoms with severe under-coordination or with strong distortion or atypical bond lengths cannot be captured with traditional techniques for the structural characterization of amorphous materials, making the defects invisible [73]. Therefore, *ab-initio* MD simulations provide valuable information, suggesting that oxygen defects in amorphous indium oxide are likely to originate from the distribution outliers, *c.f.*, Figure 6, while their specific structural characteristics may help understand the resulting differences in the formation and binding energies as well as the electronic properties of the defects and their effect on the overall transport properties of the oxide materials.

## V. IN-O POLYHEDRA SHARING AND COORDINATION MORPHOLOGY

The reduction on In coordination and the increasing fraction of under-coordinated In atoms at lower oxygen content will affect the medium-range structure, *i.e.*, how the In-O polyhedra are connected with each other. In bixbyite  $\text{In}_2\text{O}_3$ , each In atom shares two oxygen atoms with 6 In neighbors at In-In distance of 3.4 Å and also shares an oxygen atom with 6 other In atoms at In-In distance of 3.7 Å. These polyhedra connections are called edge- and corner-shared, respectively. Compared to the equal fractions of corner and edge-shared



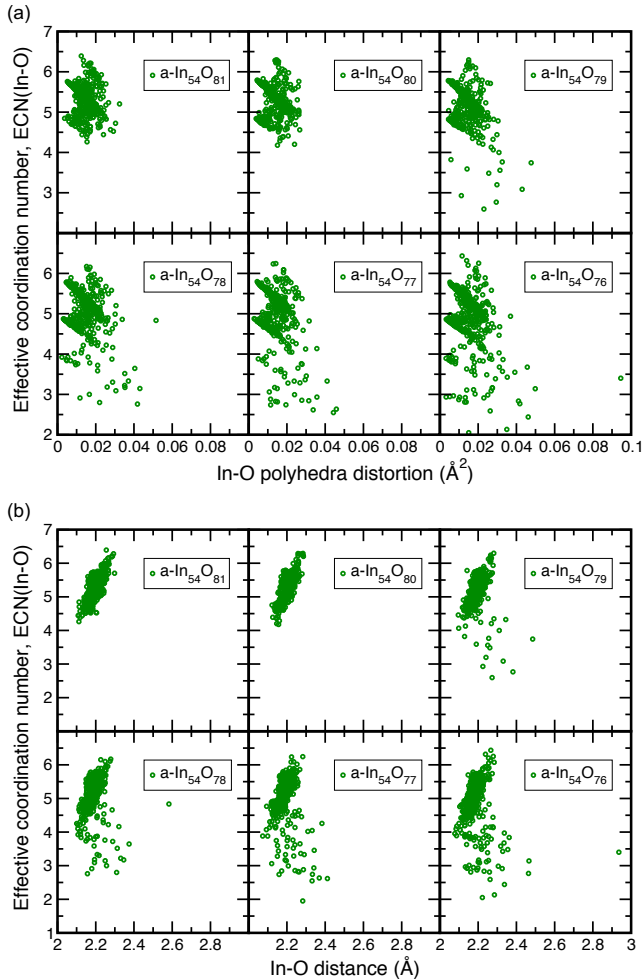


FIG. 6. The average effective coordination number (ECN) for individual In atoms in the amorphous  $\text{In}_2\text{O}_{3-x}$  (a) as a function of the time-average distortion of the In atom; and (b) a function of time-average In-O distance of the In atom. Every data point represents a time average over 3,000 MD configurations (6 ps) obtained at 300 K. For each oxygen stoichiometry, the results of 10 separate MD realizations are shown.

pairs for each In atom in crystalline  $\text{In}_2\text{O}_3$ , disorder reduces the number of edge-shared In-In pairs to about 30% in  $\text{a-In}_{54}\text{O}_{81}$ ,  $\text{a-In}_{54}\text{O}_{80}$ , and  $\text{a-In}_{54}\text{O}_{79}$ , as shown in [29]. Here we find that although the statistical variation between the 10 MD realizations for each stoichiometry may be as large as 10%, on average, the same 30:70 ratio is maintained in highly non-stoichiometric structures, Figure 7, suggesting that the overall polyhedral structure is not affected by the oxygen reduction. Note that the amount of face-shared In-In pairs is small and remains to be about 1.5% on average in all structures. Face-shared In-In connections (with three oxygen atoms shared by the In neighbors) do not occur in bixbyite  $\text{In}_2\text{O}_3$ , hence, they can be considered a structural defect caused by amorphization. Such defects, however, do not result in localized states in the band gap or near the Fermi level: although the In-In distance for the face-shared pair is shorter (about 3.18 Å) than that in

TABLE II. The number of face-, edge-, and corner-shared In-In pairs along with the total number of shared In-In pairs in amorphous  $\text{In}_2\text{O}_{3-x}$ . The values represent an average over 10 realizations and 3,000 MD configurations (6 ps) for each oxygen stoichiometry. The largest value in each category is highlighted in bold.

	Face	Edge	Corner	Total
$\text{a-In}_{54}\text{O}_{81}$	<b>5.73</b>	<b>105.94</b>	238.42	350.09
$\text{a-In}_{54}\text{O}_{80}$	5.42	102.74	243.26	<b>351.42</b>
$\text{a-In}_{54}\text{O}_{79}$	4.88	98.38	<b>245.36</b>	348.62
$\text{a-In}_{54}\text{O}_{78}$	5.28	100.28	232.96	338.52
$\text{a-In}_{54}\text{O}_{77}$	4.33	94.38	238.86	337.57
$\text{a-In}_{54}\text{O}_{76}$	4.24	96.46	229.66	330.35

elemental In (3.26 Å in tetragonal In with  $I4/mmm$  structure), the face-shared In-In pairs cannot produce In-In metallic bond because the oxygen atoms in the vicinity capture the 5s electrons from In to form the ionic In-O bonds which are stronger than the metallic In-In bond.

While the fractions of differently-shared polyhedra do not appear to change with stoichiometry, Figure 7, an interesting insight is gained from comparing the numbers of face-, edge- and corner-shared In-In pairs as a function of oxygen content, Table II. We find that the amounts of face and edge-shared pairs decrease with decreasing oxygen content, however, the reduction is not monotonic, with a notable deviation at  $\text{a-In}_{54}\text{O}_{78}$ . In marked contrast, the number of corner-shared In-In initially increases, reaching the highest value in  $\text{a-In}_{54}\text{O}_{79}$ . As a result, the largest number of total shared In-In pairs is found in  $\text{a-In}_{54}\text{O}_{80}$ . This implies that in addition to face-to-edge and edge-to-corner transformations caused by reduction in oxygen content, there are a few corner-shared pairs created, increasing the total number of shared In-In. These additional corner-shared pairs are likely to form due to longer bond distances and stronger distortions in the In-O polyhedra. We believe that these structural adjustments in the medium-range polyhedral morphology help maintain the number of fully-coordinated indium in  $\text{a-In}_{54}\text{O}_{80}$  and  $\text{a-In}_{54}\text{O}_{79}$  with respect to perfectly-stoichiometric  $\text{a-In}_{54}\text{O}_{81}$ , as discussed in the previous Section IV. When the oxygen content decreases further, the lack of oxygen cannot be sustained by additional reduction in the number of shared pairs, instead, the structure undergoes a coordination transformation characterized by a significant drop in the number of fully-coordinated In between  $\text{a-In}_{54}\text{O}_{79}$  and  $\text{a-In}_{54}\text{O}_{78}$  (see Section IV). Interestingly, the coordination transformation is accompanied by a slight increase in the number of face and edge-shared connections in  $\text{a-In}_{54}\text{O}_{78}$  which is followed by an increased number of corner-shared pairs in  $\text{a-In}_{54}\text{O}_{77}$ , likely due to the similar face-to-edge and edge-to-corner transformations that occurs at higher oxygen content, Table II. Thus, the results imply that the network morphology undergoes several subtle structural transformations when oxygen content decreases. These changes may have a pronounced effect on the electronic and transport properties of amorphous indium oxide.

Figure 8(a) shows In-In distance distribution calculated for face-, edge-, corner-, and non-shared pairs in amorphous

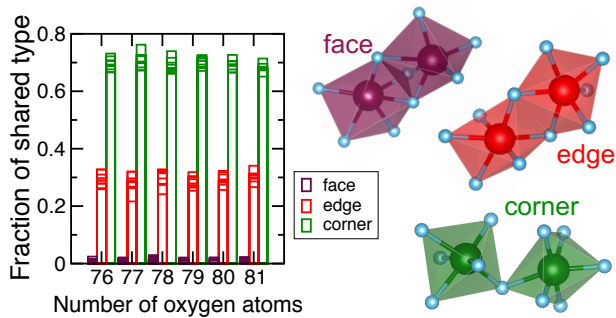


FIG. 7. Fraction of face, edge, and corner shared In-In pairs calculated for 10 separate realizations for each oxygen stoichiometry for amorphous  $\text{In}_2\text{O}_{3-x}$ . The sharing type pairs have been calculated based on the atomic coordinates of the 3,000 MD configurations (6 ps) obtained at 300 K. Examples of the face, edge and corner-shared polyhedra are also shown.

$\text{In}_2\text{O}_{3-x}$ . For each stoichiometry, the results are averaged over 10 MD realizations. We find that the edge-shared distribution peak is at 3.36 Å in all cases except for  $\text{a-In}_{54}\text{O}_{76}$ , where the peak shifts to 3.34 Å. The majority of corner-shared In-In pairs have distance of 3.6 Å and the In-O-In angle of  $110^\circ$ , while the second soft shoulder-like peak at 4.1 Å corresponds to the In-O-In angles of  $130^\circ$ . The corner-sharing distribution widens with oxygen reduction and loses the double-peak nature in  $\text{a-In}_{54}\text{O}_{77}$  and  $\text{a-In}_{54}\text{O}_{76}$ , Figure 8(a). The calculated average distances for face-, edge-, and corner-shared In-In pairs are given in Table III. As discussed above, the total number of shared In-In pairs decreases steadily starting from  $\text{a-In}_{54}\text{O}_{79}$  and continuing for higher oxygen sub-stoichiometry, Table II. The reduction signifies that the number of non-shared In-In pairs that have distances below 4.5 Å increases with oxygen reduction, Figure 8(a). The presence of non-shared In-In pairs with short distances implies that metallic bond formation becomes possible – owing to the lack of oxygen in the vicinity. It will be shown below that the metallic In-In bonds may result in electron localization and deep defect formation for isolated In-In pairs or to cause insulator-to-metal transition when the concentration of such metallic In-In pairs and the probability for their clustering increases upon oxygen reduction.

Now, we compare our results to the recent high-energy, wide-angle X-ray diffraction measurements for amorphous indium oxide [41]. In this work, fitting of the grazing-incidence pair distribution function (PDF) produced three In-In peaks at 2.69 Å, 3.28 Å, and 3.72 Å, assigned to face-, edge-, and corner-shared In-In pairs, respectively. Our theoretical results are in agreement with the edge- and corner-shared In-In distances; the larger calculated values may be attributed to the differences in density ( $7.1 \text{ g/cm}^3$  in our work vs  $4.6 \text{ g/cm}^3$  in experiment [41]). However, the average face-shared distances (3.14-3.18 Å) are notably longer than the observed first In-In peak at 2.69 Å, although the shortest face-shared distance in our calculations was found to be 2.60 Å in  $\text{a-In}_{54}\text{O}_{76}$ . Importantly, our results suggest that the presence of non-shared

TABLE III. The average In-In distance in Å for face-, edge-, and corner-shared In-In pairs in amorphous  $\text{In}_2\text{O}_{3-x}$ . The values represent an average over 10 realizations and 3,000 MD configurations (6 ps) for each oxygen stoichiometry.

	Face	Edge	Corner
$\text{a-In}_{54}\text{O}_{81}$	3.181	3.397	3.801
$\text{a-In}_{54}\text{O}_{80}$	3.183	3.387	3.830
$\text{a-In}_{54}\text{O}_{79}$	3.174	3.382	3.819
$\text{a-In}_{54}\text{O}_{78}$	3.143	3.359	3.821
$\text{a-In}_{54}\text{O}_{77}$	3.172	3.365	3.807
$\text{a-In}_{54}\text{O}_{76}$	3.148	3.360	3.812

In-In pairs with comparable distances (within 2.5–3.5 Å) and comparable concentration to that of face-shared In-In, Figure 8(a), is likely to be the reason for the large first In-In peak in experimental PDF as compared to edge- and corner-shared peaks.

In Figure 8(b), the number of edge-shared neighbors is plotted as a function of the corner-shared neighbors for individual In atoms in all amorphous  $\text{In}_2\text{O}_{3-x}$ . As mentioned above, each In atom in bixbyite  $\text{In}_2\text{O}_3$  has 12 In neighbors: 6 of them are edge-shared and 6 are corner-shared with the given In atom. It is obvious that disorder has a tremendous effect on the polyhedra sharing: even the perfectly stoichiometric  $\text{a-In}_{54}\text{O}_{81}$  structure has only 17 In atoms among 10 MD realizations, *i.e.*, out of 540 In atoms, that possess 6 edge- and 6 corner-shared neighbors. The average In atom in  $\text{a-In}_{54}\text{O}_{81}$  has 3.9 edge-shared and 8.8 corner-shared neighbors, while the outliers in the overall distribution may have 7 edge-shared and 5 corner-shared In neighbors or only 1 edge-shared and 12 corner-shared neighbors. Oxygen non-stoichiometry has little effect on the average In atoms, however, it results in appearance of severely under-coordinated In atoms, *i.e.* those with low numbers of both edge and corner-shared In neighbors. Interestingly, the appearance of a few under-coordinated In atoms (1-2 edge-shared and 7 corner-shared neighbors) in  $\text{a-In}_{54}\text{O}_{79}$  seems to be compensated by an increased number of over-coordinated In atoms (7-8 edge-shared and 4-6 corner-shared neighbors), Figure 8(b). This suggests that the amorphous oxide structures may feature intricate coordination morphology. The fraction of severely under-coordinated In atoms continues to increase significantly in  $\text{a-In}_{54}\text{O}_{78}$ ,  $\text{a-In}_{54}\text{O}_{77}$ , and  $\text{a-In}_{54}\text{O}_{76}$ . Moreover, a general trend—the lower the number of edge-shared neighbors, the higher the number of corner-shared neighbors are—can be seen in structures with higher oxygen content, *i.e.*, in  $\text{a-In}_{54}\text{O}_{81}$ ,  $\text{a-In}_{54}\text{O}_{80}$ , and  $\text{a-In}_{54}\text{O}_{79}$ . As the oxygen content decreases, the overall distribution along this trend broadens significantly that suggests an increased disorder for the medium range. Such level of disorder in the In-O polyhedra network is remarkable given the fact that the density of the structures is only 1% below the crystalline value. This highlights the ability of ionic amorphous oxides to withstand large oxygen non-stoichiometry by adjusting the sharing of In-O polyhedra in the entire cell.

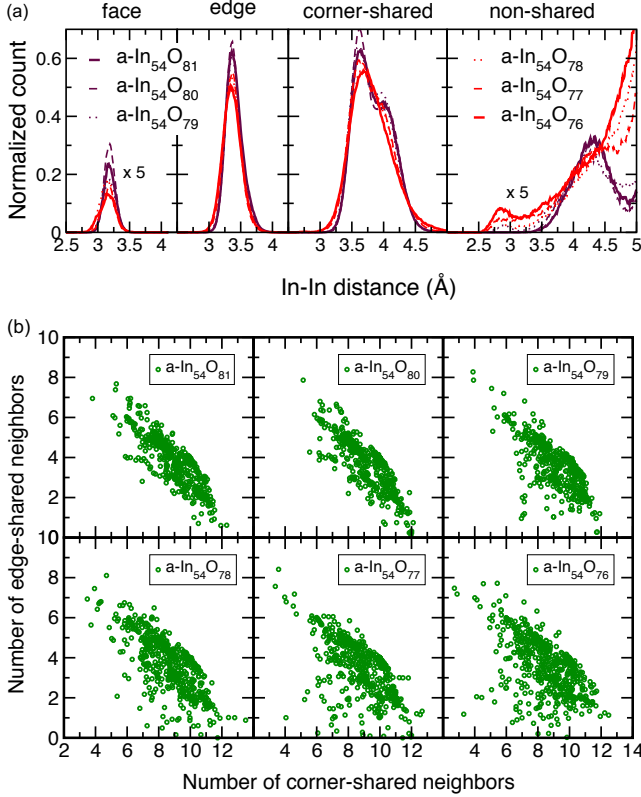


FIG. 8. (a) Distribution of face-, edge-, corner-, and non-shared In-In pairs as a function of In-In distance in amorphous  $\text{In}_2\text{O}_{3-x}$ . The type of sharing is determined based on the number of oxygen atoms that contribute to ECN of both In atoms. The results are based on 3,000 MD simulations (6 ps) at 300 K and include 10 MD runs for each  $\text{a-In}_2\text{O}_{3-x}$ . (b) The number of edge-shared In neighbors as a function of the number of corner-shared In neighbors for every In atom in the cell in amorphous  $\text{In}_2\text{O}_{3-x}$ . Every data point represents a time average over 3,000 MD configurations obtained at 300 K. The results of 10 separate MD realizations in each stoichiometry case are shown.

## VI. ELECTRONIC PROPERTIES

The calculated density of states (DOS) for fully relaxed structures of amorphous  $\text{In}_2\text{O}_{3-x}$ , Figure 9(a), shows that the stoichiometric  $\text{a-In}_{54}\text{O}_{81}$  case corresponds to an insulator with a direct band gap at  $\Gamma$  point of 1.64 eV on average over 10 realizations, each obtained from HSE06 calculations. The value of band gap ranges from 1.49 eV to 1.79 eV among the realizations, representing some sensitivity to the variable average In-O distance in each structure (ranging from 2.205 Å to 2.223 Å in optimized structures) as well as the differences in the morphology that determine the hybridization in the conduction band and, hence, its width. As expected, the Fermi level shifts into the conduction band in all non-stoichiometric structures. In  $\text{a-In}_{54}\text{O}_{80}$ , the value of the shift is 1.59 eV on average over 10 realizations; it ranges from 1.50 eV to 1.64 eV among the realizations. This value of Fermi level shift is comparable to the Burstein-Moss shift in crystalline transparent con-

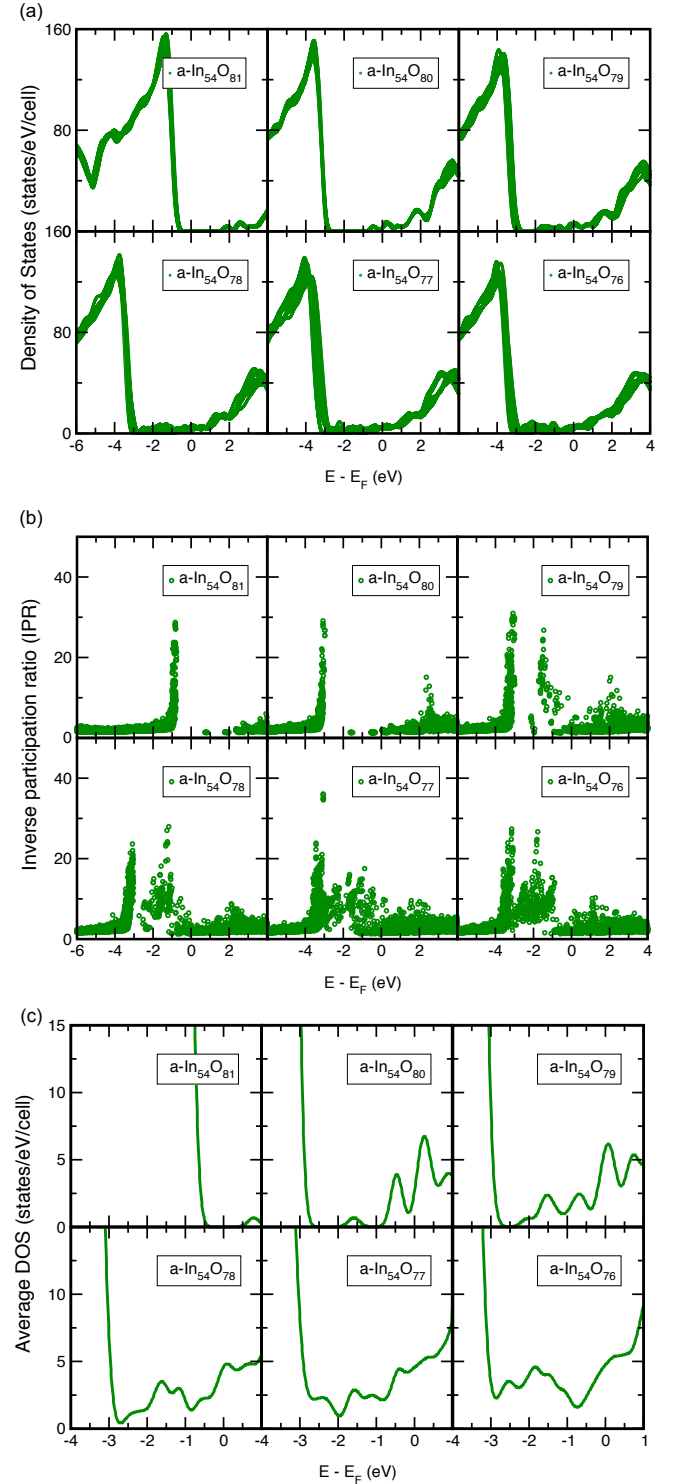


FIG. 9. Calculated (a) density of states (DOS); (b) inverse participation ratio (IPR); and (c) average DOS for the gap states for amorphous  $\text{In}_2\text{O}_{3-x}$ . All results are obtained using hybrid functional (HSE06) calculations for the structures optimized using DFT-PBE. In (a) and (b), 10 MD+DFT(HSE) realizations for each oxygen stoichiometry are shown simultaneously, whereas in (c) an average over the 10 realizations is given.

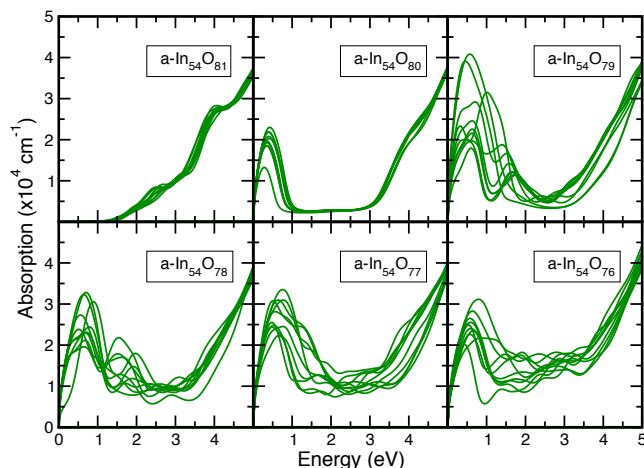


FIG. 10. Calculated optical absorption for 10 MD+DFT(HSE) realizations for each oxygen stoichiometry are shown for amorphous  $\text{In}_2\text{O}_{3-x}$ . Average over the 10 realizations. All results are obtained using hybrid functional (HSE06) calculations for the structures optimized using DFT-PBE.

ducting oxides [70], suggesting that the delocalized nature of the conduction band is preserved upon amorphization. As the oxygen content decreases, states with low density extend into the band gap (for a- $\text{In}_{54}\text{O}_{79}$ ) and fill the entire band gap for structures with lower oxygen stoichiometries. To characterize the degree of electron localization of these states, inverse participation ratio is calculated according to Eq. 4 and given in Figure 9(b). Most of the defect states within the band gap are highly localized with comparable IPR values to those at the top of the valence band (the origin of the localized states at the top of the valence band has been discussed in detail in [29]). Importantly, the localization of the states near the Fermi level—the states that are responsible for carrier transport as well as electron scattering—increases only moderately, except for a few realizations in a- $\text{In}_{54}\text{O}_{77}$  case where the electron localization is significant ( $\text{IPR} \approx 10$  near  $E_F$ , Figure 9(b)). Below, the defect states will be analyzed in more detail by identifying individual atoms that are the primary or major contributors to these states and associating the electronic features of the defect states with the structural characteristics of these atoms.

In Figure 9(c), the average DOS calculated from 10 realizations for each stoichiometry is shown. As discussed in earlier works [28], at low oxygen sub-stoichiometry, the density of states at 0 K features a characteristic gap, the so-called Coulomb gap, near the Fermi level that signifies the formation of chain-like conductivity channels. As the oxygen content decreases, the gap fills up and the DOS remains nearly constant in the vicinity of the Fermi level, as expected for a metal with a uniform charge density distribution. Accordingly, the free electron concentration, estimated as an integrated DOS within  $-0.1$  eV to  $0.1$  eV energy range, is nearly constant for a- $\text{In}_{54}\text{O}_{78}$ , a- $\text{In}_{54}\text{O}_{77}$  and a- $\text{In}_{54}\text{O}_{76}$ , Table IV. The highest free electron concentration is obtained in a- $\text{In}_{54}\text{O}_{79}$ . The values are in excellent agreement with the experimental values

TABLE IV. The integrated number of states calculated within two energy ranges: from  $-0.1$  eV to  $0.1$  eV that represent free carrier concentration and from  $-2.5$  eV to  $-1.0$  eV that corresponds to deep defect concentration. Also, the electron velocity calculated along the [111] band-like state at the energy where the band crosses the Fermi level. The calculations are based on DFT-HSE density of states averaged over 10 realizations for each oxygen stoichiometry, Figure 9(c).

	Free carriers, $\times 10^{20} \text{ cm}^{-3}$	Deep defects, $\times 10^{21} \text{ cm}^{-3}$	Electron velocity, $\times 10^5 \text{ m/s}$
a- $\text{In}_{54}\text{O}_{80}$	3.3	—	1.39
a- $\text{In}_{54}\text{O}_{79}$	6.6	0.4	1.04
a- $\text{In}_{54}\text{O}_{78}$	5.3	1.2	0.89
a- $\text{In}_{54}\text{O}_{77}$	5.4	1.1	0.58
a- $\text{In}_{54}\text{O}_{76}$	5.6	2.2	0.80

for amorphous indium oxide grown at oxygen partial pressure of 1-8 mTorr [28]. In addition, we estimate the concentration of deep strongly-localized defect states that are formed within the energy range approximately from  $-1$  eV to  $-2.5$  eV below the Fermi level, Figure 9(c) and Table IV. We find that the deep defect content is comparable to that of amorphous In-Ga-Zn-O [32].

The calculated optical absorption for amorphous  $\text{In}_2\text{O}_{3-x}$  is shown in Figure 10. At small oxygen non-stoichiometry (in a- $\text{In}_{54}\text{O}_{80}$ ), a pronounced Fermi level shift widens the optical window, and the material becomes nearly transparent within the entire visible range. The low absorption is associated with the intra-band transitions, *i.e.*, within the half-occupied conduction band formed by delocalized states, case a- $\text{In}_{54}\text{O}_{80}$  in Figure 9(b). We note here that despite the aforementioned variation in the band gap values, the optical properties of different MD+DFT(HSE) realizations are similar for 10 cases of stoichiometric a- $\text{In}_{54}\text{O}_{81}$  and also for 10 cases of a- $\text{In}_{54}\text{O}_{80}$ . In marked contrast, the optical absorption curves vary significantly for different realizations with lower stoichiometry, owing to the presence of defect states with different degree of electron localization that leads to a different Fermi level shift, Figure 9 and 10. For example, in a- $\text{In}_{54}\text{O}_{79}$ , different realizations yield notably different electronic properties: several realizations result in (i) further Fermi level shift up into conduction states; (ii) further optical band gap widening; and (iii) further increase of the carrier concentration (as signified by a higher Drude peak at about  $0.5$  eV)—as compared to the cases of a- $\text{In}_{54}\text{O}_{80}$ . At the same time, other realizations at this oxygen stoichiometry show a reduction in the optical gap and an increased absorption near  $1.5$ - $2.5$  eV, Figure 10. The latter is associated with a formation of a deep state inside the fundamental band gap, an electron trap. The absorption within the IR and visible ranges continues to gradually increase with oxygen reduction, leading to a complete transition to metallic behavior found in all realizations in a- $\text{In}_{54}\text{O}_{76}$  case, Figure 10. In all structures with oxygen stoichiometry below  $2.926$  (oxygen defect concentration of  $11.5 \times 10^{20} \text{ cm}^{-3}$  and above), structural variations associated with the different coordination morphology (*i.e.*, the spacial distribution of the under-coordinated In atoms) will lead to pronounced differences between the realizations yielding significantly different

optical absorption profiles, overall optical transmission, and the total number of free carriers. This again highlights the necessity for adequate statistical representation using multiple realizations or significantly larger supercells, since a single calculation in a 100-200-atom cell may produce misleading conclusions.

## VII. ELECTRON LOCALIZATION AND STRUCTURE-PROPERTY RELATIONSHIPS FOR METALLIC FORMATIONS

To analyze the localized states that arise in  $a\text{-In}_{54}\text{O}_{79}$ ,  $a\text{-In}_{54}\text{O}_{78}$ ,  $a\text{-In}_{54}\text{O}_{77}$ , and  $a\text{-In}_{54}\text{O}_{76}$ , Bader charge contributions from every In atom is calculated for the occupied defect states (located within up to 3 eV below the Fermi level, Figure 9(b)) and plotted as a function of the effective coordination number of the given In atom, Figure 11. (Note that here the ECN, effective distance and distortion values discussed in this section are calculated based on the atomic coordinates in the optimized 0 K structures for which the electronic properties were calculated.) We find that the largest Bader charge contribution to the defect state in each realization is from a low-coordinated In atom,  $\text{ECN} < 5$ . The ECN value calculated as an average over the In coordination of the largest Bader contributor in each of the 10 realizations for different stoichiometry, decreases gradually from 3.63 to 3.61, to 3.39, to 3.25 for  $a\text{-In}_{54}\text{O}_{79}$ ,  $a\text{-In}_{54}\text{O}_{78}$ ,  $a\text{-In}_{54}\text{O}_{77}$ , and  $a\text{-In}_{54}\text{O}_{76}$ , respectively. This is consistent with the decreasing overall ECN calculated for all In atoms, Table I, and the growing number of In atoms with extremely low coordination, Figure 6, when the oxygen content decreases. A clear dependence of the charge localization on  $\text{ECN}(\text{In})$  is observed in  $a\text{-In}_{54}\text{O}_{79}$ , *i.e.*, for the oxygen stoichiometry of 2.926 and oxygen defect concentration of  $11.5 \times 10^{20} \text{ cm}^{-3}$ : in this case, the largest Bader charge contributions (about  $1e^-$ ) are associated with the lowest ECN values ( $\text{ECN} < 4$ ), whereas the majority of In atoms with high coordination ( $\text{ECN} > 4$ ) have low Bader charge contributions to the defect state, namely, less than  $0.1e^-$ , Figure 11. At lower oxygen content, a broad range of In coordination numbers have large Bader charge of about  $0.5\text{-}1e^-$ , namely, from  $\text{ECN}=5.0$  to  $3.5$  in  $a\text{-In}_{54}\text{O}_{78}$  and from  $\text{ECN}=4.5$  to  $2.0$  in  $a\text{-In}_{54}\text{O}_{77}$  and  $a\text{-In}_{54}\text{O}_{76}$ , Figure 11. At the same time, an increasing number of severely under-coordinated In atoms (with  $\text{ECN} \approx 4$  and  $\text{ECN} \approx 3$ ) have moderate or orders-of-magnitude smaller Bader charge (below  $0.1e^-$ ) as the oxygen sub-stoichiometry increases, Figure 11. Therefore, ECN value alone is not a sufficient descriptor to predict the charge localization and, consequently, to explain the deep traps in highly non-stoichiometric amorphous indium oxide. Other structural characteristics of individual In atoms should be considered in combination with ECN in order to predict localized defects.

In addition to ECN, we analyzed the average In-O distance and distortion (or distance variance within a given InO polyhedron), *c.f.*, Figure 6(a,b). Indium atoms with a longer than average In-O distance appear to have larger Bader charge contributions, in agreement with our earlier findings for stoichiometric  $a\text{-In}_{54}\text{O}_{81}$  [29]. Specifically, for the In atoms that have

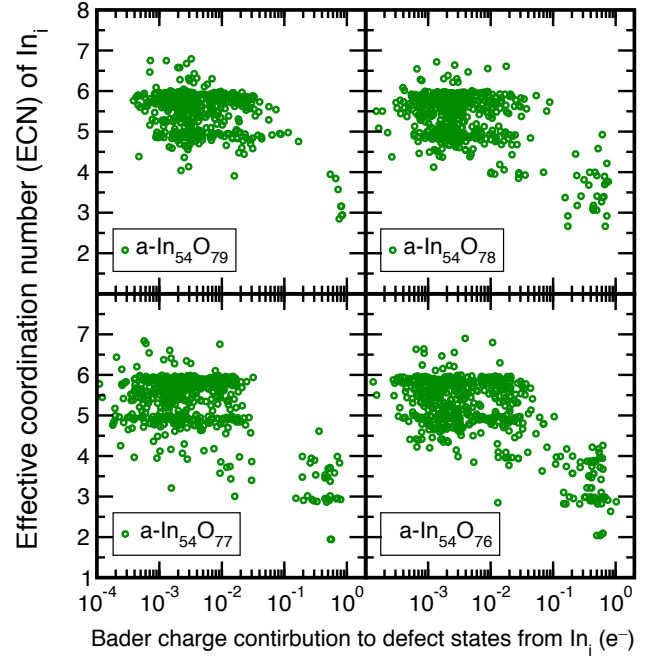


FIG. 11. The effective coordination number of individual In atoms as a function of the Bader charge contributions from the atom to the defect state(s) located in the band gap at up to 3 eV below the Fermi level. Each state holds  $2e^-$ . All 54 In atoms in each of the 10 supercells are shown for each oxygen stoichiometry; only the largest Bader charge contribution to the defect state(s) for each In atom is shown. The results are obtained using hybrid functional (HSE06) calculations for the structures optimized using DFT-PBE approach.

defect Bader charge of  $0.2e^-$  or greater, the average ECN, average effective In-O distance and average distortion are, respectively, 3.46, 2.25 Å and  $0.006 \text{ \AA}^2$  in  $a\text{-In}_{54}\text{O}_{79}$ ; 3.63, 2.26 Å and  $0.020 \text{ \AA}^2$  in  $a\text{-In}_{54}\text{O}_{78}$ ; 3.28, 2.26 Å and  $0.017 \text{ \AA}^2$  in  $a\text{-In}_{54}\text{O}_{77}$ ; and 3.31, 2.27 Å and  $0.019 \text{ \AA}^2$  in  $a\text{-In}_{54}\text{O}_{76}$ . These values differ significantly from the overall structural characteristics in  $a\text{-In}_2\text{O}_{3-x}$ , Table I. Therefore, not only a small ECN, but also longer than expected effective In-O distances that can be categorized as “outliers” in the ECN-vs-distance plot, Figure 6(b), as well as larger than usual polyhedral distortions, Figure 6(a), are the reasons for higher Bader charge values. It must be noted that the distortion considered in this work as the distance variance within a given InO polyhedron, does not account for specific symmetry or distribution of the oxygen atoms around the central In, and therefore, it not a reliable parameter. For example, in one of the  $a\text{-In}_{54}\text{O}_{76}$  realizations, we find two In neighbors that have similar ECN values of 3.63 and 3.95; similar average In-O distance of 2.19 Å and 2.18 Å; and polyhedra distortion of  $0.072 \text{ \AA}^2$  and  $0.002 \text{ \AA}^2$ , respectively, yet, their largest Bader charge is  $0.02e^-$  and  $0.61e^-$ , respectively. A closer inspection of the oxygen environments around the In atoms reveals that the strongly distorted polyhedra contains two oxygen atoms at longer-than-expected distances but directed towards the second In, effectively screening the former In atom from the latter, thus, reducing its Bader charge. This finding explains the observation

that some low-coordinated In atoms have small Bader charge, Figure 11.

Moreover, the coordination of individual In atoms or a combination of several structural characteristics do not show correlation with the energy of the defect state within the electronic structure. For example, we find that in  $a\text{-In}_{54}\text{O}_{76}$ , a low-ECN In atom (ECN=2.95, effective In-O distance 2.20 Å and distortion 0.0026 Å<sup>2</sup>) is the largest Bader contributor to a defect state located at -2.3 eV with respect to the Fermi level, *i.e.*, with  $E_F$  at zero. At the same time, this realization has a deeper defect located at -3.0 eV, and the largest Bader contribution to this state is from an In atom with a larger ECN, 3.95 (In-O distance 2.18 Å and distortion 0.0016 Å<sup>2</sup>). It should be noted that the results also reveal that the Bader charge contributions from individual In atoms do not correlate with how deep the defect state associated with the In atom is, suggesting that further analysis is required.

The mutual distribution of the abundant under-coordinated In atoms must be taken into account in order to explain the degree of charge localization and the resulting diverse electronic properties. First, in addition to In-O coordination, we consider the structural characteristics of next nearest neighbors of the low-coordinated In atoms. Specifically, we find that the largest (above  $0.1e^-$ ) Bader charge contributions in each realization are from In atoms that on average (*i.e.*, among 10 realizations) have  $\text{ECN} \approx 3.5$  and also have at least one low-coordinated In neighbor with  $\text{ECN} \approx 4.1$  that is located at a short In-In distance of 3.4 Å. These results are in agreement with our earlier findings for the localized states in  $a\text{-In}_{54}\text{O}_{79}$  where the energy location of the defect state below the Fermi level was found to correlate not only with how low the ECN value of an In atom is, but also with how low the ECN value of its under-shared In neighbor is and how short the distance between the two In atoms is [29]. In other words, the In-In distance between the two low-coordinated In atoms and whether or not they share oxygen atom(s) are important factors that contribute to the formation of isolated In-In metallic bonds and should be considered to determine the energy location of the associated deep electron traps within the band gap in  $a\text{-In}_{54}\text{O}_{79}$  [29]. It should be noted here that the In-In distance alone, *i.e.*, without taking into account the In coordination, cannot predict the electron localization. First of all, a face-shared In-In pair is a common structural defect in amorphous indium oxide at any oxygen stoichiometry, Figures 7 and 8(a). As mentioned in Section V, the average In-In distance for a face-shared pair is 3.16 Å, while the shortest face-shared distance is found to be 2.60 Å. This is significantly shorter than the In-In distance in metallic elemental In, 3.26 Å. However, the face-shared connections are formed when the two In atoms share three oxygen atoms with each other. The presence of the oxygen atoms effectively screens the In atoms from each other: the formation of the six ionic In-O bonds inhibits a direct interaction between the In orbitals, *i.e.*, it prevents the formation of a metallic In-In bond. Therefore, face-shared In-In pairs should be excluded from consideration as a cause of electron localization.

In this work, we focus on a combination of low ECN, short In-In distances, and no oxygen sharing between pairs

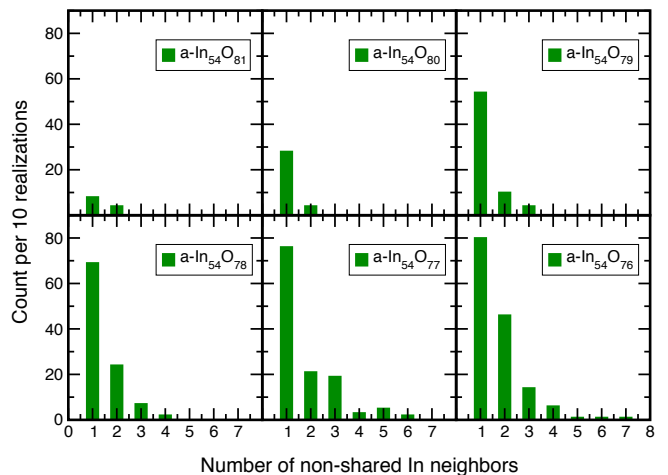


FIG. 12. The number of non-shared In neighbors that are located at the distance of 4.5 Å or below from each other and both are under-coordinated with oxygen ( $\text{ECN} < 5.2$ ). The results are calculated based on 10 MD realizations for each oxygen stoichiometry using the amorphous  $\text{In}_2\text{O}_{3-x}$  structures optimized within DFT-PBE. The total number of In atoms within 10 realizations is 540.

of In atoms in order to study the effect of clustering of increasingly abundant under-coordinated In atoms in highly non-stoichiometric oxides on the formation of deep localized states. To do this, we set the following structural criteria that may allow In atoms to form direct metallic bonds with the In neighbors: for every under-coordinated In atom ( $\text{ECN} < 5.2$ ), we find all under-coordinated In neighbors ( $\text{ECN} < 5.2$ ) that are at the In-In distance of 4.5 Å or below and do not share any oxygen atoms between them. Here, one should recall that the In-In distance within 3.1 Å to 3.8 Å is typical for edge-shared In-In pairs (two oxygen atoms shared the In neighbors) and the In-In distance within 3.3 Å to 4.5 Å is typical for corner-shared In-In pairs (one oxygen atom shared by the In neighbors), Figure 8. Therefore, two In atoms located at a distance of 4.5 Å or below from each other without sharing an oxygen should be examined as potential non-shared In-In defect that may result in a metallic In-In bond. For comparison, we remind here that the In-In distance in elemental In metal with tetragonal  $I4/mmm$  structure is 3.26 Å. Note, the ECN limiting value of  $\leq 5.2$  may appear quite high since a large fraction of In atoms with coordination of 4.5 to 5.2 have small Bader charge contributions, below  $0.1e^-$ , Figure 11. However, we would like to capture the small fraction of “outliers”, the In atoms that have ECN within this range, but contribute within  $0.5\text{-}0.6e^-$  to the defect state Bader charge, Figure 11. We anticipate that the other structural features—longer-than-usual In-O distances, short In-In distances, and under-sharing—will help us capture the important contribution from these “outliers”.

First, we calculate the percentage of the In atoms that are non-shared according to the criteria set above: it is 2%, 6%, 13%, 19%, 23%, and 28% in  $a\text{-In}_{54}\text{O}_{81}$ ,  $a\text{-In}_{54}\text{O}_{80}$ ,  $a\text{-In}_{54}\text{O}_{79}$ ,  $a\text{-In}_{54}\text{O}_{78}$ ,  $a\text{-In}_{54}\text{O}_{77}$ , and  $a\text{-In}_{54}\text{O}_{76}$ , respectively, out of the total 540 In atoms in 10 MD configurations for each stoi-

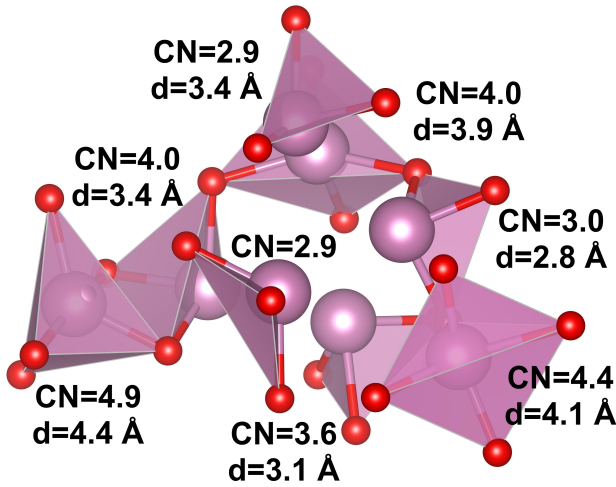


FIG. 13. An In atom that does not share any oxygen atoms with 7 In neighbors. All the In atoms in the cluster have low effective coordination numbers (labeled as CN) and short In-In distances to the central In atom. This example is from one of the 10 MD realizations for  $a\text{-In}_{54}\text{O}_{76}$  after structural optimization. The network diagram for the metallic cluster is shown in Figure 14(c).

chiometry. This means that nearly a third of all In atoms in  $a\text{-In}_{54}\text{O}_{76}$  has at least one In neighbor at the In-In distance below  $4.5 \text{ \AA}$  that it does not share an oxygen atom with. The number of the In atoms with a single non-shared In neighbor increases from 8 (in  $a\text{-In}_{54}\text{O}_{81}$ ) to 80 (in  $a\text{-In}_{54}\text{O}_{76}$ ), calculated among the 540 In atoms in 10 MD configurations for each stoichiometry, that corresponds to 1.5% and 15%, respectively, Figure 12. The number of In atoms with 2 or more non-shared In neighbors also increases with oxygen reduction, reaching as many as 7 neighbors found in one realization for  $a\text{-In}_{54}\text{O}_{76}$ , Figure 12. The In atom that does not share any oxygen atoms with 7 In neighbors is illustrated in Figure 13(a) where the effective coordination numbers and In-In distances to the central In atom are given. Here we must stress an important difference between  $a\text{-In}_{54}\text{O}_{77}$  and  $a\text{-In}_{54}\text{O}_{76}$ : the number of 2-neighbor non-shared under-coordinated In atoms doubles in the latter case, signifying that at this oxygen stoichiometry the In-In metallic chains become more prevalent and also longer. Indeed, among 10 realization for  $a\text{-In}_{54}\text{O}_{76}$ , we find two configurations where there are only 1 and 2 neighbor non-shared under-coordinated In atoms. In both cases, the network diagram represents a set of chains that never cross with each other, and one of the chains consists of 7 non-shared under-coordinated atoms with no loops, Figure 14(a). An even longer chain is found in another configuration for  $a\text{-In}_{54}\text{O}_{76}$  where 11 under-coordinated In atoms are all connected in one single chain, Figure 14(b). In  $a\text{-In}_{54}\text{O}_{77}$ , however, the longest chain consists of 5 under-coordinated non-shared In atoms and overall the chains are more scarce and shorter. Therefore, the oxygen stoichiometry between  $a\text{-In}_{54}\text{O}_{77}$  and  $a\text{-In}_{54}\text{O}_{76}$  marks the transition to metallic networks with abundant chain-like formations. On the other hand, star-like formations, where the chains cross when the central In atom has

more than 2 neighbors, gradually appear with higher oxygen non-stoichiometry: we find 3-branch stars in  $a\text{-In}_{54}\text{O}_{79}$ ; 3 and 4-branch stars in  $a\text{-In}_{54}\text{O}_{78}$ ; 3, 4, 5 and 6-branch stars in  $a\text{-In}_{54}\text{O}_{77}$ ; and 3, 4, 5, 6, and 7-branch stars in  $a\text{-In}_{54}\text{O}_{76}$ , Figure 12. Three characteristic examples of  $a\text{-In}_{54}\text{O}_{76}$  configurations with a long chain and no crossing between four different chains; the longest chain with two 4-atom stars and one 3-atom stars (giving rise to two loops); and a network with 7-branch star and multiple interconnected loops are shown in Figure 14. We note that the structures with higher oxygen content are similar with the exception for a smaller number of star branches or loops and shorter chains and, hence, may be considered as a part of the diagrams shown in Figure 14.

Among 10 realizations for  $a\text{-In}_{54}\text{O}_{76}$ , the distribution of the metallic non-shared under-coordinated In pairs is very diverse. In addition to the three examples we show in Figure 14, we find that other realizations often have several chains that are not connected with each other. In fact, only a single realization results in a single chain with all non-shared under-coordinated In atoms connected, Figure 14(b). The remaining 9 configurations have 2, 2, 3, 3, 3, 3, 4, 4, and 5 independent chains not connected to each other. Each chain consists of 2 or up to 11 atoms. Four configurations do not have any loops within their chains; another four configurations have 1-3 loops that connect 3-4 In atoms within the chain; and only two configurations have pronounced clustering with 8-9 loops, shown in Figure 14(a,c). While an infinite number of distinct atomic configurations should be expected for a disordered structure, it is clear that amorphous indium oxide tends to spread out the individual metallic bonds within the amorphous cell in percolation-like single-atom chain formations. A significant fraction of the realizations for  $a\text{-In}_{54}\text{O}_{76}$  do not feature strong metallic clustering. This finding is consistent with earlier results for  $a\text{-In}_{54}\text{O}_{80}$  where the oxygen defect is found to be a delocalized shallow donor where the lack of oxygen is shared between as much as a third of In atoms with low coordination ( $\text{ECN} < 5.0$ ) instead of resulting in a strongly localized state as in crystalline indium oxide with an oxygen vacancy [29]. The tendency for a more uniform coordination distribution in amorphous indium oxide arises from the weak ionic In-O bonding combined with bond reconfiguration facilitated by the lack of periodicity. The metallic chain-like networks is likely to be the reason for a higher electron velocity in  $a\text{-In}_{54}\text{O}_{76}$  as compared to  $a\text{-In}_{54}\text{O}_{77}$ , Table IV, because such morphology supports percolation for the extended conductivity paths.

Bader charge calculations reveal that 84% of the under-coordinated In atoms ( $\text{ECN} < 5.2$ ) with a single non-shared In neighbor ( $\text{ECN} < 5.2$  and In-In distance below  $4.5 \text{ \AA}$ ) among 10 MD realizations of  $a\text{-In}_{54}\text{O}_{76}$  contribute below  $0.1e^-$  to the occupied defect states located within up to 3 eV below the Fermi level in the conducting oxides, *c.f.*, Figure 9(b). Among the under-coordinated In atoms with two non-shared under-coordinated In neighbors, about 46% have Bader charge contributions below  $0.1e^-$ . All under-coordinated In atoms with 3, 4, 5, 6, or 7 non-shared under-coordinated In neighbors contribute more than  $0.1e^-$  and up to about  $1e^-$  for the most localized state. This finding clearly indicates that cluster-

ing is playing an important role in localization. However, above  $0.1e^-$ , the Bader charge values do not directly correlate with the number of non-shared In neighbors. For example, the In atom with 7 non-shared In neighbors has the largest Bader contribution of  $0.27e^-$  to one of the defect states, whereas the two largest Bader charge contributions,  $1.03e^-$  and  $0.83e^-$ , are from In atoms that have only two non-shared under-coordinated In neighbors (note, the examples belong to different realizations).

To understand the relatively low Bader charge on the In atom with 7 non-shared In neighbors, we create a graph plot using the structural criteria set above: we find all In atoms that have low ECN (below 5.2) and are non-shared with other low-ECN In atoms ( $ECN < 5.2$ ) being at the In-In distance below  $4.5 \text{ \AA}$  from each other and plot a network-like graph plot showing the ECN values inside circles to represent under-coordinated In atoms and connecting the atoms that are non-shared using lines that show the In-In distance. The result is shown in Figure 14(c). We find that the under-coordinated In atom with 7 non-shared In neighbors is part of a cluster of under-coordinated In atoms with similar ECN (2.85, 2.90, 2.96, 3.56, 3.96) and that several of the non-shared connections within the cluster have similar In-In distances (2.71, 2.80, 3.03, 3.05, 3.43, and  $3.53 \text{ \AA}$ ), Figure 14(c). As a result, the first four In atoms in the cluster have nearly equal Bader charge ( $0.27e^-$ ,  $0.42e^-$ ,  $0.38e^-$ ,  $0.44e^-$ ,  $0.02e^-$ , respectively to the ECN values above). Importantly, the clustering of In atoms with alike coordination at alike non-shared distances is the reason for the defect to be closer to the Fermi level: among three defect states for this realization of  $a\text{-In}_{54}\text{O}_{76}$ , the given defect is located at  $-1.4 \text{ eV}$ . This is nearly  $1 \text{ eV}$  higher than the deepest defect for this realization that is located at  $-2.5 \text{ eV}$  and is associated with an In atom that has Bader charge of  $0.75e^-$ , the largest value for these configuration. The latter In atom also has a low  $ECN=2.91$  and is non-shared with 4 In neighbors, one of which has  $ECN=4.09$  and is located at the shortest distance of  $2.82 \text{ \AA}$ . However, the other three non-shared In neighbors have higher ECN values, 4.41, 4.85, and 5.13, and are at a notably longer distances,  $3.72$ ,  $3.85$ , and  $4.25 \text{ \AA}$  from the given In with largest Bader charge. This arrangement makes the two In atoms with lowest ECN isolated and leads to stronger localization at the corresponding state associated with the two atoms, Figure 14(c). For completeness of our analysis, we also consider an intermediate defect state for the same realization. The defect state is located at  $-2.1 \text{ eV}$  below the Fermi level and has the largest Bader charge contribution ( $0.44e^-$ ) from an In atom that has  $ECN=3.56$  and a longer-than-expected In-O distance of  $2.22 \text{ \AA}$ . Although the ECN value is notably higher than those for its two non-shared In neighbors, 2.85 and 2.96, located at  $3.05 \text{ \AA}$  and  $3.53 \text{ \AA}$  from the given In atom, it has a third non-shared neighbor with  $ECN=3.99$  and located at  $2.87 \text{ \AA}$ . Hence, this state corresponds to a very short In-In non-shared connection between two In atoms with relatively low ECN but surrounded by two In with even lower ECN but at a longer distances. The mixed nature of the ECN and distance values may explain the intermediate energy location of the defect ( $-2.1 \text{ eV}$ ) that is between  $-2.5 \text{ eV}$  and  $-1.4 \text{ eV}$ . The atoms are part of the com-

plex illustrated in Figure 14(c). A closer analysis reveals that several of the In atoms in the defect state have their oxygen bonds pointing outward and away from a line connecting the In atoms, thus, allowing for direct overlap of the In- $5s$  orbitals that favors the formation of metallic In-In bond.

The above results help explain why the calculated Bader charge contributions from the In atoms with severe under-coordination,  $ECN \approx 3$  and  $ECN \approx 2$ , may be relatively low, below  $0.2e^-$  for the state, Figure 11, and also why the deep defect states may be split by more than  $1 \text{ eV}$  in energy despite similar ECN values and similar number of non-shared neighbors for the In atoms associated with each defect. In addition to extreme structural characteristics of individual In atoms when the In-O coordination, In-O and In-In distances, polyhedra distortion, and/or under-sharing belong to the tails of the respective distributions, Figures 6 and 8, one has to take into account the spacial distribution of the “outliers” and their environment, *i.e.*, the structural features of the surrounding In neighbors, in order to explain the resulting charge localization. An isolated under-coordinated In-In pair—the one for which all other In neighbors have significantly higher ECN, share one or two oxygen atoms with the two In atoms, and are at an In-In distances that fall within the corresponding corner- or edge-shared distribution—will result in a deeper electron trap as compared to a cluster that consists of more than two In atoms with similar ECN and similar In-In distances, even if the ECN values are lower and the In-In distances are shorter in the latter case. In other words, the energy location of a defect moves toward the Fermi level as the number of In atoms in a cluster of neighbors with similar low ECN and similar short In-In distances increases. Stronger interaction between alike “outliers” reduces the electron localization of the defect state.

Based on the results for different oxygen stoichiometries, clustering of low-coordinated In atoms is likely to occur in  $a\text{-In}_{54}\text{O}_{76}$ ,  $a\text{-In}_{54}\text{O}_{77}$ , and  $a\text{-In}_{54}\text{O}_{78}$ , but not in  $a\text{-In}_{54}\text{O}_{79}$ , where the under-coordinated In atoms are the minority defects, isolated from each other within the amorphous structure, hence, the corresponding states are strongly localized—as evident from the large Bader charges for most of the low-coordinated In atoms ( $ECN < 4.0$ ), Figure 11, and also from the narrow energy range where the defect states are located, Figure 9(b). At low oxygen stoichiometries, the increased number of under-coordinated In atoms and broad distribution of their ECN values leads to intricate spacial arrangements of these In atoms, from clustering to rings to percolation-like chains formed by the under-coordinated In atoms with short-distant non-shared connections. Schematic graph plots are employed to illustrate the diverse morphology of under-coordinated non-shared In-In pairs in  $a\text{-In}_{54}\text{O}_{76}$ . The structure discussed above, Figure 14(c), has In atom with 7 non-shared neighbors; the cluster is also connected to 4 In atoms with 4 non-shared neighbors resulting in multiple 3, 4, and 5-atom loops. Another realization has only two 3-atom loops and a long chain of non-shared under-coordinated In atoms, Figure 14(b). This arrangement spreads out the lowest-ECN shortest In-In distance pairs into separate defect structures, making the corresponding defect states to be closer to each other in energy, at  $-1.2 \text{ eV}$ ,  $-1.6 \text{ eV}$ , and  $-1.9 \text{ eV}$ , with an additional deep state at  $-2.9 \text{ eV}$ .



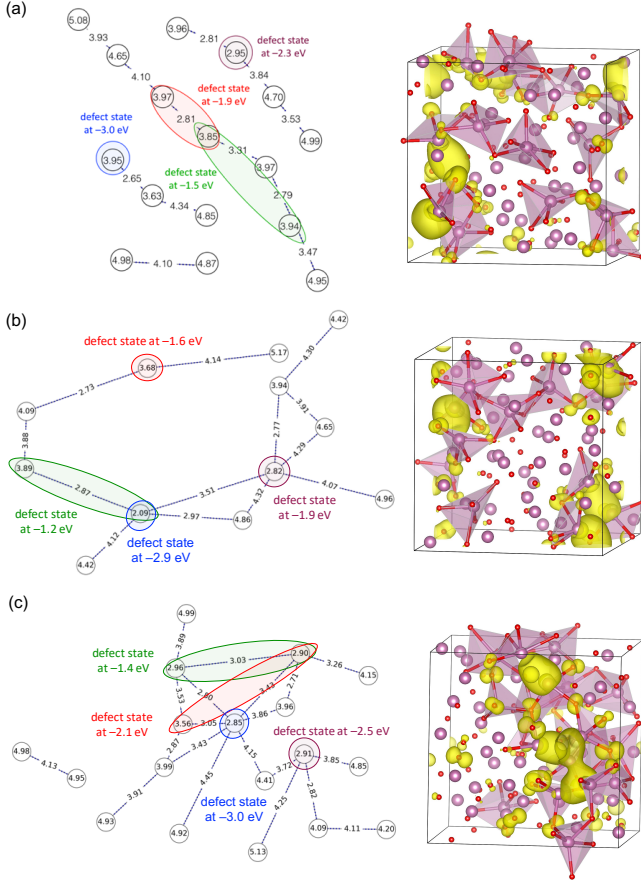


FIG. 14. Schematic representation of non-shared under-coordinated In atoms in three realizations for  $a\text{-In}_{54}\text{O}_{76}$  after structural optimization. For the graph plots, only non-shared In-In pairs that consist of In atoms with  $\text{ECN} < 5.2$  and have the In-In distance below  $4.5 \text{ \AA}$  were selected. Individual ECN values are shown inside the circles and the In-In distances (in  $\text{\AA}$ ) for non-shared connections are shown along the lines. Also, the main contributors (those with the Bader charge of  $0.2e^-$  or above) to defect states are highlighted and the energy of the corresponding defect state with respect to  $E_F=0 \text{ eV}$  is given. In each case, the charge density distribution calculated for the four defect states is shown on the right.

Similarly, the configuration with no star-like crossing and the longest chain, Figure 14(a), has one deep state at  $-3 \text{ eV}$  and three localized states,  $-1.5 \text{ eV}$ ,  $-1.9 \text{ eV}$ , and  $-2.3 \text{ eV}$ . While photo-illumination with visible or UV light may excite all of the defects, the shallower states may be sensitive to applied voltage or thermal stress, causing instabilities.

The widest coordination distribution among different realizations is found in  $a\text{-In}_{54}\text{O}_{77}$ , Figure 4(a). Accordingly, this oxygen stoichiometry shows the widest distribution of the defect formation energies, Figure 4(b), and in agreement with our discussion above, the  $a\text{-In}_{54}\text{O}_{77}$  cases exhibit the widest energy spread of the defect states and the highest localization of the states in the vicinity of the Fermi level among all stoichiometries, Figure 9(b). This finding highlights an important structure-property relationship in amorphous oxide semiconductors.

## VIII. COMPARISON OF METALLIC FORMATIONS IN CRYSTALLINE AND AMORPHOUS OXIDES

As mentioned in the introduction, highly non-stoichiometric crystalline  $\text{In}_2\text{O}_{2.5}$  grown in argon atmosphere shows metallic nanoclusters embedded in bixbyite indium oxide matrix [19]. Similarly, nanocomposite In-Sn-O films exhibit phase separation between the stoichiometric crystalline oxide with insulating properties and the embedded metallic (In and Sn) nano-inclusions with percolation-like conductivity and a superconducting transition at  $6 \text{ K}$  [20–23].

In amorphous indium oxide, the formation of metallic bonds occurs already in nearly-stoichiometric oxides, *i.e.*, at oxygen stoichiometry of 2.926: in  $a\text{-In}_{54}\text{O}_{79}$ , the shortest In-In distance for a pair of non-shared In atoms is found to be  $2.81 \text{ \AA}$ —significantly shorter than the shortest non-shared In-In distance ( $3.58 \text{ \AA}$ ) in crystalline  $\text{In}_2\text{O}_{2.94}$  with an oxygen vacancy defect [29] and also shorter than the In-In distance in elemental In metal ( $3.26 \text{ \AA}$ ). As the oxygen stoichiometry decreases, the number of non-shared In neighbors for under-coordinated In atoms increases, Figure 12, and in  $a\text{-In}_{54}\text{O}_{76}$  ( $\text{In}_2\text{O}_{2.815}$ ), percolation-like distribution of the non-shared In-In metallic formations becomes intricate and diverse, Figure 14, with a strong tendency for single-atom chains, as discussed in the previous section. This ability of the amorphous indium oxide to spread out individual metallic bonds throughout the disordered structure instead of promoting their clustering that would enable growth of metallic nano-inclusions is the key feature that distinguishes the amorphous material’s response to oxygen reduction from the behavior observed in crystalline oxides. Indeed, crystalline indium oxide exhibits phase separation between stoichiometric insulating  $\text{In}_2\text{O}_3$  and the embedded metallic In nanoclusters detected by X-ray diffraction analyses [19]. In marked contrast, in amorphous indium oxide, the number of fully coordinated ( $\text{ECN} > 5.5$ ) In atoms is only 50% even in the perfectly stoichiometric  $a\text{-In}_{54}\text{O}_{81}$ , and it decreases to 34% for  $a\text{-In}_{54}\text{O}_{76}$ . The low numbers of fully-coordinated In atoms prevent the nucleation of bixbyite  $\text{In}_2\text{O}_3$  where all In atoms are octahedrally coordinated ( $\text{ECN}=5.6\text{-}6.0$ ). Thus, the results of this work reveal that not only the metallic In-In bond distribution is relatively uniform within the highly non-stoichiometric oxide structure, but also that the In coordination in the entire oxide matrix is affected by oxygen deficiency leading to a more uniform coordination morphology as compared to crystalline nanocomposites.

We note here that the amorphous structures with higher oxygen stoichiometries, 3.000 and 2.963, exhibit only weak (unstable) In-In pairs with shortest non-shared distances of  $3.65 \text{ \AA}$  and  $3.53 \text{ \AA}$ , respectively, among 10 DFT-PBE optimized structures for each stoichiometry. The In-In distances belong to corner-shared distribution, Figure 8(a), yet, these pairs of In do not share any oxygen atoms with each other, hence, we can classify them as under-shared. The metallic bonding for these non-shared In-In pairs is weak (given the relatively long In-In distances) and do not cause substantial electron localization, Figure 9(b). We should also mention that the shortest non-shared In-In distances during MD run at

300 K are 3.15 Å and 3.23 Å for the above oxygen stoichiometries, respectively; however, such short-distant “bonds” appear only for a very short periods of time of several fs, and hence are unstable.

The presence and distribution of metallic networks reported in this work highlight two important characteristics of amorphous indium oxide. First, owing to the shallow metal-metal defects even in weakly sub-stoichiometric  $\text{In}_2\text{O}_{3-x}$ , the observed carrier concentration in amorphous indium oxide is very high,  $3\text{--}5 \times 10^{20} \text{ cm}^{-3}$  for the samples grown in oxygen partial pressure of 1–8 mTorr using pulsed laser deposition (PLD) method [27, 29, 74]. Our calculated free carrier concentrations, Table IV, are in excellent agreement with the measurements. Moreover, the number of carriers decreases only moderately, to  $6 \times 10^{19} \text{ cm}^{-3}$ , when the oxygen partial pressure is increased to as much as 16 mTorr. This is in marked contrast to crystalline indium oxide, where the carrier concentration is two orders of magnitude lower,  $5 \times 10^{18} \text{ cm}^{-3}$ , when grown by PLD at  $p(\text{O}_2)=8 \text{ mTorr}$  [27, 29, 74]. A high carrier density of  $8 \times 10^{20} \text{ cm}^{-3}$  can be achieved in crystalline indium oxide only when samples are grown in oxygen-free atmosphere and when oxygen stoichiometry is as low as 2.5 [19]. Second, we show that oxygen stoichiometry has a pronounced effect on the coordination morphology and distribution of metallic networks, as evident from the calculated electron velocity as a function of oxygen sub-stoichiometry, Table IV. This explains the observed high sensitivity of the carrier mobility on oxygen environment in amorphous indium oxide: the mobility changes from 9 to 50  $\text{cm}^2/\text{Vs}$  when the oxygen partial pressure increases from 1 to 8 mTorr [28]. For comparison, the electron mobility in stoichiometric  $\text{In}_2\text{O}_3$  deposited in oxygen-rich atmosphere is 5.5  $\text{cm}^2/\text{Vs}$  and it increases to 15.5  $\text{cm}^2/\text{Vs}$  in oxygen-deficient samples with oxygen stoichiometry of 2.5 [19]. The opposite mobility trends suggest that the scattering mechanisms are different in crystalline and amorphous oxides: in crystalline phases the mobility is primarily limited by scattering on ionized impurities, whereas morphology and phonons are likely to govern the electron transport in amorphous oxides [28].

### IX. HYDROGEN COMPENSATION IN HIGHLY-NONSTOICHIOMETRIC AMORPHOUS OXIDE

In this work, we also study the changes in the structural and electronic properties of highly-nonstoichiometric indium oxides upon compensation with hydrogen. Hydrogen is common in amorphous metal oxides deposited by sputtering due to water vapor presence and also in samples that were grown by laser deposition techniques at low oxygen partial pressure and not encapsulated from the environment or brought in contact with H-containing layers in a device [75–78]. In amorphous In-Ga-Zn-O prepared by sputtering, hydrogen anion species and hydrogen in the form of hydroxyl group were reported to each have concentrations of  $>10^{20} \text{ cm}^{-3}$  [79], while an order of magnitude higher concentration of hydrogen (about  $5 \times 10^{21} \text{ cm}^{-3}$  or up to 7 at.%) was studied in amorphous indium oxide samples [77]. Substitutional  $\text{H}^-$  was suggested to be respon-

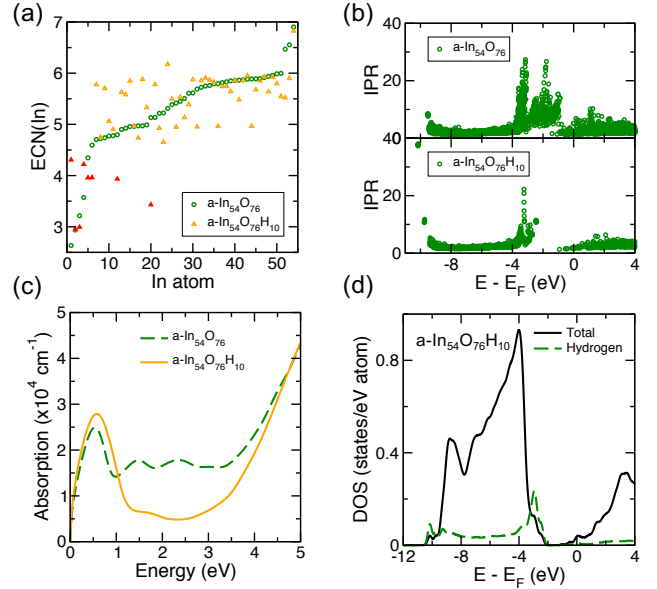


FIG. 15. (a) Effective coordination numbers for individual In atoms with oxygen neighbors in the lowest-energy realization for  $a\text{-In}_{54}\text{O}_{76}$  (circle) and for the same In atoms after H doping and structural relaxation in  $a\text{-In}_{54}\text{O}_{76}\text{H}_{10}$  (triangle). The In atoms that have one or more H neighbors at distances shorter than 1.95 Å, are represented with filled red triangle symbols. Calculated (b) inverse participation ratio (IPR); (c) optical absorption; and (d) total and partial density of states (DOS) for amorphous  $\text{In}_{54}\text{O}_{76}$  and  $a\text{-In}_{54}\text{O}_{76}\text{H}_{10}$ . The electronic properties are obtained using hybrid functional (HSE06) calculations for the structures optimized using DFT-PBE.

sible for negative bias illumination stress in amorphous metal oxides [80–82].

To determine the role of hydrogen in charge compensation and defect passivation, ten H radicals were added to the amorphous  $\text{In}_{54}\text{O}_{76}$  structure with the lowest total energy (among 10 realizations at the highest oxygen non-stoichiometry considered above). The initial locations of H atoms were determined as random positions with only two constrains: (i) the nearest-neighbor (In or O) distance to the initial H location is at least 1.7 Å (which is comparable to the typical In-H bond length [83] in amorphous In-Ga-O), at the same time, it was found to be shorter than 2.1 Å, in accord with earlier work [83]; and (ii) the initial H-H distances are long enough (4.1 Å on average) to correspond to a fairly uniform distribution of ten H radicals within the supercell. The random yet uniform placement of H atoms ensures that each H has a freedom to relax towards or away from under-coordinated In atoms. The resulting structure,  $a\text{-In}_{54}\text{O}_{76}\text{H}_{10}$ , corresponds to H concentration of  $5.8 \times 10^{21} \text{ cm}^{-3}$ . Prior to 0 K relaxation of the H-doped structure, ab-initio molecular dynamics simulations at 300 K were performed for the initial structure containing ten H atoms for 5,000 steps using integration step of 0.5 fs. It has been shown that MD simulations help find stable H defects in energetically-preferable locations and, at the same time, optimize the structural morphology of amorphous metal oxides by facilitating bond reconfiguration [83]. After the MD simula-

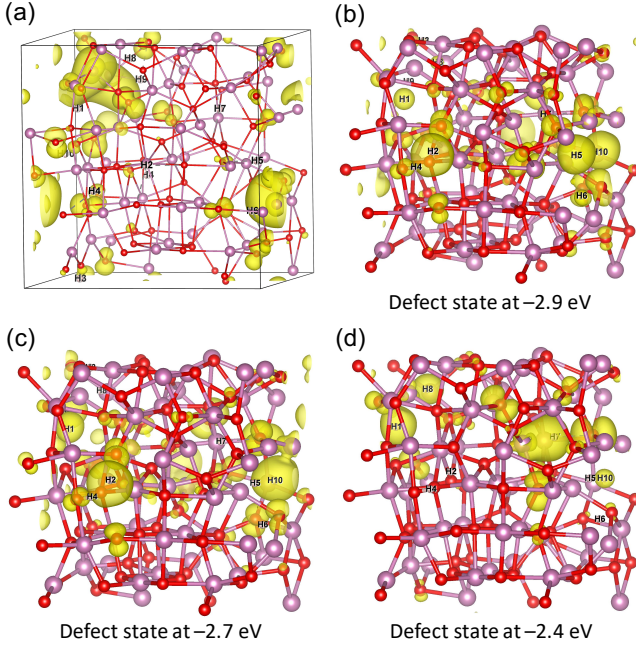


FIG. 16. (a) Initial locations of H with respect to the strongly localized defects in H-free structure of  $a\text{-In}_{54}\text{O}_{76}$  showing that none of 10 H radicals were placed directly at the defects represented by yellow charge density contours. (b,c,d) Charge density distribution calculated for the deep localized states formed near the top of the valence band in  $a\text{-In}_{54}\text{O}_{76}\text{H}_{10}$ .

tions, the H-doped configuration was relaxed using DFT-PBE approximation followed by the HSE06 calculations to determine the electronic and optical properties of the H-doped oxide. The results are summarized in Figures 15 and 16.

First, we find that out of ten H atoms added to the  $\text{In}_{54}\text{O}_{76}$  structure, 9 formed In-H-In defects and one formed In-OH defect. The shortest In-H distance for the former defects ranged from 1.69 Å to 1.90 Å, representing a weak In-H bonding, and the O-H distance for the latter defect is 1.00 Å. The calculated charge transfer confirms that hydrogen in the In-H-In defects acts as an acceptor, accumulating an additional electron density from nearby In atoms, whereas  $\text{OH}^-$  with a strong covalent bonding corresponds to H being a donor. The results are in agreement with previous investigations of H defects in amorphous In-Ga-O [83]. From the structural analysis we find that the presence of H affects the coordination of the majority of In atoms in the supercell, not only those in the vicinity of hydrogen, Figure 15(a). Among the In atoms that have one or more H neighbors at distances shorter than 1.95 Å, several increase their coordination with oxygen, and for several the coordination does not change. At the same time, a few In atoms reduced their coordination with oxygen upon H doping, Figure 15(a). Strikingly, the coordination of many In atoms that do not have a hydrogen atom in their vicinity changed after H doping. This signifies that the entire amorphous structure undergoes a significant bond reconfiguration due to H doping. A notable fraction of In atoms increase their coordination from below 5 to well above 5.5, pointing out that the coordina-

tion morphology changes with H doping. The results highlight the fact that placing H at random initial positions throughout the structure and not directly at the localized defects, Figure 16(a), not only models a realistic hydrogenation process, but also reveal the important role of structural reconfiguration in facilitating H passivation of strongly localized defects.

As expected, hydrogen is attracted to the oxygen-deficient regions with groups of under-coordinated under-shared In atoms, *c.f.*, Figure 14 and Section VII. The average In-O coordination of the In atoms that are the nearest neighbors of an H atom in relaxed  $a\text{-In}_{54}\text{O}_{76}\text{H}_{10}$ , was 3.54 prior to H doping. This is significantly lower than the average In-O coordination for the H-free structure, namely, 5.30 (in the PBE optimized case). Accordingly, hydrogen effectively passivates the strongly localized states located within the band gap (located at  $-1$  eV to  $-3$  eV in H-free structure) and forms acceptor-like states near the top of the valence band, at  $-2.4$  eV to  $-2.9$  eV below the Fermi level, Figure 15(b). The H passivation of the under-coordinated under-shared In atoms significantly reduces the optical absorption within the visible range as compared to the highly-nonstoichiometric H-free case, Figure 15(c). The calculated total and partial density of states, Figure 15(d), reveals that the H states contribute primarily near the top of the valence band. Charge density distributions calculated for the localized defect states above the top of the valence band confirm that the electron localization occurs on several H atoms as well as their under-coordinated In atoms and/or non-bonding O-*p*-orbitals, Figure 16(b,c,d).

In addition to restoring optical transparency in the visible region, hydrogen doping is likely to significantly improve the stability of the material's response to thermal stress or applied voltage [84–86] because it narrows the range of activation energies of the defect states that trap the electrons and pushes the defect states from  $-1$  eV or below in H-free case to  $-2.4$  eV or below after H doping, Figure 15(b). Whether the H-states located near the top of the valence band, would be sensitive to photo-illumination with energies above 2.5 eV to play a role in photo-switching transients as suggested earlier [87–92], will be investigated in a separate work.

Importantly, hydrogen doping not only passivates the strongly localized gap states, but also helps improve the electron mobility due to more uniform charge density distribution in the conduction band associated with a wide-spread coordination rearrangement caused by H-doping, *c.f.*, Figure 15(a). From the electronic structure calculations we find that the states in the conduction band in  $a\text{-In}_{54}\text{O}_{76}\text{H}_{10}$  have low IPR that reflects their delocalized nature. Comparing to the H-free case, the IPR values near the Fermi level are reduced by more than two times upon H doping, Figure 15(b). Analysis of the medium range structure reveals that H incorporation suppresses clustering of under-coordinated non-shared In-In pairs. The majority of the under-coordinated In atoms have only a single under-coordinated In that it does not share an oxygen with while being at a distance below 4.5 Å. Accordingly, H doping results in an increase of the average In-In distance for the under-coordinated ( $\text{ECN} < 5.2$ ) non-shared In-In pairs from 3.55 Å before H doping to 3.75 Å after H incorporation. The results signify that hydrogen further pro-

notes the tendency for single-atom percolation-like chains of metallic In-In bonding, contributing to a better electron transport. Indeed, the electron velocity calculated along the [111] band-like state at the energy where the band crosses the Fermi level, increases from  $7.6 \times 10^4$  m/s for the H-free configuration to  $9.7 \times 10^4$  m/s after H doping.

We stress here that the formation of a single donor  $\text{OH}^-$  defect in  $\text{a-In}_{54}\text{O}_{76}\text{H}_{10}$  leads to the conductive state with Fermi level located at 0.9 eV above the conduction band bottom and a large concentration of free carriers as signified by the height of the Drude peak in the calculated absorption, Figure 15(c). Indeed, the integrated density of states calculated within  $-0.1$  eV to 0.1 eV energy range that represents free carrier concentration, is  $6.0 \times 10^{20} \text{ cm}^{-3}$  which is larger as compared to H-free  $\text{a-In}_{54}\text{O}_{76}$ ,  $5.6 \times 10^{20} \text{ cm}^{-3}$ , Table IV. Importantly, the results imply that unlike crystalline indium oxide where H serves as a dopant upon O substitution, hydrogen is not a donor in amorphous oxide, instead it affects carrier concentration indirectly, by controlling the degree of electron localization and binding energy of oxygen defects associated with under-coordinated In-In.

Finally, we find that the presence of extended metallic networks in highly-non-stoichiometric indium oxide leads to formation of defect complexes such as In-H-H-In and In-OH-H-In with H-H distances of 2.4 Å and as short as 1.5 Å, respectively. These defects are likely to be less stable than the most common In-H-In and In-OH defects found in this work and reported earlier [79, 83] and may play an important role in H mobility and structural reconfiguration, hence, call for further investigations of the formation of H defect complexes and their stability at elevated temperatures.

## X. CONCLUSIONS

In summary, the structural and electronic properties of amorphous  $\text{In}_2\text{O}_{3-x}$  with  $x=0-0.185$  obtained via *ab-initio* molecular dynamics simulations and accurate hybrid density-functional calculations, are thoroughly investigated to establish the formation and microscopic features of oxygen defects in the disordered metal oxide. The results of this work reveal the key feature that distinguishes the amorphous material's response to oxygen reduction from the behavior observed in crystalline oxides, namely, the tendency of the disordered ionic oxide to lower the coordination of a large fraction of In atoms and, at lower oxygen content, to spread the

individual metallic In-In bonds associated with highly-under-coordinated non-shared pairs or clusters of In atoms throughout the amorphous structure in a percolation-like single-atom chains.

Because of the collective response of the disordered metal oxide to the lack of oxygen, multiple descriptors for the local (nearest-neighbor) In structure (such as the effective In-O coordination, In-O distance or In-O polyhedral distortion) must be considered in combination with next-nearest neighbor(s) distances, coordination and sharing in order to accurately predict the degree of electron localization or the binding energy of the defects. Based on the derived structure-property relationships, we illustrate how the metallic network morphology gradually becomes more complex as the oxygen content decreases and identify the key features that lead to electron localization.

The results of this work provide a microscopic explanation of an increased number of free carriers combined with a good carrier mobility in the disordered indium oxide as compared to its crystalline counterpart. The extended nature of metallic percolation-like networks supports coexistence of shallow and localized defects, whereas annealing in oxygen environment or hydrogen compensation will promote a more uniform coordination morphology with no or deep defects (at 2-3 eV below the Fermi level) that cannot scatter free electrons. Our calculated carrier concentrations, electron velocities, and deep defect densities as a function of oxygen content are in excellent agreement with available experimental observations.

Given the striking differences between the structural and electronic properties of oxygen defects in crystalline and amorphous indium oxide, one should expect significant changes in carrier concentration and mobility during crystallization which occurs in  $\text{In}_2\text{O}_3$  at low temperature [27]. Last but not least, understanding the structural features of metallic formations will help future studies of hydrogen passivation, the formation of H defect complexes, and H mobility throughout the disordered oxide as well as the relaxation dynamics in both H-free and H-doped indium oxide.

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