PHYSICAL REVIEW B **72**, 125204 (2005)

First-principles study of Sn and Ca doping in $CuInO_2$

Li Liu
Institute of High Performance Computing, 1 Science Park Road, #01-01 The Capricorn, Singapore 117528, Singapore and Department of Materials Science, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260, Singapore

Kewu Bai
Institute of High Performance Computing, 1 Science Park Road, #01-01 The Capricorn, Singapore 117528, Singapore

Hao Gong
Department of Materials Science, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260

Ping Wu*
Institute of High Performance Computing, 1 Science Park Road, #01-01 The Capricorn, Singapore 117528, Singapore
(Received 26 May 2005; published 7 September 2005)

The roles of Ca and Sn doping for *p*- and *n*-type $CuInO_2$ were studied from first principles DFT calculations, which may lead to a better understanding of the dopant effects and further help to speed up the progress of new doping techniques. Currently Ca and Sn dopants are widely used in $CuInO_2$ experiments, but the reported carrier concentrations were still too low to support practical device design. In this theoretical approach, we demonstrated that Ca is a deep acceptor and Sn is a deep donor which are unlikely to account for the enhanced electrical conductivity in experiments. We further propose that amorphous In_2O_3 may be partially responsible for the difference between the experiment and modeling.

DOI: 10.1103/PhysRevB.72.125204 PACS number(s): 71.55.−i, 61.72.Ji, 71.15.Mb

I. INTRODUCTION

Being transparent yet conductive simultaneously, transparent conductive oxides (TCOs) are widely used in a number of applications like low-emissivity windows, front-surface electrodes for solar cells and flat-panel displays, "smart windows," defrost windows in vehicles, and glass touch-control panels.[1] However, most of the applicable TCOs are *n*-type.

Since the discovery of delafossite-type TCO of $CuAlO_2$ with *p*-type conductivity in 1997,[2] there has been great interest in the study of TCOs with delafossite structure. Among them, $CuInO_2$ is of special interest due to its verified doping bipolarity,[3–6] the capability of being doped to both *n*- and *p*-type. This property offers superiority to a semiconductor into "device" applications, because homogeneous *p*-*n* junctions are convenient to fabricate and stable in service. Yanagi *et al.*[4] later fabricated a homogeneous transparent *p*-*n* junction with this material. According to most of the reports, the conductivity values of Ca- and Sn-doped $CuInO_2$ are in order of 10^{-3} Scm^{-1} (except the 10^{-6} Scm^{-1} report[6] on $CuInO_2$:Ca), which can be improved one magnitude higher by optimizing the deposition parameters.[5] Activation energy of *n*-type Sn-doped $CuInO_2$ is much lower than that of *p*-type Ca-doped one[3,6] whereas the carrier concentration in $CuInO_2$:Sn is higher than that of $CuInO_2$:Ca.[6] Band gap of the material was estimated as 3.9 eV.[3] Although a single phase of composition $CuInO_{2.67}$ can be produced,[7] the parameter range for the growth of high quality film is very narrow[5] and the film may decompose during PLD.[3]

Despite the interesting bipolar dopability of $CuInO_2$, however, few reports concentrated on the theoretical study on $CuInO_2$ compared with the prototype of *p*-type delafossite TCO, $CuAlO_2$. Theoretical studies on ZnO, another promising TCO candidate of homogeneous *p*-*n* junctions, greatly outnumbered the theoretical studies on $CuInO_2$, partially due to the relatively simple chemical composition and the crystal structure of ZnO. Therefore, we chose $CuInO_2$ delafossite as our subject of interest.

Theoretical method is of especial priority in the defect physics study due to its superiority in control. However, only two reports on the theoretical study of defect physics for the delafossite family are available, despite the mysterious *p*-type conductivity in the on-stoichiometric $CuAlO_2$, a prototype of delafossite TCO. Katayama-Yoshida *et al.*'s study[8] on $CuAlO_2$ suggested V_{Cu} and Be_{Al} with lower impurity levels are promising point defects for higher *p*-type conductivity. However, the supercell employed contains only 32 atoms, which is probably insufficient to avoid artificial interaction between defects, based on our supercell size convergence test.[9] The other theoretical report on the defect physics of this group of compounds was given by Nie *et al.*[10] They calculated the formation energy for some typical intrinsic defects (V_{Cu}, V_O and Cu_i) in $CuGaO_2$ and compared with their former point defect calculation on ZnO. They suggested that a great reduction in self-compensation plus lower acceptor formation energy stand for *p*-type conductivity in $CuM^{III}O_2$ delafossites. However, almost no calculation details or concrete data on formation energy or defect levels were provided.

Previously, we presented our study of the isolated intrinsic point defect in $CuInO_2$.[12] Asymmetry in terms of intrinsic doping was found. In this work, we aim to simulate the effect of doping from a first-principles calculation. As most of the experiments[3–5] doped Ca^{2+} and Sn^{4+} to $CuInO_2$ for *p*- and

 ©2005 The American Physical Society

n-type semiconductivity, these two types of dopants become our subject of interest.

II. METHODOLOGY

A. Defect formation energy and defect level (Ref. 11)

In the intrinsic point defect study on $CuInO_2$,[12] it shows that interstitials and cation antisites at O position have very high energy barrier to overcome; dopants in the supercell are therefore studied mainly as substitutes at Cu/In cation position in $CuInO_2$.

For a neutral substitute in $CuInO_2$, the formation energy $\Delta H_f(\alpha)$ depends on the chemical potential μ of the elements (see next section):

$$\Delta H_f(\alpha,q=0) = E(\alpha,q=0) - E_0(\mathrm{CuInO_2}) + (\mu_\mathrm{c} + \mu_\mathrm{c}^0) - (\mu_\mathrm{d} + \mu_\mathrm{d}^0), \quad (1)$$

where $E(\alpha,q=0)$ is the total energy of the supercell containing the neutral defect α. $E_0(\mathrm{CuInO_2})$ is the total energy of the same supercell free of any defect. μ_d^0 and μ_c^0 are the standard chemical potentials of the dopant (Ca/Sn) and the cation (Cu/In) being substituted by the dopant, while μ_d and μ_c are the chemical potential of them.

To obtain the formation energy of a charged defect, total energy has to be calculated for four cells: a supercell with a charged defect $\alpha[q]$ of the total energy $E^{M-q}(\alpha,q)$; a defect supercell without introducing extra charges $[E^M(\alpha,q=0)]$; a perfect supercell without introducing point defect or extra charge $[E^N(\mathrm{CuInO_2})]$ and a supercell free from point defects but with one of component atoms charged to $-q[E^{N+q}(\mathrm{CuInO_2},-q)]$. In a supercell calculation, $\Delta H_f(\alpha,q)$ is given by:

$$\Delta H_f(\alpha,q) = \Delta H_f(\alpha,q=0) + \delta E(\alpha,q) + \delta E(\mathrm{CuInO_2},-q) + qE_F. \quad (2)$$

The first term on the right hand side of Eq. (2) is the formation energy for neutral point defect [Eq. (1)]. The second and third terms are as follows:[12]

$$\delta E(\alpha,q) = E^{M-q}(\alpha,q) - E^M(\alpha,q=0)$$

$$\delta E(\mathrm{CuInO_2},-q) = E^{N+q}(\mathrm{CuInO_2},-q) - E^N(\mathrm{CuInO_2}).$$

The defect transition levels $\varepsilon_\alpha(q/q')$ can be obtained as

$$\varepsilon_\alpha(q/q') = [\Delta E(\alpha,q) - \Delta E(\alpha,q')]/(q'-q). \quad (3)$$

B. Limits on atomic chemical potential

Chemical potentials determine the off-stoichiometry of the system and depend on different parameters such as partial pressure and growth conditions. From our previous study on the intrinsic point defect in $CuInO_2$,[12] the chemical potential ranges of the three components were determined as: $-1.34 \leqslant \mu_\mathrm{O} \leqslant 0$, $-0.67 \leqslant \mu_\mathrm{Cu} \leqslant 0$, and $-4.10 \leqslant \mu_\mathrm{In} \leqslant -2.09$.

In our study of $CuInO_2$:Sn and $CuInO_2$:Ca, SnO_2($P42/MNM$) and CaO ($FM3$-M) were chosen as the sources of dopants, respectively. Both Ca/Sn and their oxides were calculated on their ground state structures. The structure parameters and bulk properties were compared and verified to be in good agreement with the experimental data. Thus, the standard values of μ^0 for Ca (fcc) and Sn (diamond-like) are −1.91 eV and −3.83 eV, respectively. Formation energy values for CaO and SnO_2 are −6.14 eV and −5.08 eV. By balancing the chemical potential of oxygen in the dopant source and in the ternary compound, we can estimate the chemical potential ranges as $-6.14 \leqslant \mu_\mathrm{Ca} \leqslant -4.81$ and $-5.08 \leqslant \mu_\mathrm{Sn} \leqslant -2.40$. It should be note that the chemical potential of oxygen is not expected to be greatly influenced by the trace doping confined by the isolated dopant condition in our study.

C. Calculation details

All the calculations were performed using the plane wave basis Vienna *ab initio* Simulation Package (VASP) code.[13] The spin-polarized periodic density functional calculations (DFT) was parameterized in the local-density approximation (LDA), with the exchange-correlation functional proposed by Perdew and Zunger[14] and corrected for nonlocality in the generalized gradient approximation (GGA) using Perdew-Wang 91 functional.[15] The interaction between the core and valence electrons is described using the ultrasoft pseudopotentials (USPP) introduced by Vanderbilt[16] and provided by Kresse and Hafner.[17] The next uppermost states of $\mathrm{Cu}(3d,4s)$, $\mathrm{In}(4d,5s,5p)$, $\mathrm{O}(2s,2p)$, $\mathrm{Ca}(3s)$, and $\mathrm{Sn}(4d,5s,5p)$ were explicitly treated as parts of the valence states.

A similar method as the intrinsic point defect study[12] was employed to build supercells in this study. A $3\times3\times1$ supercell containing 108 atoms and the relaxation ranges adopted in the previous study on $CuInO_2$ were used. To ensure the same reference eigenvalue ε_i used in the calculation, the same cutoff energy and k point sampling as for defect-free supercell were employed.

III. ISOLATED EXTRINSIC POINT DEFECTS

Based on the same formalism as the intrinsic point defect study, substitute defect formation energy $\Delta H(\alpha,q)$ [Eq. (1) or Eq. (2) for neutral or charged defects] and defect transition levels [Eq. (3)] were obtained and listed in Table I. $\Delta H_f(\alpha,q)$ values are given for both before and after the band gap (BG) correction.[12] The value of $\Delta H_f(\alpha,q)$ before BG correction gives reasonable evaluation of the relative abundance of the defect, whereas the ones after BG correction are mainly for a proper defect level within the corrected BG. The effect of BG correction on our conclusions will be discussed later.

Figure 1 shows the dependence of defect formation energy (after BG correction) on the E_F position in oxygen rich and oxygen poor conditions. By changing E_F we can simulate the effect of changes in dopant concentration. $\Delta H_f(\alpha,q)$ varies as a function of doping level. The slope of the lines in the figures corresponds to the charge state of the defect. For each defect, the line for a particular charge state is shown over the range where this charge state has the lowest energy

TABLE I. Formation energy [Eq. (2)] of Ca or Sn substitutes on Cu or In positions when E_F locates at the VBM and defect transition levels. Formation energy $\Delta H_f(\alpha,q)$ is given at different charge state and chemical environment. $\Delta H_f(\alpha,q)$ values before and after BG corrections are for the evaluation of the relative abundance and the defect levels, respectively. All the defect transition levels listed in are those within the band gap. The unit is eV.

Defect type	$\Delta H_f(\alpha,q)$: before BG correction		$\Delta H_f(\alpha,q)$: after BG correction	
	O rich	O poor	O rich	O poor
Ca_{In}^{0}	−0.75	−0.08	−0.75	−0.08
Ca_{In}^{0}	−0.35	0.32	−0.35	0.32
Defect transition levels: $(-1/0)=E_V+0.40$ eV				
Sn_{In}^{+1}	1.38	0.71	1.38	0.71
Sn_{In}^{0}	0.90	0.23	1.61	0.94
Defect transition levels: $(0/+1)=E_C-1.16$ eV				
Ca_{Cu}^{+1}	2.86	2.20	2.86	2.20
Ca_{Cu}^{0}	2.56	1.89	3.27	2.60
Defect transition levels: $(0/+1)=E_C-0.99$ eV				
Sn_{Cu}^{+3}	9.01	7.01	9.01	7.01
Sn_{Cu}^{+2}	6.01	4.01	6.72	4.72
Sn_{Cu}^{+1}	4.67	2.66	6.09	4.08
Sn_{Cu}^{0}	4.61	2.60	6.74	4.73
Defect transition levels: $(0/+1)=E_C-0.74$ eV				

of all possible charge states. The kinks thus correspond to the transitions between charge states.

From Table I and Fig. 1, both dopants were found to have lower formation energy at In positions, as most experiments suggested. Being a large cation, Ca^{2+} may tend to be unstable in the linear coordination sites,[18,19] whereas Sn^{4+}, a much smaller cation, is even harder to substitute Cu^{+} position. As Ca is a donor-like impurity if substituting Cu, but an acceptor-like if substituting In, it is very likely for Ca to substitute In and act like an acceptor. Sn, on the other hand, substitutes In and acts as a donor. Figure 2 shows the formation energy of eight intrinsic point defects in $CuInO_2$, half donor-like and half acceptor-like.[12] In general, acceptor-like intrinsic point defects have lower formation energies compared with door-like counterparts. Acceptor-like intrinsic point defects have lower formation energy in oxygen rich conditions, whereas donor-like ones are easier to form in oxygen poor conditions. Similar to what was found for the intrinsic defects,[12] acceptor-like defect Ca_{In} is easier to produce in oxygen rich conditions whereas donor-like defect Sn_{In} is quite opposite. This means, by controlling the partial pressure of oxygen during the fabrication process, we can introduce *n*- or *p*-type defects or suppress their formation intentionally.

From Fig. 1, we may also find the defect transition level for Ca_{In} is at 0.4 eV, a rather deep acceptor level. However, as Ca_{In} has very low formation energy from this calculation, $CuInO_2$:Ca could have higher carrier concentration than the undoped sample, especially when it was heavily doped in the experiment. Increase of carrier concentration predicted by

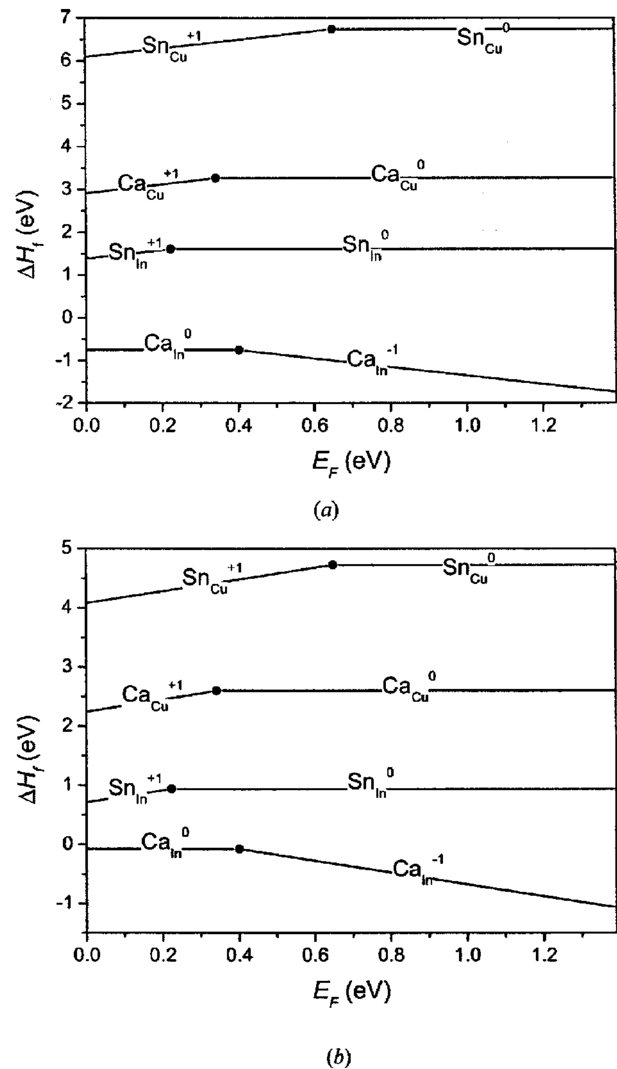

FIG. 1. Formation energy of Ca or Sn dopant substituting Cu or In, as a function of E_F in (a) oxygen rich and (b) oxygen poor conditions. Charge state q determines the slope of each line segment. Solid dots denote values of E_F where transition between charge states occurs.

our calculation is in consistence with Sasaki and Shimode's experimental work on $CuInO_2$:Ca.[6] They found the carrier concentration of Ca doped sample is one magnitude larger than that of the non doped one. On the other hand, Sn_{In} produces a very deep donor level with an activation energy of >0.6 eV. This means Sn_{In} point defect alone does not support an improved n-type carrier concentration and conductivity.

Furthermore, we can see that, similar to the intrinsic point defects, the donor-like substitutes (Ca_{Cu}, Sn_{In}, and Sn_{Cu}) have lower formation energy in oxygen poor conditions; whereas the acceptor-like substitutes (Ca_{In}) have lower formation in oxygen rich conditions. This explains some experimental observations in the Yanagi *et al.* study.[3] In their work of depositing Sn doped $CuInO_2$ thin film, they found the optimal deposition condition in terms of optoelectronic properties of $CuInO_2$:Sn is the lowest possible oxygen partial pressure for a stable film.

FIG. 2. Formation energy of intrinsic defects of donor-like (a), (b) and acceptor-like (c), (d) as a function of oxygen chemical potential when E_F is at the CBM (a), (c) or the VBM (b), (d).

Moreover, as the position of E_F moves from the VBM to the CBM, donor-like substitutes become harder to produce, whereas acceptor-like ones easier to form. E_F moving towards the CBM indicates an increase of electron concentration. Therefore, increasing electron concentration makes donor-like impurity harder to produce, but acceptor-like impurity easier to form and compensate free electron carriers. A similar process occurs while increasing hole concentrations for a *p*-type semiconductor. This represents the so-called compensation effect.

IV. DISCUSSIONS

A. Formation of $CuInO_2$ from Cu_2O and In_2O_3

As mentioned in our previous work on intrinsic point defect in $CuInO_2$, this ternary compound shows metastability compared with its end-point binary compounds.[12] This will be further explored in this section.

Let us consider the reaction of fabricating $CuInO_2$ from the end-point binary compounds, Cu_2O and In_2O_3 as follows:

$$Cu_2O + In_2O_3 \xrightarrow{\Delta H} 2CuInO_2. \quad (4)$$

Taking the calculated formation energy of the end-point binary compounds (−1.337 eV and −8.193 eV) and $CuInO_2$ (−4.737 eV), we may find the theoretical ΔH for the reaction is:

$$\Delta H = 2 \times \Delta H_f[CuInO_2] - (\Delta H_f[Cu_2O] + \Delta H_f[In_2O_3]) = 0.056\ \text{eV}.$$

Thus, the formation of the ternary compound $CuInO_2$ is found to be comparable with that of the end-point binary compounds in terms of energy. In other words, $CuInO_2$ is metastable compared with the end-point binary compounds Cu_2O and In_2O_3.

The result is consistent with the fact that it is difficult to fabricate $CuInO_2$ by solid state reactions from the end-point binary compounds in Shimode's[20] and Hahnn's[21] studies. In Shimode's study, solid state reactions could produce $CuInO_2$ neither in the Cu_2O–In_2O_3 system nor in the Cu_2O–$In(OH)_3$ system, although many other delafossite compounds had

been successfully fabricated from the according end-point binary oxides. As a result, $CuInO_2$ is often produced through ion-exchange reaction method with the alkali ternary compounds like $LiInO_2$ at high temperature. However, if the reaction of Eq. (4) is not energetically favorable, its reverse process could be expected to readily occur.

B. Band gap correction and its effect on defect transition levels

Due to the ground-state feature of DFT method, calculated band gap values are generally underestimated, so that the calculated band gap has to be corrected. Then the band gap is scissored in the middle and then sewn with the CBM shifting 0.71 eV upwards. As the calculated minimum direct band gap is 0.68 eV at Γ, the direct gap becomes 1.39 eV after band gap correction. Both the defect levels and the formation energy values were corrected accordingly.[12]

The relative position of each defect level to the corresponding band edges could not be affected by this correction as we explained in the intrinsic point defect study.[12] Hence the conclusions about them as shallow or deep levels would not be varied. Furthermore, the conclusions about the defect formation energy and their relative abundance are robust to the band gap correction. From Table I we can find the formation energy values of each substitute type before and after the band gap correction. Compared with Ca (Sn) substitute at Cu site, the formation energy of its In site counterpart is at least 1.57 (1.96) eV lower before band gap correction in all charge states and both chemical environment limits. Hence, $Ca_{In}(Sn_{In})$ is the stable state for Ca (Sn) doped $CuInO_2$. Therefore, the conclusions on the extrinsic point defects do not be affected by the band gap correction either in terms of shallow or deep level or their relative abundance.

C. Further discussions on doped $CuInO_2$: Comparing with the available experimental results

Our calculation on Ca^{2+} doped $CuInO_2$ shows that Ca_{In} substitute is the stable and abundant state for Ca^{2+} dopant. It produces an acceptor state at 0.41 eV above the VBM, a fairly deep acceptor level in $CuInO_2$. This is consistent with the experimental result that $CuInO_2$ became *p*-type conductive after doping Ca^{2+} into the material. Furthermore, Sn_{In} forms a rather deep donor level in the band gap. Hence we do not expect higher carrier concentration in $CuInO_2$:Sn. But in Sasaki's work,[6] they found carrier concentrations are comparable in $CuInO_2$:Ca and $CuInO_2$:Sn. There must be other explanations for the experimental observation. Some factors have to be involved into our consideration while comparing the calculation results with the experiments.

First, the conductivity of doped $CuInO_2$ experimentally measured is very low, i.e., $\sim 10^{-3}$ S cm^{-1} in Yanagi's report[3] and 6×10^{-2} S cm^{-1} after improving the film quality by Ginley *et al.*[5] Moreover, it was quite heavily doping (5 at %) into $CuInO_2$ in both the experiments mentioned above. Some factors may account for the low conductivity in a heavily doped semiconductor, like the low carrier mobility, deep dopant level, high defect formation energy,[22] or limited solubility of dopants.[19]

Second, heavy doping (5 at %) not only pushes the defect levels nearer to the related band edges,[22] but also makes the problem in the ternary compound even more complicated. One possible effect of heavily doping is the agglomerating of or interacting between dopants, which will surely influence the defect levels. The extrinsic defect concentration in our calculation, however, is less than 1% (one defect in a supercell of 108 atoms). We should also note that interaction between defects of heavily doped materials could not be simulated through employing a small supercell. Therefore, theoretical study on heavily doped $CuInO_2$ needs to be examined in future work.

Another result from heavily doping is the formation of defect complex. As a first systematic point defect calculation work on $CuInO_2$, only isolated point defects were examined here. Other types of point defects, like defect pair formed by or between intrinsic point defects and dopants are necessary to be studied for a thorough understanding of the experimental observations.

Third, the XRD spectra in the experimental reports do not preclude the existence of In_2O_3, especially amorphous one. Inspired by the Ginley[5] and Yanagi reports[3] that deposited films could be a mixture of $CuInO_2$ and In_2O_3 in certain conditions, we suggest that small amount of In_2O_3 may account for the experimental observations. Moreover, according to the Ginley[5] report that In_2O_3 coexists in the deposited $CuInO_2$:Ca for a deposition temperature of 600 °C or above, the Yanagi report[4] of single phase $CuInO_2$ delafossite of the thin film fabricated at more than 873 K may be susceptive. Our calculation result on the thermal instability of $CuInO_2$ with respect to its end-point binary compound also justifies this suspicion. $CuInO_2$ could decompose during film deposition.

Both In_2O_3:Sn and In_2O_3 with oxygen deficiency are proven to be n-type TCOs with high mobility, even in amorphous phase.[23,24] With In_2O_3 binary compound in the $CuInO_2$:Sn film, increased electron concentration and conductivity could be expected, although Sn has a deep donor level in the ternary compound. Moreover, we can explain the observation that the conductivity of $CuInO_2$:Sn film is greatly reduced when $P_{O_2} > 2$Pa if coexistence of In_2O_3 is assumed. External O_2 partial pressure can determine the electricity of amorphous In_2O_3 because V_O is the source of carriers in amorphous In_2O_3.[23] In addition, dopant Sn may constrain the formation of V_{In}, the intrinsic defect with shallow acceptor level, and greatly reduce the self-compensation effect.

The existence of amorphous In_2O_3 in the deposited films can also explain the observations of the non doped or Ca doped films. The low carrier concentration of non doped sample could result from compensation effect of intrinsic *p*-type defects (that is abundant in $CuInO_2$) and the *n*-type carriers in In_2O_3. For $CuInO_2$:Ca, large amount of Ca, a *p*-type dopant with low formation energy, could eliminate the electrons released by In_2O_3, but *p*-type carrier concentration is also reduced. Furthermore, because of the possible existence of secondary phase in the ternary compound, conductivity values measured in all the experiments are low for both $CuInO_2$:Ca and $CuInO_2$:Sn.

Last but not least, our calculation based on DFT is about the properties at ground state, while most experimental data

were measured at ambient temperature or even higher temperatures. Temperature is another factor that will affect the relative position of defect levels.

V. CONCLUSIONS

Theoretical calculations on isolated extrinsic point defects in $CuInO_2$ were carried out for their formation energies and defect transition levels using plane-wave basis set, pseudopotential technique, and the supercell approach.

Two dopants, Ca and Sn, were studied as substitutes while their oxides as dopant sources. The calculations on these extrinsic point defects show that both Ca and Sn have lower formation energy at In position, coincident with the assumptions made in most of experimental studies on doped $CuInO_2$. Both Ca_{In} and Sn_{In} form rather deep defect levels in the band gap. Comparing our calculation results with the experimental observations, we found something hard to explain within isolated point defect study alone. We suggest amorphous In_2O_3 may stand for the experimental observation of insulating non-doped $CuInO_2$ and comparable carrier concentration in $CuInO_2$:Ca and $CuInO_2$:Sn. This is also based on our result on metastability of $CuInO_2$ compared with its end-point binary compounds. Moreover, $CuInO_2$ was 5 times more heavily doped in experiments than in our theoretical calculations. With higher concentration of dopants, interactions between dopants or formation of defect complex are unavoidable, which surely influence the defect formation energy and the defect level positions. Further theoretical calculations on defect complexes are necessary for a thorough understanding on the doped $CuInO_2$. Other factors like temperature may also affect the calculation results.

ACKNOWLEDGMENTS

This work was sponsored by the Agency of Science, Technology and Research of Singapore (A*STAR).

---

*Corresponding author. Electronic address: wuping@ihpc.a-star.edu.sg

[1] B. G. Lewis and D. C. Panine, MRS Bull. **20**, 22 (2000).

[2] H. Kawazoe, M. Yasukawa, H. Hyodo, M. Kurita, H. Yanagi, and H. Hosono, Nature (London) **398**, 939 (1997).

[3] H. Yanagi, T. Hase, S. Ibuki, K. Ueda, and H. Hosono, Appl. Phys. Lett. **78**, 1583 (2001).

[4] H. Yanagi, K. Ueda, H. Ohta, M. Orita, M. Hirano, and H. Hosono, Solid State Commun. **121**, 15 (2002).

[5] D. Ginley, B. Roy, A. Ode, C. Warmsingh, Y. Yoshida, P. Parilla, C. Teplin, T. Kaydanova, A. Miedaner, C. Curtis, A. Martinson, T. Coutts, D. Readey, H. Hosono, and J. Perkins, Thin Solid Films **455**, 193 (2003).

[6] M. Sasaki and M. Shimode, J. Phys. Chem. Solids **64**, 1675 (2003).

[7] S. Park and D. A. Keszler, J. Solid State Chem. **173**, 355 (2003).

[8] H. Katayama-Yoshida, T. Koyanagi, H. Funashima, H. Harima, and A. Yanase, Solid State Commun. **126**, 135 (2003).

[9] L. Liu, Master thesis, National University of Singapore, 2005.

[10] X. L. Nie, S-H. Wei, and S. B. Zhang, Phys. Rev. Lett. **88**, 066405 (2002).

[11] A. S. Foster, V. B. Sulimov, F. L. Gejo, A. L. Shluger, and R. M. Nieminen, Phys. Rev. B **64**, 224108 (2001); S-H. Wei and S. B. Zhang, *ibid.* **66**, 155211 (2002); A. F. Kohan, G. Ceder, D. Morgan, and C. G. Van de Walle, Phys. Rev. B **61**, 15019 (2000); G. A. Baraff and M. Schluter, Phys. Rev. Lett. **55**, 1327 (1985); S. B. Zhang and J. E. Northrup, *ibid.* **67**, 2339 (1991); D. B. Laks, C. G. Vandewalle, G. F. Neumark, P. E. Blochl, and S. T. Pantelides, Phys. Rev. B **45**, 10965 (1992).

[12] L. Liu, K. W. Bai, H. Gong, and P. Wu, Chem. Mater. 2005 (resubmitted).

[13] G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996); Phys. Rev. B **54**, 11169 (1996).

[14] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[15] J. P. Perdew and Y. Wang, Phys. Rev. B **33**, R8800 (1986); J. P. Perdew, in *Electronic Structure of Solids '91*, edited by P. Ziesche and H. Eschrig (Akademie, Berlin, 1991).

[16] D. Vanderbilt, Phys. Rev. B **41**, R7892 (1990).

[17] G. Kresse and J. Hafner, J. Phys.: Condens. Matter **6**, 8245 (1994).

[18] L. E. Orgel, J. Chem. Soc. **1958**, 4186 (1958).

[19] B. J. Ingram, B. J. Harder, N. W. Hrabe, and T. O. Mason, Chem. Mater. **16**, 5623 (2004).

[20] M. Shimode, M. Sasaki, and K. Mukaida, J. Solid State Chem. **151**, 16 (2000).

[21] H. Hahnn and C. Lorent, Z. Anorg. Allg. Chem. **279**, 281 (1955).

[22] C.-T. Sah, *Fundamentals of Solid-State Electronics* (World Scientific, Singapore, 1991).

[23] B. Pashmakov, B. Claflin, and H. Fritzsche, J. Non-Cryst. Solids **164-166**, 441 (1993); P. K. Song, H. Akao, M. Kamei, Y. Shigesato, and I. Yasui, Jpn. J. Appl. Phys., Part 1 **38**, 5224 (1999).

[24] R. E. Johanson and S. O. Kasap, J. Vac. Sci. Technol. A **20**, 1027 (2002).