Dopant chemical potential modulation on oxygen vacancies formation in In_2O_3 : A comparative density functional study

Zhi Gen Yu^{a,*}, Jian Sun^b, Michael B. Sullivan^a, Yong-Wei Zhang^a, Hao Gong^c, David J. Singh^d

^a*Institute of High Performance Computing, Singapore 138632*

^b*Faculty of Material Science and Chemistry, China University of Geosciences, Wuhan 430074, P. R. China*

^c*Department of Materials Science and Engineering, National University of Singapore, 21 Lower Kent Ridge Road, Singapore 117543*

^d*Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6056, USA*

Abstract

We report first principles calculations aimed at understanding the dopant chemical potential modulation on the oxygen vacancy formation in In_2O_3 . Relaying on our results, it implies that oxygen vacancies are deep donors in undoped In_2O_3 and change to shallow donors with embedded Zn and Al in contrast to previous expectations of native carrier from oxygen vacancy. Our results well explain the anomalous carrier concentration increase in Zn and Al codoped In_2O_3 . Our proposed models reveal the chemical potential modulation on oxygen vacancy formation and lead to a natural oxygen vacancy formation mechanism in the presence of metallic dopants in In_2O_3 .

Keywords: Dopant, Oxygen vacancy, In_2O_3

PACS: 61.72.Bb, 61.72.jd, 71.15.Nc, 73.61.Le

1. Introduction

In_2O_3 is one of the archetypal transparent conducting oxide (TCO) materials, and indium tin oxide (ITO) has been widely used in electronics including liquid crystal displays, photovoltaic devices, and light emitting diodes [1–4]. Recently, it has attracted more attention to develop substitute materials to ITO containing reduced amount or indium-free TCOs. $\text{ZnO-In}_2\text{O}_3$ (IZO) and $\text{ZnO-Al}_2\text{O}_3\text{-In}_2\text{O}_3$ (AIZO) are potential substitute materials to ITO. Compared with ITO, IZO/AIZO attracts more attention due to its unique advantages of larger work function, wider wavelength window of higher optical transmittance, less indium content, and especially favorable for flexible electronics [5–7]. However, even fundamental material properties such as band gap and native *n*-type conductivity sources are controversial and uncertain, e.g. defect models for the oxygen vacancy in In_2O_3 are inconclusive [8, 9]. Early theoretical models had systematic errors on the formation energy of defects and the band gap using standard *ab initio* methods, and hence it is unworkable to predict accurate ionization energies of defects. Although several advanced methods and scientific corrections were employed in defect formation calculations, the results and final conclusions were inconclusive.

*Corresponding author at: Institute of High Performance Computing, Singapore 138632

Email address: yuzg@ihpc.a-star.edu.sg (Zhi Gen Yu)

For example, reported formation energies ΔH of the neutral oxygen vacancy V_O^0 under oxygen poor conditions were 0.69, 1.0 and 1.23 eV using different approximations [9]. While ΔH of V_O^0 under oxygen rich conditions were 4.17 and 5.67 eV [8, 10].

Even though there were numerous experimental reports on IZO and AIZO [7, 11–16], no reliable defect model exists that would account for anomalously increased carrier concentration in IZO and AIZO since divalent Zn substituting In possibly acts as “electron killer” [12]. Owing to dopings are associated with many properties of host materials, the chemical modulation on oxygen vacancies formation is very important, which may govern electric properties of In_2O_3 based TCOs. The chemical modulation on native defects in colloidal lanthanide-doped Ga_2O_3 and zinc-blende CdS photocatalysts have been reported [17, 18]. Doped ions are extrinsic point defects in metals embedded In_2O_3 , and thus dopants would exert an influence on oxygen vacancy formation. With these results in mind, we undertake a comprehensive study on oxygen vacancy formation in indium based TCOs aims for understanding of chemical modulation and conductivity physics underlying to the experimental observations. We develop predictive oxygen vacancy formation models for undoped In_2O_3 , $\text{Zn}_1\text{In}_{31}\text{O}_{48}$ (Zn doped In_2O_3), and $\text{Al}_1\text{Zn}_1\text{In}_{30}\text{O}_{48}$ (Zn and Al codoped In_2O_3) by using well-converged, state-of-the-art density functional calculations.

2. Computational Methods

It is well-known that underestimated band gap in semiconductors or insulators obtained from plain DFT yields systematic errors on defect ionization energies and formation energies. Especially for In_2O_3 , the binding energies of the bands related to the semicore In- d orbital are underestimated by plain DFT and result an underestimated band gap in In_2O_3 : The calculated band gap of In_2O_3 is only ~ 1.2 eV using plain DFT, which is much less than the experimental value of 2.6–2.9 eV. In order to investigate the effect of underestimated band gap on the defect formation, the HSE06 functional [19], a robust method was developed through admixing 25% of exact nonlocal Hartree-Fock exchange to the generalized Perdew-Burke-Ernzerhof [20] functional as implemented in the plane-wave code VASP [21]. For comparison, we performed oxygen vacancy defect calculations based on both PBE and HSE06 functionals to investigate the dopant chemical potential modulation on oxygen vacancy formation as well as ionization energy. The valence electrons were described in terms of *Kohn-Sham* single-electron orbitals and were expanded in plane-wave basis with a cutoff energy of 500 eV, and a $2 \times 2 \times 2$ k -point mesh was found to achieve the sufficient convergence. Core electrons were defined within the projector-augmented-wave (PAW) methodology [22, 23].

Bixbyite In_2O_3 supercells with 32 In atoms and 48 O atoms as shown in Figure 1 were used to calculate defect formation energies, the optimized lattice constants are 10.27 Å from PBE functionals and 10.24 Å from HSE06 functionals both are close to the experimental value of 10.12 Å. The sufficient supercell size would suppress defect-defect interactions in supercell with three dimensional periodic boundary conditions (PBC). Charged defects calculations were considered by optimizing defects contained supercells constraining lattice parameters with different numbers of electrons exchanged between Bloch states and a homogeneous jellium background, ensuring that the charge neutrality of the supercells in conserved. Nonetheless we included finite-size corrections for charged defect interactions [24]. Furthermore, it was reported that the qualitative results do not change by finite-cell-size corrections [9]. Here, we consider that 80-atom supercell size is sufficient for HSE calculations, and it was adopted widely for In_2O_3 defect calculations in the DFT community [8–10, 25].

3. Results and discussion

The defect formation energy E_f in a bulk system is defined as a function of the Fermi level E_e and the charged state q ,

$$E_f = E^{\text{def}} - \sum H_i \mu_i - \sum D_i \mu_i + q(E_V + E_e), \quad (1)$$

where E^{def} is the total energy of defect system, $\sum H_i \mu_i$ and $\sum D_i \mu_i$ are the sum of the number host atoms H_i and defect atoms D_i multiply their individual chemical potential μ_i , respectively. E_V is the eigenvalue of the

Table 1. Comparisons of calculated bulk unit cell parameters and formation energy of bixbyite In_2O_3 ($\Delta H_f^{\text{In}_2\text{O}_3}$), wurtzite ZnO (ΔH_f^{ZnO}) and corundum Al_2O_3 ($\Delta H_f^{\text{Al}_2\text{O}_3}$) with experiments.

		PBE	HSE06	Experimental
In_2O_3	a (Å)	10.27	10.24	10.12
	$\Delta H_f^{\text{In}_2\text{O}_3}$ (eV)	-9.75	-8.28	-9.76
ZnO	a (Å)	3.25	3.27	3.25
	c (Å)	5.24	5.23	5.20
	ΔH_f^{ZnO} (eV)	-3.63	-3.32	-3.68
Al_2O_3	a (Å)	4.71	4.55	4.76
	c (Å)	12.80	12.78	12.91
	$\Delta H_f^{\text{Al}_2\text{O}_3}$ (eV)	-16.80	-16.21	-16.39

Figure 1. Conventional cell of In_2O_3 bixbyite structure and local lattice structure of (a) pristine In_2O_3 , (b) V_O in undoped In_2O_3 , (c) V_O in $\text{Zn}_1\text{In}_{31}\text{O}_{48}$, and (d) V_O in $\text{Al}_1\text{Zn}_1\text{In}_{30}\text{O}_{48}$, respectively. In atoms locate at $8b$ sites labeled by In_1 and at $24b$ sites labeled by In_2 .

valence band maximum of bulk In_2O_3 . The calculated DFT band gap is 1.17 eV from PBE functionals and 2.51 eV from HSE06 functionals. The latter has good agreement with the experimental value of 2.60–2.9 eV [26, 27]. Hence, considering the accurate band gap obtained by using HSE06 functionals in this study, we expect our conclusions on the defect transition energy based on HSE06 functional calculations to be robust.

The limited chemical potential ranges of Equation (1) are decided by the thermodynamic condition. For In_2O_3 , at equilibrium, we have $2\mu_{\text{In}} + 3\mu_{\text{O}} = \Delta H_f^{\text{In}_2\text{O}_3}$, where $\Delta H_f^{\text{In}_2\text{O}_3}$ is the compound formation energy relative to O_2 and solid metallic In as shown in Table 1. In In_2O_3 , in order to suppress the host elements phases such as oxygen gas and metallic indium formation, the chemical potential of In (O) would be in the range of $\frac{1}{2}\Delta H_f^{\text{In}_2\text{O}_3} \leq \mu_{\text{In}} \leq 0$ ($\frac{1}{3}\Delta H_f^{\text{In}_2\text{O}_3} \leq \mu_{\text{O}} \leq 0$), corresponding to the In(O)–poor and –rich growth condition, respectively. For the $\text{Zn}_1\text{In}_{31}\text{O}_{48}$ and $\text{Al}_1\text{Zn}_1\text{In}_{30}\text{O}_{48}$ systems, the chemical potentials of Zn and Al are governed by O in order to resist its corresponding oxides formation in the host, the bounds imposed by formation of ZnO and Al_2O_3 should be: $\mu_i \leq 0$ ($i = \text{Zn}, \text{Al}$), $\mu_{\text{Zn}} + \mu_{\text{O}} \leq \Delta H_f^{\text{ZnO}}$ and $2\mu_{\text{Al}} + 3\mu_{\text{O}} \leq \Delta H_f^{\text{Al}_2\text{O}_3}$. It is worth noting that the chemical potentials of Zn and Al in $\text{Zn}_1\text{In}_{31}\text{O}_{48}$ and $\text{Al}_1\text{Zn}_1\text{In}_{30}\text{O}_{48}$ systems are lower than those in their respective oxide compounds, ZnO and Al_2O_3 , under the oxygen poor condition. Which is caused by different formation energies of three compounds, $\frac{1}{3}\Delta H_f^{\text{In}_2\text{O}_3} > \Delta H_f^{\text{ZnO}} > \frac{1}{3}\Delta H_f^{\text{Al}_2\text{O}_3}$, and the chemical potential of oxygen in In_2O_3 is slightly higher than that in ZnO and Al_2O_3 under oxygen poor growth condition and which leads to the chemical potentials of Zn and Al are less than these in metallic Zn and Al, respectively. Such as, under oxygen poor growth condition, the chemical potential of Zn and Al should be equal to $(\frac{1}{2}\mu_{\text{ZnO}} - \mu_{\text{O}}^{\text{In}_2\text{O}_3})$ and $(\frac{1}{4}\mu_{\text{Al}_2\text{O}_3} - \frac{3}{2}\mu_{\text{O}}^{\text{In}_2\text{O}_3})$, respectively. Here $\mu_{\text{O}}^{\text{In}_2\text{O}_3}$ notes the oxygen

Figure 2. The formation energies of V_O as a function of the Fermi level in In_2O_3 under the oxygen rich condition ($\mu_O = 0$ eV) and the oxygen poor condition ($\mu_O = \frac{1}{3}\Delta H_f^{In_2O_3}$) by using PBE (top) and HSE06 functional calculations (bottom). The lines with positive and zero slopes refer to V_O^{2+} and V_O^0 , respectively. The valence band maximum (VBM) is set to zero. Vertical sparse pattern is denoted the bottom of the conduction band (the experimental band gap of 2.6 eV was used for discussion).

chemical potential in In_2O_3 . All values are adopted to calculate oxygen vacancy formation energy in three considered systems. The calculated lattice constants and formation energies of ZnO and Al_2O_3 are shown in Table 1. Comparing between the theoretical and the experimental values, we consider the basic settings are correct and our results would be reliable.

In this study, we mainly focus on oxygen vacancy formation modulated by locally chemical environment and only oxygen formation energy is explicitly discussed. In the bixbyite structure In_2O_3 , all O atoms are four-fold coordinated and surrounded by three In atoms as shown in Figure 1. In order to explore scientific mechanisms on anomalously increased carrier concentration in Zn and Al codoped In_2O_3 , we mainly study three types of oxygen vacancy formation: Type I: V_O in undoped In_2O_3 as shown in Figure 1(b); Type II: $V_O + Zn_{In}$, V_O in $Zn_{10}In_{31}O_{48}$: Zn substitutional In combining with one V_O in In_2O_3 as shown in Figure 1(c); Type III: $V_O + Zn_{In} + Al_{In}$, V_O in $Al_1Zn_{10}In_{30}O_{48}$: Al substitutional In combining with type II defect as shown in Figure 1(d). We calculate the defect binding energies of type II and type III, and the results are -1.09 eV and -1.45 eV, respectively. The negative binding energy show that V_O is energetically binding with Zn_{In} and Al_{In} . The formation energy of V_O as a function of the Fermi energy obtained from plain DFT (PBE)

and HSE06 functional calculations are shown in Figure 2. In which, we choose the variable of the Fermi energy with the range of the forbidden gap of 3.6 eV which was considered an optical band gap [26]. The results shown in Figure 2 reveal the existence of doubly positive V_O^{2+} and neutral V_O^0 defects. Comparing the results as shown in Figure 2, we find that the HSE06 and PBE functionals provide different descriptions on the oxygen vacancy formation in pristine and Zn or/and Al embedded In_2O_3 .

Under the oxygen rich growth condition, the formation energy of V_O^{2+} in In_2O_3 is 1.78 eV when the Fermi energy is zero using PBE functionals as shown in Figure 2(a), and -1.38 eV using HSE06 functional calculations as shown in Figure 2(c); which causes a big different ionization energy of oxygen vacancy, 1.16 eV using PBE vs. 2.39 eV using HSE06 above the top of the valence band. Consequently, we predict V_O transition energy in undoped In_2O_3 is 1.44 eV from PBE and 0.21 eV from HSE06 functionals below the bottom of the conduction band (with respect to the experimental band gap of 2.60 eV). No matter what functional is used, the calculated ionization energy of oxygen vacancy in undoped In_2O_3 is much higher than the active energy at 300 K (~ 0.26 meV). Hence, we suggest that oxygen vacancies are deep donors and may not contribute to the native *n*-type conduction in undoped In_2O_3 . Our theoretical results are consistent with the results reported by Lany and Zunger [8]. However, our results are inconsistent with the results reported by Ágoston and co-authors [9], in which, they reported oxygen vacancies were deep donors. The possible reasons leading to the inconsistent conclusions on the oxygen vacancy are using different band gap correction schemes and valence electrons configurations. It was seen that the band gaps were varied by using different approximations, such as LDA, GGA, and HSE, including or excluding *In-d* valence electrons also produces the different band gaps even using the same approximation, and the oxygen vacancy was consider a shallow donor based on the calculation results using HSE03 functional without considering *In-d* electrons [9]. In our study, we use HSE06 functional and consider *In-d* electrons and our calculated ionization energy leads to the conclusion that oxygen vacancy in In_2O_3 is a deep donor, unlikely to provide free electrons at room temperature. It is worth noted that the repeat calculations using the same method as Ref. [9] lead to the conclusion of the oxygen vacancy in In_2O_3 is a deep donor with a localized wavefunctions [8].

With Zn and Al embedding, the formation energy and transition energy of V_O are remarkable. Using PBE functionals, we find V_O with embedded Zn in the type II has the lowest formation energy among three types when the Fermi level close to the bottom of the conduction band. Based on the reduced formation energy of oxygen vacancy on Zn embedded In_2O_3 , we consider that embedding Zn may promote oxygen vacancy formation especially on *n*-type conduction while the Fermi level close to the the bottom of the conduction band. While using HSE06 functionals, we find V_O with embedded Zn and Al in the type III has the lowest formation energy among three cases when the Fermi level close to the bottom of the conduction band. The formation energy of V_O is increased with oxygen partial pressure (the chemical potential) increase. We further explore that type II defect has a lower formation energy than that of isolated V_O , which may be caused by the chemical potential modulation of embedding Zn. The lower formation energy of V_O in metal oxides originates from the formation of stable metal-metal bonds neighbors of oxygen vacancy defects, which leads to a strong local atomic relaxation and energy lowering of the doubly occupied a_1^2 gap level [28].

To further understand the observed dopant chemical modulation on oxygen vacancy formation in In_2O_3 , we analyze the physical origin of the ionization energy of oxygen vacancy in In_2O_3 , ZnO and Al_2O_3 , respectively. When nearest-neighbouring In atoms are replaced by Zn and/or In as shown in Figure 1, the locally chemical environment of V_O is varied in contrast to that in pristine In_2O_3 . For simplifying, the following discussions are made based on the band alignment of three pure oxides for predicting V_O ionization level shift in different chemical environments. The valence band offset (VBO) of ZnO/ In_2O_3 was reported around 0.29 eV according to the transitivity rule [30], and VBO of ZnO/ Al_2O_3 was around 0.8 eV [31]. Based on the reported values of VBO and the experimental band gaps of ZnO (3.4 eV), In_2O_3 (2.93 eV [32]) and Al_2O_3 (8.8 eV [33]), we figure out the band alignment for three oxides and the schematic diagram is shown in Figure 3. The red lines in Figure 3 represent the ionization energy level of V_O in respective oxides, they are 2.72 eV (this work) in In_2O_3 , 2.7 eV in ZnO [34] and 6 eV in Al_2O_3 [35]. Notably, we find that the ionization energy level of V_O in In_2O_3 is higher than that in ZnO but is lower than that in Al_2O_3 . When nearest-neighbouring In atom is replaced by Zn ($\text{Zn}_1\text{In}_{31}\text{O}_{48}$), the locally chemical environment would be

Figure 3. Schematic diagram of the band alignment for ZnO-In₂O₃-Al₂O₃.

partial of ZnO and which modulates the ionization energy of V_O in $Zn_1In_{31}O_{48}$ shifts down following the dotted line along the green arrow. While, when nearest-neighbouring In atoms are replaced by Al and Zn ($Al_1Zn_1In_{30}O_{48}$), the locally chemical environment would be partial ZnO and Al_2O_3 . Due to the ionization energy level of V_O in Al_2O_3 is much higher than that in In_2O_3 and ZnO, and we find that it is possible to push V_O into the conduction band in $Al_1Zn_1In_{30}O_{48}$ following the dashed line along the red arrow. Our HSE06 functional results on the ionization energies of V_O as shown in Figure 2(c) and Figure 2(d) support and are consistent with our proposed the dopant chemical modulation mechanism. Relying on the results as shown in Figure 3, we conclude that a higher concentration of embedded Al may further modulate V_O to degenerate states and increase the carrier concentration. This conclusion was proved by our previous experimental study, in which we found that the carrier concentration was increased with the Al concentration increase (from 4% to 11%) [16]. In addition, the localizations of wavefunction of the occupied V_O^0 in In_2O_3 , $Zn_1In_{31}O_{48}$ and $Al_1Zn_1In_{30}O_{48}$ obtained by using HSE06 functionals as shown in Figure 4 also prove the dopant chemical modulation working in oxygen vacancy formation. We find that V_O in In_2O_3 has localized wavefunction, which is consistent with other theoretical result [8]. However, the wavefunction of V_O keeps localized in $Zn_1In_{31}O_{48}$ but it changes to delocalized in $Al_1Zn_1In_{30}O_{48}$ with embedding Zn and Al. The delocalized wavefunction is a typical characteristic of the shallow defect. Using HSE06 functional, the calculated ionization energies of V_O are 0.21, 0.30 and -0.21 eV below or above (negative value) the bottom of the conduction band, compared with 1.44, 1.9 and 2.0 eV obtained from PBE functional calculations, corresponding to V_O in In_2O_3 , $Zn_1In_{31}O_{48}$ and $Al_1Zn_1In_{30}O_{48}$, respectively.

PBE and HSE06 functionals provide the same trend on the formation energy of V_O in pristine In_2O_3 under the oxygen-poor growth condition. The isolate V_O would be predominant as shown in Figure 2(b) and Figure 2(d) without embedding Zn and Al. However, the predicted ionization energies of 0.21 eV from HSE06 functional and 1.44 eV from PBE functional with respect to the bottom of the conduction band suggest that V_O is a deep donor and unlikely to be one of primary sources of n -type carriers in undoped In_2O_3 even under oxygen poor growth condition. Our result on V_O ionization energy in In_2O_3 obtained from HSE06 functionals is consistent with experimental observation [12] and reported theoretical predictions [8]. Although another conclusion has been drawn that V_O is likely to be a shallow and abundant donor in undoped In_2O_3 [9, 29]. We also find that V_O may form in $Zn_1In_{31}O_{48}$ and $Al_1Zn_1In_{30}O_{48}$ due to its low formation energy. However, V_O formation energy is increased with embedding Zn and Al compared with undoped In_2O_3 under the oxygen-poor growth condition. The anomalous increase on the formation energy of V_O is caused by the chemical potential modulation from Zn and Al, which would be increased when the oxygen potential decrease.

Based on the ionization and formation energies obtained using HSE06 functionals as shown in Figure 2(c) and Figure 2(d), we may calculate equilibrium concentrations of defects and free carriers [8, 36]. Here, we do not use the PBE functional results due to unreliable ionization energies primarily caused by

Figure 4. Hybrid-functional (HSE06) results for wavefunction localizations of the occupied V_O^0 defects in undoped In_2O_3 , $\text{Zn}_1\text{In}_{31}\text{O}_{48}$ and $\text{Al}_1\text{Zn}_1\text{In}_{30}\text{O}_{48}$ from left to right. Here, In, O, Zn, and Al atoms are denoted by purple, red, green and yellow balls.

Figure 5. Theoretical prediction on the concentration of defects (top shown) and electron density (bottom shown) as a function of growth temperatures. The left side figures show the oxygen-rich conditions ($\mu_O = 0$ eV) and the right side figures shown the oxygen poor condition ($\mu_O = \frac{1}{3}\Delta H_f^{\text{In}_2\text{O}_3}$). The electron density $n(T_g)$ due to thermal excitation across the band gap is shown for comparison (dotted line)

the underestimated band gap. Only the calculated concentrations of defects and free carriers based on the HSE06 functional results are simulated and shown in Figure 5. The calculated formation energies of three neutral defects are 3.39, 2.9 and 0.93 eV, corresponding to V_O , $V_O + Zn_{In}$ and $V_O + Zn_{In} + Al_{In}$, respectively. While V_O forms at concentrations up to the 10^{19} cm^{-3} (10^{10} cm^{-3}) ranges under the oxygen-poor (-rich) growth condition when the growth temperature is 1600 K. Even though the donor level of V_O is deep at room temperature, it was found that in undoped In_2O_3 an interesting deep-shallow transition caused by the pronounced reduction of band gap with temperature, bringing the donor level closer to the bottom of the conduction band [8]. Hence a high electron concentration in undoped In_2O_3 may exist at high temperature.

The prediction has the same trend as our experimental results on IZO and AIZO amorphous thin films, in which it was found that the measured carrier concentrations were increased [7, 15, 16]. Based on our results as shown in Figure 4, e.g., under the oxygen rich condition, when the growth temperature is $T = 1200 \text{ K}$ (when $\mu_O = 0 \text{ eV}$), it is found that $Al_1Zn_1In_{30}O_{48}$ has the highest carrier concentration up to 10^{18} cm^{-3} , and $Zn_1In_{31}O_{48}$ has a higher carrier concentration (up to 10^{10} cm^{-3}) than undoped In_2O_3 (up to 10^8 cm^{-3}). The similar trend was reported by Yaglioglu and co-authors [12]. The difference between theoretical and experimental electron concentration may show that V_O is unlikely to be the intrinsic n -type dopant in In_2O_3 at low growth temperature. Alternatively, we suggest that V_O is a deep donor defect state in In_2O_3 , the measured high conductivity on In_2O_3 and AZO may contribute by unintentional H [37].

4. Conclusions

In summary, we studied the formation of oxygen vacancies in In_2O_3 , $Zn_1In_{31}O_{48}$ and $Al_1Zn_1In_{30}O_{48}$ by using PBE and HSE06 functionals calculations. We found that the oxygen vacancy formation is modulated by the chemical potential of embedded Al and Zn. Meanwhile, we developed dopant chemical potential modulation models based on our HSE06 functional results. The proposed models well explain the anomalous carrier concentration increase in Zn and Al codoped In_2O_3 and might be used to choose alternative elements to replace In for reducing amount or indium-free TCOs.

5. Acknowledgements

This research was sponsored by A*STAR of Singapore and computational source was provided by ACR-C. Z. G. Yu thanks Dr. S.-H. Wei from NREL for useful discussions and suggestions on the band structure alignment.

References

- [1] K. Normura, *et al.*, Science 300 (2003) 1269.
- [2] A. Tsukazaki *et al.*, Nature Mater. 4 (2005) 42.
- [3] Z. W. Pan, Z. R. Dai, Z. L. Wang, Science 291 (2001) 1947.
- [4] Y. Li, Y. Bando, D. Golbery, Adv. Materi. 15 (2003) 581.
- [5] H. K. Kim, Surf. Coat. Technol. 203 (2008) 652.
- [6] Y. S. Park, H. K. Kim, S. W. Jeong, W. J. Cho, Thin Solid Films 518 (2010) 3071.
- [7] J. Sun, W. S. Lai, H. Gong, J. Appl. Phys. 111 (2012) 083712.
- [8] S. Lany, A. Zunger, Phys. Rev. Lett. 98 (2007) 045501; 106 (2011) 069601.
- [9] P. Ágoston, K. Albe, R. M. Nieminen, M. J. Puska, Phys. Rev. Lett. 103 (2009) 245501; 106 (2011) 069602.
- [10] P. Reunchan, X. Zhou, S. Limpijumnong, A. Janotti, C. G. Van de Walle, Current Appl. Phys. 11 (2011) S296.
- [11] B. Kumar, H. Gong, R. Akkipeddi J. Appl. Phys. 98 (2005) 073703.
- [12] B. Yaglioglu, Y.-J. Huang, H.-Y. Yeom, D. C. Paine, Thin Solid Films 496 (2006) 89.
- [13] A. J. Leenheer *et al.*, Phys. Rev. B 77 (2008) 115215.
- [14] M. P. Taylor *et al.*, Adv. Funct. Mater. 18 (2008) 3169.
- [15] J. Sun, H. Gong, Appl. Phys. Lett. 97 (2010) 092106.
- [16] J. Sun, Y. Huang, H. Gong, J. Appl. Phys. 110 (2011) 023709.
- [17] T. Wang, A. Layek, L.D. Hosein, V. Chirmanov, P. V. Padovanovic, J. Mater. Chem. C 2 (2014) 3212.
- [18] J. Wu, J. Zheng, P. Wu, R. Xu, J. Phys. Chem. C, 115 (2011) 5675-5682.
- [19] J. Heyd, G. E. Scuseria, and M. Ernzerhof, J. Chem. Phys. 118 (2003) 8207; J. Chem. Phys. 124 (2006) 219906.
- [20] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.

- [21] G. Kresse, J. Furthmüller, *Comput. Mater. Sci.* 6 (1996) 15.
- [22] P. E. Blöchl, *Phys. Rev. B* 50 (1994) 17953.
- [23] G. Kresse, D. Joubert, *Phys. Rev. B* 59 (1999) 1758.
- [24] C. Freysoldt, J. Neugebauer, C. G. Van de Walle, *Phys. Rev. Lett.* 102 (2009) 016402.
- [25] A. Walsh, D. O. Scanlon, *Phys. Rev. B* 88 (2013) 161201(R).
- [26] A. Walsh *et al.*, *Phys. Rev. Lett.* 100 (2008) 167402.
- [27] F. Fuchs and F. Bechstedt, *Phys. Rev. B* 77, 155107 (2008).
- [28] S. Lany, A. Zunger, *Phys. Rev. B* 72 (2005) 035215.
- [29] P.D.C. King, T.D. Veal, D.J. Payne, A. Bourlange, R.G. Egdell, C. F. McConville, *Phys. Rev. Lett.* 101 (2008) 116808.
- [30] H.P. Song, G.L. Zheng, A.L. Yang, Y. Guo, H.Y. Wei, C.M. Li, S.Y. Yang, X.L. Liu, Q.S. Zhu, Z.G. Wang, *Solid State Commun.* 150 (2010) 1991.
- [31] J. W. Liu, A. Kobayashi, K. Ueno, J. Ohta, H. Fujioka, M. Oshima, *e-J. Surf. Sci. Nanotech.* 10 (2012) 165.
- [32] P. D. C. King, T. D. Veal, F. Fuchs, Ch. Y. Wang, D. J. Payne, A. Bourlange, H. Zhang, G. R. Bell, V. Cimalla, O. Ambacher, R. G. Egdell, F. Bechstedt, C. F. McConville, *Phys. Rev. B* 79 (2009) 205211.
- [33] J. Robertson, K. Xiong, S. J. Clark, *Phys. Status Solidi B* 243 (2006) 2054.
- [34] V. Soriano, D. Galland, *J. Status solidi (b)* 2 (1976) 739.
- [35] V.A. Pustovarov, T.V. Perevalov, V.A. Gritsenko, T.P. Smirnova, A.P. Yelisseyev, *Thin Solid Films* 519 (2011) 6319.
- [36] C. G. Walle, J. Neugebauer, *J. Appl. Phys.* 95 (2004) 3851.
- [37] S. Limpijumnong, P. Reunchan, A. Janotti, C. G. Van de Walle, *Phys. Rev. B* 80 (2009) 193202.