Density-functional theory study of stability and subgap states of crystalline and amorphous Zn–Sn–O

Wolfgang Körner [a,*], Christian Elsässer [a,b]

[a] Fraunhofer Institute for Mechanics of Materials IWM, Wöhlerstr. 11, 79108 Freiburg, Germany
[b] Institute for Applied Materials, Karlsruhe Institute of Technology, Kaiserstr. 12, 76131 Karlsruhe, Germany

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ABSTRACT

We present a density-functional theory analysis of stoichiometric and nonstoichiometric crystalline and amorphous Zn–Sn–O systems (c-ZTO, a-ZTO) which connects structural features with electronic properties in order to contribute to the understanding of the recently discovered subgap states in a-ZTO and other amorphous oxide films. In particular we show that defect levels originating from oxygen vacancies are too high in energy to be responsible for levels above the valence band edge. We offer an explanation for the experimentally seen decrease of subgap states with increasing oxygen content. From our analysis of the energetic stability of c- and a-ZTO compounds with different Zn/Sn ratios the decomposition of $ZnSnO_3$ into Zn_2SnO_4 and SnO_2 at sufficiently high temperatures is conceivable. Moreover, our results indicate that a lowering of the mass density of an a-ZTO sample leads to a rising of the conduction band edge.

1. Introduction

Amorphous oxide semiconductors begin to replace classical (poly-)crystalline transparent conducting oxides because they are easy and cheap to fabricate. Moreover they fulfill additional requirements for products such as organic light emitting diodes or rollable thin-film-transistor liquid-crystal displays on flexible substrates, namely uniform morphology and low deposition temperature (below 200 °C). The multi-component amorphous oxide semiconductors In–Zn–O and In–Ga–Zn–O (IGZO) have attracted much attention since they show so far the best performances [1,2] concerning electrical conductivity and optical transparency. However, the Zn–Sn–O (ZTO) system is an attractive, cheap alternative since it is indium free and additionally provides good thermal stability, mechanical strength and good chemical stability under reducing atmosphere [3–6].

In spite of the promising ZTO examples mentioned above various open questions remain. For instance: How is the band gap changing with the density or porosity of the amorphous structure? Several experimental groups have found that amorphous systems show similar or even bigger band gaps than their crystalline counterparts which contradicts the common notion that disorder should reduce the band gap [7–9].

What is the origin of the subgap states which for example play a role in thin film transistors [10]? According to Refs. [1 and 11] the impact of disorder in amorphous oxide semiconductors on the conduction band (CB) edge is small since it mainly consists of metal s-states, whereas the valence band (VB) edge mainly consisting of direction dependent oxygen 2p states is strongly affected by structural disorder. They conclude that for amorphous oxide semiconductors the disorder leads to sharp CB tails whereas the VB tails are broad which apparently agrees with experimental findings (see e.g. the results of Erslev et al. [12] for a-SnZnO$_x$). However, the subgap states found in ZTO [12,13] and IGZO [10,14,15] are not covered by those general considerations on disorder. Theoretical investigations hint at localized defects, namely oxygen vacancies [16,17] and under-coordinated oxygen atoms [19], as possible sources of deep states above the VB.

In this paper we extend our analysis [19] of the origin of the subgap states for oxygen rich and oxygen poor amorphous Zn–Sn–O (a-ZTO) models. By clarifying the origin of the subgap states we can explain the experimentally seen decrease of subgap states by going to oxygen-rich conditions [13].

A commonly done approach to answer questions like those posed above is the calculation of the density of states (DOS) of the c- and a-ZTO model systems with the local-density approximation (LDA) of the density functional theory (DFT) [17,18]. In our work, going beyond this, we use a self-interaction correction (SIC) scheme for LDA since recent theoretical work [20–23] has shown that LDA has limited predictive power for wide band gap semiconductors due to its inherent artificial self-interaction. In addition to the DOS, we analyze the total energies of the c- and a-ZTO model systems to give answers to stability questions.

* Corresponding author.
E-mail address: wolfgang.koerner@iwm.fraunhofer.de (W. Körner).

2. Theoretical approach

2.1. 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 method [25–28] with the same calculation setup as in our previous papers [19–21]. We have taken the LDA for exchange-correlation as parameterized by Perdew and Zunger [29]. For Zn, Sn and O optimally smooth norm-conserving pseudopotentials [31] are constructed, and a mixed-basis of plane waves and nonoverlapping localized orbitals are used. Due to the localized orbitals a plane-wave cutoff energy of 20 Ry (1 Ry = 13.606 eV) is sufficient to obtain well converged results. For the k-point sampling of the Brillouin-zone integrals Monkhorst–Pack meshes of $3 \times 3 \times 3$ and a Gaussian broadening of 0.2 eV are used. The DOSs of the supercells were evaluated with the same mesh and a Gaussian smearing of 0.1 eV.

We solve the self-interaction problem of LDA (or generalized gradient approximation) by an implementation of the SIC in the pseudopotentials [20,30]. This does not increase the computational effort and thus is applicable to 100-atom supercells. Our implementation uses a factor α measuring the deviation from the atomic SIC and weight factors w_is accounting for occupation of the individual valence orbitals. All this is explained in detail in Ref. [20]. For all oxides in this paper we used $\alpha = 0.8$. For c-ZnO and a-ZnO, correcting Zn 3d, O 2s and 2p, we used Zn(0, 0, 1) and O(1, 0.8, 0) where the bracket terms denote (w_0, w_1, w_2). Correspondingly, for SnO$_2$ in the rutile structure and a-SnO$_2$ we used Sn(0, 0, 1) and O(1, 0.93, 0). We had to modify the w_1 of oxygen accounting for the SIC of the 2p orbitals with respect to the O potential of ZnO in order to reproduce the band gap for crystalline SnO$_2$. The main reason for the necessary adjustment is probably the change from fourfold tetrahedral coordination in the wurtzite structure of ZnO to sixfold octahedral coordination in the rutile structure of SnO$_2$. For all ternary Zn–Sn–O compounds we have chosen Zn(0, 0, 1), Sn(0, 0, 1) and O(1, 0.9, 0) which lead to an electronic band gap of 3.8 eV [19] for ZnSnO$_3$ which is well in the middle of the experimentally found 3.7 eV [32] and 3.9 eV [33]. In order to identify the energetic position of the various deep levels that appear in the DOS of a-ZTO samples we aligned the deep lying and well localized Zn 3d or Sn 4d bands with the bands of the corresponding c-ZTO.

2.2. Crystalline and amorphous Zn–Sn–O models

As reference and starting point for the generation of the amorphous model systems we constructed the following crystalline supercells: ZnO (wurtzite-type (P6$_3$mc), 72 atoms), c-Zn$_2$SnO$_4$ (inverse-spinel-type [34] (P4$_1$22), and normal-spinel-type (Fd3m), 56 atoms), c-ZnSnO$_3$ (lithium-niobate-type [35] (R3c), and ilmenite-type (R-3), 60 atoms) and hypothetical c-ZnSn$_2$O$_5$ (pseudobrookite-type [37] (Cmcm), 64 atoms) and SnO$_2$ (rutile-type (P4$_2$mnm) and α-quartz-type (P3$_2$21), 72 atoms). In the hypothetical α-quartz structure the Sn atoms are in tetrahedral position in contrast to the octahedral position in the real rutile structure which makes it a useful additional reference for low density a-SnO$_2$ in which the tetrahedral coordination dominates.

Following methodologically the pioneering work of Nomura et al. [36], we generated a-ZnO, a-Zn$_2$SnO$_4$, a-ZnSnO$_3$, a-ZnSn$_2$O$_5$ and a-SnO$_2$ structures by performing classical molecular dynamics (MD) with the GULP code [39]. Empirical interionic Buckingham potentials were employed whose rigid ion potential parameters are given in Table 1. The MD started at 5000 K and was subsequently cooled down in steps of 10 K per ps with time steps of 2 fs at constant temperature and constant pressure.

For each Zn–Sn–O composition we generated a set of 5 small cells (denoted samples A–E) with the atom numbers of the above listed crystalline counterparts and a set of 3 big cells (448, 480 or 512

atoms). For each set we determined the radial distribution functions (RDFs) for all atom species and verified that the average RDFs of the small cells coincide well with the average RDFs of the big cells in order to exclude the idea that the amorphous structures depend on the supercell sizes. Since for all compositions the RDFs of small and big supercells agreed (see e.g. Ref. [19] for a-ZnSnO$_3$) we continued our analysis with the small cells which are tractable with DFT with reasonable computational effort. The small amorphous supercell models were then structurally relaxed using LDA by shifting the atoms according to the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm [38] until the residual forces on all atoms were less than 0.005 Ry/B$_0$ (B$_0$ = 0.529 Å).

For ZnO and SnO$_2$ we generated two further sets of 5 amorphous structures by MD simulations with the initial temperature of 5000 K but with the constraint of constant volume (instead of constant pressure) in order to study the electronic structure of amorphous sets of different mass densities. We distinguish the sets of a-ZnO and a-SnO$_2$ by their average volume increase with respect to the single crystal written in brackets. We denote them by a-ZnO (8%) (constant pressure), a-ZnO (31%) (constant volume), a-SnO$_2$ (16%) (constant volume) and a-SnO$_2$ (41%) (constant pressure).

In order to study oxygen-poor and oxygen-rich amorphous structures we introduced O, Zn or Sn vacancies. We generated 5 oxygen deficient, 5 zinc deficient and 5 tin deficient a-ZTO supercells by removing either an O, a Zn or a Sn atom from stoichiometric a-ZnSnO$_3$ supercells which we denote by a-ZnSnO$_3$:V$_O$, a-ZnSnO$_3$:V$_{Zn}$ and a-ZnSnO$_3$:V$_{Sn}$ (samples A–E). Following the example of Kamiya et al. [16] additional sets of 5 samples were created by melting the nonstoichiometric structures at 5000 K and cooling them in steps of 10 K per ps with time steps of 2 fs at constant temperature and constant pressure. These samples in which the O, Zn and Sn holes are annihilated are denoted by a-ZnSnO$_3$:V$_{O(anh)}$, a-ZnSnO$_3$:V$_{Zn(anh)}$ and a-ZnSnO$_3$:V$_{Sn(anh)}$ (samples A–E).

3. Results and discussion

3.1. Atomic structures

The calculated structural parameters of the single crystals given in Table 2 deviate by less than 2% from experimental values. There exists no crystalline structure for ZnSn$_2$O$_5$. We have built ZnSn$_2$O$_5$ in the hypothetical pseudobrookite (Cmcm) structure and checked its energetic instability. Our optimized lattice parameters are a = 3.92 Å,

Table 1
Buckingham potential parameters used for the molecular dynamics simulations taken from Ref. [24]. Potential form: $V_{ij} = A_{ij} \cdot \exp(-r_{ij}/\rho_{ij}) - C_{ij}r_{ij}^{-6}$.

Ion pair	A_{ij} (eV)	ρ_{ij} (Å)	C_{ij} (eV·Å^6)
Zn^{+2}–O^{-2}	499.3	0.3595	0.0
Sn^{+4}–O^{-2}	938.7	0.3813	0.0
O^{-2}–O^{-2}	22,764.3	0.149	43.0

Table 2
Structure parameters calculated with LDA. The lattice parameters a and c are given in Å and the internal parameters u are dimensionless. Experimental values are given in brackets.

	ZnO wurtzite	Zn$_2$SnO$_4$ inverse spinel	ZnSnO$_3$ lithium niobate	SnO$_2$ rutile
a	3.23 (3.258)[a]	8.62 (8.648)[b]	5.29 (5.262)[c]	4.81 (4.737)[d]
c	5.16 (5.22)[a]		14.11 (14.003)[c]	3.21 (3.19)[d]
u	0.38 (0.382)[a]		0.286 (0.2859)[c]	0.307 (0.307)[d]

[a] Ref. [45].
[b] Ref. [34].
[c] Ref. [35].
[d] Ref. [46].