We present a microscopic interpretation for the appearance and behaviour of subgap states in stoichiometric and oxygen-deficient, amorphous In-Zn-O (a-IZO) and In-Sn-O (a-ITO) derived from a density functional theory analysis using a self-interaction-correction scheme. Our findings concerning the defect structures and the resulting deep levels are qualitatively similar to earlier results on a-IGZO and a-ZTO and in agreement with recent experimental results. Based on our extensive set of DFT results for In-, Sn-, Zn- based oxides we develop a general concept of the subgap states which is applicable to these systems. Electronic defect levels in the lower half of the band gap are created by undercoordinated oxygen atoms while local oxygen deficiencies cause defect levels in the upper part of the band gap.

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I. INTRODUCTION

Amorphous oxide semiconductors (AOS) have become technologically important materials due to their easy and cheap synthesis by thin film deposition methods. Indium based oxides like In-Ga-Zn-O (IGZO), In-Zn-O (IZO) and In-Sn-O (ITO) have shown the best performance so far concerning both electrical conductivity and optical transparency.

The optical and electrical properties of active layers made of AOS strongly depend on and are altered by the presence of subgap states. Such deep levels within the energy band gap of the semiconductor cause a reduction in transparency. They can form flat bands above the valence band maximum (VBM) and thereby reduce the mobility of holes. A theoretical understanding of the origin of these deep levels within the band gap and their relation to structural defects is important in order to find the right means for improving the properties of the material under investigation.

The origin of the subgap states in the prominent a-IGZO and also in related oxides is experimentally not resolved and still an open matter of debate. Previous theoretical investigations by Kamiya et al. based on local-density approximation (LDA) to density functional theory (DFT) hint at oxygen vacancies as possible sources of deep states above the VB. Our previous studies on a-IGZO and a-ZTO suggest a different picture connecting the subgap states above the VB to undercoordinated oxygen atoms. This is in line with recent theoretical studies using LDA+U, GW, or hybrid-functional approaches as well as with a very recent experimental work of Sallis et al.

In this paper we give an answer to the question of the structural origin of these deep lying levels for a-ITO and a-IZO, and from this we derive a general concept applicable to In-, Sn, Zn-based oxides including the results of our previous studies on a-IGZO and a-ZTO. To our knowledge there does not exist any study on deep levels in a-IZO or a-ITO. In that respect our results are a prediction for the level structure which we generalize to a generically valid picture for AOS.

For our study we have used of a self-interaction-corrected LDA (SIC–LDA) approach. This choice is motivated by recent theoretical work which has shown that both common approximations, LDA and the generalized gradient approximation (GGA), have limited predictive power for wide band gap semiconductors resulting from their inherent self-interaction error. SIC–LDA over-
comes this limitation and yields electronic band structures with band gaps that are in good agreement with experiments.\textsuperscript{20,26} The paper is organized as follows. Section II is dedicated to the theoretical framework of the SIC–LDA and the computational generation of amorphous structures. Our results on atomic and electronic structures are presented and discussed in Sec. III. Sec. IV gives a summary and conclusions.

II. THEORETICAL APPROACH

A. SIC-LDA calculations

The total-energy and electronic-structure calculations in this work are performed on the basis of DFT using the computational mixed-basis pseudopotential (MBPP) method\textsuperscript{31–34} with the same calculation setup as in our previous papers.\textsuperscript{18–20,26,27} We have taken the LDA for exchange-correlation as parameterized by Perdew and Zunger.\textsuperscript{35} For the ionic cores of In, Sn, Zn, and O, optically smooth norm–conserving pseudopotentials\textsuperscript{36} were used and for the electronic valence and conduction bands a mixed basis of plane waves and nonoverlapping localized orbitals were employed. Due to the localized orbitals a plane–wave cutoff energy of 20 Ry (1Ry = 13.606 eV) is sufficient to obtain converged results. For the k-point sampling of the Brillouin-zone integrals a Monkhorst-Pack mesh of $3 \times 3 \times 3$ points and a Gaussian broadening of 0.2 eV were used. The electronic DOS of the supercells were evaluated with the same mesh and a Gaussian smearing of 0.1 eV. In order to compare the DOS for different amorphous samples, we aligned the DOS in energy according to low lying bands (Zn 3d, e.g.).

We corrected the self-interaction error of LDA by an incorporation of the SIC into the pseudopotentials. This approach is explained in detail in Refs. [26,37]. The SIC procedure depends on weight factors $w_l$ accounting for the occupation of the individual s, p and d valence orbitals. For a-IZO, correcting only occupied In 4d, Zn 3d, O 2s, and O 2p states, we used $In(0, 0, 1)$, Zn$(0, 0, 1)$, and $O(1, 0.85, 0)$ weightings where the bracket terms denote $(w_s, w_p, w_d)$. For a-ITO, we took the same settings as for a-IZO and used Sn$(0, 0, 1)$, thereby correcting the Sn 4d orbitals like in our recent study on ZTO.\textsuperscript{19,20}

B. Models for amorphous IZO and ITO

For a-IZO we have constructed cubic supercell models consisting of 8 formula units (f.u.) of In$_2$O$_3$ and 16 f.u. of ZnO therefore giving the total composition In$_{16}$Zn$_{16}$O$_{40}$ with 72-atoms. For a-ITO we took 7 f.u. of In$_2$O$_3$ and 14 f.u. SnO$_2$ yielding cubic supercells of total composition In$_{14}$Zn$_{14}$O$_{40}$ with 77 atoms. The amorphization procedure was done by means of classical molecular dynamics (MD) simulations with the GULP code\textsuperscript{38} following methodologically the pioneering work of Nomura et al.\textsuperscript{39} The MD simulations were started at 5000 K and subsequently cooled down in steps of 10 K per ps with time steps of 2 fs at constant temperature and constant volume. The resulting structures were subsequently relaxed with LDA (for further details see Refs. [19,20]).

We have generated a total of 24 stoichiometric amorphous IZO and ITO structures (12 each). In order to study a volume dependence the one half of the sample cells (samples A – F) have a volume increase of 10% relative to the volume estimated from bulk densities ($V_{\text{bulk}}$) and the other half has a volume increase of 30% (samples G – L). This corresponds to mass densities of 5.63 g/cm$^3$ and 4.77 g/cm$^3$ for the IZO samples and 6.27 g/cm$^3$ and 5.30 g/cm$^3$ for ITO.

In order to study oxygen-poor amorphous structures we generated a second set of samples by removing a single O atom from each stoichiometric IZO or ITO supercell before applying the amorphization procedure. The resulting ensemble of 24 samples are marked by an additional $V_{O(\text{anh})}$ namely a-IZO:$V_{O(\text{anh})}$ (samples A – L) and a-ITO:$V_{O(\text{anh})}$ (samples A – L). Like in previous studies, the index (anh) indicates that the introduction of holes is followed by an annihilation step with MD (see e.g. Ref.20).

III. RESULTS AND DISCUSSION

A. Characterization of the atomic structure

Table I contains the averaged coordination numbers of our structurally relaxed stoichiometric a-ITO and a-IZO supercell samples. In crystal structures, In and Sn ions usually occupy six-fold coordinated octahedral positions

<table>
<thead>
<tr>
<th></th>
<th>a-ITO 110% $V_{\text{bulk}}$</th>
<th>130% $V_{\text{bulk}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Sample A-F)</td>
<td>(Sample G-L)</td>
</tr>
<tr>
<td>In–O</td>
<td>5.65</td>
<td>5.02</td>
</tr>
<tr>
<td>Sn–O</td>
<td>5.52</td>
<td>4.84</td>
</tr>
<tr>
<td>O–(In, Sn)</td>
<td>2.13</td>
<td>1.69</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>a-IZO 110% $V_{\text{bulk}}$</th>
<th>130% $V_{\text{bulk}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Sample A-F)</td>
<td>(Sample G-L)</td>
</tr>
<tr>
<td>In–O</td>
<td>5.01</td>
<td>4.36</td>
</tr>
<tr>
<td>Zn–O</td>
<td>4.06</td>
<td>3.71</td>
</tr>
<tr>
<td>O–(In, Zn)</td>
<td>2.52</td>
<td>2.10</td>
</tr>
</tbody>
</table>

TABLE I: Coordination numbers of the LDA-relaxed amorphous ITO and IZO structures. The given values for the amorphous compounds are the averages of each six stoichiometric samples generated. The cut-off value for counting nearest neighbours was 3Å for In–O, Sn–O and Zn–O pairs.
whereas Zn ions take four-fold coordinated tetrahedral sites. This tendency is reflected for the amorphous structures with coordination numbers of about 5 for In and Sn and a coordination number of about 4 for Zn. Oxygen prefers to have tetrahedral coordination with four neighbours in crystalline structures like in c-IGZO or c-ZnO or three neighbours like in c-SnO2.18,20

However, in the amorphous a-IZO and a-ITO samples some oxygen atoms are undercoordinated, meaning that they have only two or three near neighbouring metal atoms while one or two metal atoms are more remote (exceeding distances of 2.2 Å). Representative examples of the generated amorphous structures are shown in Fig. 1 for ITO and in Fig. 2 for IZO. Both structures contain undercoordinated oxygen atoms which are highlighted in yellow.

Another class of local imperfections in the amorphous structures are undercoordinated metal atoms or even small metal clusters. The 1Sn-defect, i.e. an isolated undercoordinated Sn atom surrounded by less than six O atoms, is illustrated in Fig. 1 for the case of a-ITO. Defect complexes of two metal atoms which we denote by M-M (with M=Sn, Zn, or In) consist of two metal atoms lying next to each other, without any bridging O atom in-between. An example of a Zn-Zn defect is marked in yellow in Fig. 1.

In our previous study on a-IGZO we have even encountered a 3In defect complex which consists of three clustered In atoms.18 In real amorphous samples even bigger metal clusters of all kinds can be imagined.

Before turning to the subgap states we shortly comment on the characteristic band tails attributed to the general disorder which are found for all stoichiometric and oxygen poor amorphous samples. This reduction of the band gap, relative to crystalline counterparts, is mainly caused at the VB tail whereas disorder-induced effects at the CB tail are negligible. This can be explained by the general reasoning that the directional dependence of the orbitals forming the respective bands is quite different.1,41 The spherical 4s or 5s orbitals of the metal atoms which mainly form the CB are rather insensitive to structural disorder and thus only small CB tails are encountered. In contrast, the upper part of the VB is mainly formed by direction-dependent O 2p orbitals which are more strongly influenced by disorder so that significantly bigger band tails result. The same behaviour has also been reported for a-IGZO and a-ZTO.11,18,20,23–25 Hereby, Noh et al.23 have explicitly connected the mechanism of the VB broadening with the mutual orientation of oxygen p-orbitals.

Superimposed on top of the band tails several localized deep levels can be identified which are spread over the whole band gap. For our sets of a-ITO and a-IZO we observe an increasing probability for finding such deep levels when going to larger cell volumes, i.e. lower densities. But the deep levels remain close to the band edges. The samples A-F show fewer subgap levels than the respective samples G-L. However, this trend is weak and the number of test samples is still too small for reliable statistics.

1. Undercoordinated O atoms

A defect complex which is frequently encountered in our amorphous samples is the undercoordinated O atom. Two representative cases are sample A of a-ITO and sample K of a-IZO which contain three undercoordinated oxygen atoms each. The corresponding DOS, shown in Figs. 3 and 4, have two peaks superimposed on the VB tail.42 By analyzing the local DOS of all the individual atoms the origin of the subgap state can be directly linked to specific undercoordinated O atoms. The undercoordinated atom that causes the deepest levels at 0.5 eV shown in Fig 3 has only two bonds with metal atoms. It is marked in yellow in Fig. 1.

In contrast, Kamiya et al.15,16 attributed the deep and fully occupied localized states above the VB to oxygen vacancies. We believe that the weak point in their study of a-IGZO is their use of the LDA approximation. LDA is known to be not reliable for electronic states in these oxide systems18–20,26–29 since already the band gap is severely underestimated. Taking into account the SIC leads presumably to a more accurate and reliable picture. Summing up all our results on a-ZTO19,20, a-IGZO18, a-ITO and a-IZO we can consistently assign all the deep
levels in the lower half of the band gap to undercoordinated oxygen atoms. This picture is in line with another study on IGZO by Noh et al.\textsuperscript{21}

In our study of polycrystalline ZnO we showed that such defects can also appear at grain boundaries.\textsuperscript{30} For all grain boundaries that have undercoordinated oxygen atoms at the boundary plane we found occupied deep levels in the lower half of the band gap.

Note that the miscoordination of oxygen atoms leads to both the VB tail states and the deep levels discussed in this section. The degree of undercoordination is a continuous function and depends on the local atomic arrangement. However, the pronounced peaks in the DOS of figure 3 and 4 can be related to individual undercoordinated oxygen atoms since a projection of the total DOS on local orbitals assign up to 70\% of the peak area to one specific oxygen atom. On the other hand, the DOS of an average miscoordinated oxygen atom does not show a peak structure but a DOS spread over a wide range of the VB.

Furthermore, for a-IGZO higher-energy configurations of pairs of neighboring miscoordinated oxygen atoms have been considered which also give rise to localized deep levels above the VB edge.\textsuperscript{11,22,23,25}

2. Undercoordinated metal atoms - local oxygen deficiencies

Another class of defect states is related to local oxygen deficiencies situated nearby one, two or more metal atoms. These defects can also be described as tiny metal clusters. Sketches of generic defects of one or two metal atoms are given in Fig. 4 of Ref. [18]. According to our SIC analysis, the corresponding deep levels always lie in the upper half of the band gap. The DOS of the a-ITO sample A in Fig. 3 contains defect levels due to a 1Sn defect. As a further example in Fig. 4, the defect levels in the DOS of the a-IZO sample K originate from a Zn-Zn defect.

In the a-IZO and a-ITO samples we observe a slight increase in the number of deep defect levels in the upper half of the band gap when going from stoichiometric to oxygen-poor samples leading to a higher probability for the formation of the metal related defects described above. This effect is stronger in a-IGZO\textsuperscript{18} and most pronounced in a-ZTO.\textsuperscript{20}

In a-ITO the 1Sn-defect appeared several times but no larger metal clusters were found. In a-IZO we encountered most frequently defects of two metal atoms (mainly of In-Zn type). Between these metal atoms of interest there is no separating O atom and their distances are about 2.5–3.5 Å. Sample D of a-IZO:V\textsubscript{O(anh)} contained an In-2Zn defect, i.e. consisting of a small cluster of one In and two Zn atoms.

The energy positions of all these defects are not unique. It is clear that the energy position of a defect level is not only determined by species and number of metal atoms directly involved but also by the local atom arrangement.

In a recent experimental study on a-IGZO, Sallis et al.\textsuperscript{9} connect the deep levels below the CB to nanocrystalline indium. This interpretation fits well to our SIC results for defect levels and is further supported by theoretical results by Kang et al.\textsuperscript{24} However, according to our findings a-IGZO, a-ZTO, a-ITO and a-ITO not only In clusters produce high lying defect levels but various kinds of metal atom aggregations. Hopefully this can be clarified by future experiments.
3. Treatment of defects: annealing in an oxygen-rich atmosphere and hydrogen doping

As mentioned before, there is a slight increase in the number of deep defect levels caused by more metal related defects when going from stoichiometric to oxygen-poor samples. Since the presence of deep levels inside the band gap in general decreases the transparency of the material\textsuperscript{8,10} it is desirable to reduce their number by additional treatment. One possibility is annealing in oxygen-rich atmosphere which was indeed confirmed to have a positive effect, see e.g. Ref.\textsuperscript{[10]}. The addition of oxygen reduces the number of miscoordinated metal atoms or metal clusters and hence reduces the number of deep levels in the upper half of the band gap.

However, increasing the oxygen content favors the formation of undercoordinated oxygen atoms in the amorphous structures which again leads to subgap states close to the VB edge. For those defects we propose the treatment with hydrogen which can be realized experimentally by wet annealing\textsuperscript{16}. In order to simulate this procedure we added H atoms near undercoordinated O atoms and subsequently relaxed the supercells structures. This results in the disappearance of the respective localized deep levels which are shifted into the VB (see Fig. 3). It is achieved by saturating the oxygen through the creation of an O-H bond with a relaxed length of about 1.0 Å. Clearly, this procedure is not restricted to a-IZO or a-ITO. For a-IGZO\textsuperscript{18} and a-ZTO\textsuperscript{19,20} we indeed reported the same effects. Such a disappearance of deep levels above the VB has been observed in experiments (see Fig. 3b of Ref. [10]). This corroborates our hypothesis of undercoordinated oxygen atoms being the origin of the deep levels in the lower half of the band gap.

Note that for a-IGZO we have shown that hydrogen doping is not efficient for the defects related to local oxygen deficiencies.\textsuperscript{18} The deep levels due to the In-Zn defect in a-IGZO move down in energy but remain deep and well visible above the VB tail.

A further, general effect of H doping is the upshift of the Fermi level (see small arrows in Fig. 3 indicating the occupation). The supply of extra charge carriers and a Fermi level in the conduction band increases the electrical conductivity. This has been observed experimentally as well.\textsuperscript{43,44}

IV. SUMMARY AND CONCLUSIONS

We have studied the subgap levels of stoichiometric and nonstoichiometric amorphous model-structures of ITO and IZO using a SIC-LDA approach to DFT. The results are in line with those of previous studies of a-ZTO\textsuperscript{18,19} and a-IGZO.\textsuperscript{11,20,21,23–25} The general concept that arises for the electronic structure around the band gap of transparent AOS is schematically drawn in Fig. 5. All analyzed In-, Sn-, and Zn-based amorphous oxides show broad VB tails which spread up to about 1 eV relative to the VB edges of their crystalline counterparts. The CB tails, on the other hand, are negligible. Our SIC results confirm quantitatively the general qualitative reasoning that this different behaviour has its origin in the direction dependence of the orbitals underlying the bands.\textsuperscript{1,41}

According to our calculations the subgap states which can appear in addition to the band tails can be divided into two main types. In the lower half of the band gap the deep localized defect levels are related to undercoordinated O atoms. Experimental support of this reasoning was recently provided by Sallis et al.\textsuperscript{8} who have found a positive correlation between the oxygen composition and the subgap intensity.

Subgap states in the upper part of the band gap are caused by defects related to local oxygen deficiencies (D\textsubscript{O}). These defect levels originate from clustering of metal atoms which come close without a separating oxygen atom in between. This picture is in line with recent results of Sallis et al.\textsuperscript{8} in which the origin of the subgap states is further resolved and the subgap density below the CB edge is linked to nanocrystalline indium. Their interpretation agrees with the levels we have found for the 3In defect and similar local metal-metal-clustering.

According to this general concept we interpret the experimentally reported subgap DOS of Hsieh et al.\textsuperscript{13} which continuously extends from the VB to about 1.5 eV as connected to undercoordinated O atoms while the extra subgap DOS at 0.1-0.3 eV below the CB minimum observed in Ref. [14] corresponds well to the metal cluster defects.

Finally, we have shown that the addition of hydrogen reduces deep defect levels due to undercoordinated O atoms which is in accordance with experiments.\textsuperscript{10} Hydrogen atoms preferably bind to the undercoordinated O atoms and compensate their electron deficit.

Not included so far in our calculation is another de-
fect model named weakly-bonded oxygen which has been reported experimentally by Ide et al., and includes a negatively charged defect state. This defect is different from the defects in our amorphous model systems since they are all charge neutral. So there is potential for future extensions to amorphous model systems including charged defects and subsequent relaxations.

Acknowledgments

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