Carbon as a Shallow Donor in Transparent Conducting Oxides

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Carbon is a common unintentional impurity in oxide semiconductors. We use hybrid density functional theory to calculate the electronic and structural properties of carbon impurities in ZnO, In_2O_3, and Ga_2O_3—materials that are used as transparent conductors. In each of these semiconducting oxides we find that carbon is most likely to occupy the cation site under most electronic and chemical potential conditions. In ZnO, C_{Zn} acts as a shallow double donor and exhibits large local breathing-mode relaxations. In In_2O_3 and Ga_2O_3, C acts as a shallow donor and moves off the cation site to become three-fold oxygen coordinated. In all three oxides, C_{cation} exhibits modest formation energies, indicating that these species will be likely to incorporate. Our results indicate that C impurities are suitable donor dopants in these oxides, and will contribute to background n-type conductivity if unintentionally present.

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I. INTRODUCTION

The optical transparency and high electron mobility of ZnO, In_2O_3, and Ga_2O_3 enable the use of these materials as transparent conducting oxides (TCO) and in transparent transistors. Control over their electrical conductivity is still a major issue [1]. The materials almost always exhibit n-type conductivity, even when not intentionally doped. p-type doping has not been established due to the lack of appropriate shallow acceptors and the tendency for spontaneous hole trapping [2]. Even in applications that do not require ambipolar doping, such as transparent conducting contacts [3], transparent thin-film transistors [4], or polariton lasers [5], better control of n-type conductivity is highly desirable.

Unintentional n-type conductivity has often been attributed to native point defects, in particular to oxygen vacancies [6, 7]. In ZnO and Ga_2O_3, recent theoretical and experimental investigations indicate that impurities, not native defects, are the source of conductivity [8–11]. In In_2O_3, the role of native defects is still under debate [1, 12]. In all of these oxides, however, doping can be due to the unintentional incorporation of donors, and a number of impurities have been put forward as likely sources, including H [13–16] and Si [11, 17].

Surprisingly, carbon has received less attention as an unintentional dopant, in spite of the fact that is ubiquitous in growth and processing environments. Oxide films are frequently grown by metal-organic chemical vapor deposition (MOCVD) or atomic layer deposition (ALD), making carbon contamination from organic precursors very plausible. In ZnO, C impurities have been detected in as-grown samples in some studies [18], though secondary ion mass spectroscopy (SIMS) measurements have difficulty detecting C, possibly due to high detection thresholds (3 x 10^{18} cm^{-3} in Ref. 15). In Ga_2O_3 grown by ALD, reduction of C contamination below 1% has proven difficult [19]. *Intentional* C-doping of ZnO has been linked with increases in n-type conductivity [20].

A few theoretical studies of carbon impurities in ox-

ides have been reported, all based on density functional theory (DFT), but not all possible atomic configurations or charge states were explored. In the case of ZnO and In_2O_3, previous work either did not consider all C configurations [20, 21], or did not consider that C impurities could assume charge states other than neutral [22, 23]. In order to ascertain the behavior of impurities in semiconductors, it is crucial to allow for the possibility of charged defect states. Considering all relevant charge states in each possible atomic configuration of the defect is essential for determining what effect the defect will have on the electrical properties of the semiconductor. To our knowledge there have been no previous theoretical studies of C in Ga_2O_3.

Sakong and Kratzer [24] did consider the possibility of charged C impurities in ZnO. They found C on the Zn site (C_{Zn}) to be the most stable configuration for a wide range of Fermi-level (E_F) positions in the gap, but reported unusual results for the electronic behavior of C_{Zn}. C_{Zn} is expected to be a double donor in ZnO, but Sakong and Kratzer [24] found it to convert to an acceptor when the Fermi level was higher than 2.5 eV above the valence-band maximum (VBM) of ZnO. These calculations [24] were performed with DFT+U, which yields a ZnO band gap of only 1.65 eV, calling into question the validity of the results in Ref. 24. As shown in previous work [9, 17, 25], employing a method that correctly predicts the electronic band structure and the positions of the band edges (on an absolute energy scale) is essential for the quantitative prediction of formation energies and transition levels of defects and impurities in semiconductors.

Here we use DFT calculations with a hybrid functional to provide a reliable description of C impurities in ZnO, In_2O_3 and Ga_2O_3. We explore both substitutional (C_{cation} and C_O) and interstitial (C_i) configurations of the C impurity, and consider all possible charge states of each configuration. By analyzing the stability of the different configurations as a function of Fermi level and chemical potentials, we are able to predict the low-

est energy configuration and the effects on the electrical properties of the TCOs. In each case, we find that C impurities strongly prefer to occupy the cation site, where they act as shallow donors. (We note that in SnO_2, another widely-used TCO, C would not be expected to give rise to free electrons since it is isoelectronic with the Sn cation.)

II. COMPUTATIONAL DETAILS

Our calculations are based on DFT [26, 27] and projector-augmented wave potentials [28, 29] as implemented in the VASP code [30]. We use the screened hybrid functional of Heyd, Scuseria, and Ernzerhof (HSE) [31]. The hybrid mixing parameter was set to 36% for ZnO, 35% for Ga_2O_3, and 32% for In_2O_3, which results in an accurate values of band gaps and structural parameters [11, 17]. Using these parameters, the band gaps are calculated to be 3.35 eV for ZnO, 4.87 eV for Ga_2O_3, and 3.04 for In_2O_3. For ZnO, $3d$ electrons were treated as valence electrons, while for Ga_2O_3 and In_2O_3, semicore d states were treated as core electrons. The isolated C impurities were simulated using 96-atom wurtzite supercells for ZnO, 120-atom monoclinic supercells for Ga_2O_3, and 80-atom bixbyite supercells for In_2O_3. A cutoff of 400 eV was used for the plane-wave basis set and two special k-points for Brillouin zone integrations. All relaxations were performed consistently with the HSE functional.

The likelihood of incorporating an impurity in ZnO is determined by its formation energy. For the incorporation of C on the Zn site (C_{Zn}), the formation energy is given by [32]:

$$E^f(C_{Zn}^q) = E_{tot}(C_{Zn}^q) - E_{tot}(ZnO) - \mu_C + \mu_{Zn} \\ + qE_F + \Delta^q, \quad (1)$$

where $E_{tot}(C_{Zn}^q)$ is the total energy of the supercell containing one C_{Zn} in charge state q, and $E_{tot}(ZnO)$ is the total energy of a perfect crystal in the same supercell. The Zn atom that is removed from the crystal is placed in a reservoir of energy μ_{Zn}, referenced to the energy of bulk Zn. The C atom that is added is taken from a reservoir with energy μ_C, referenced to the energy of bulk C (diamond). E_F is the Fermi level referenced to the VBM of the host. Finite-size charge-state corrections (represented by the Δ^q in Eq. 1) are performed as described in Refs. 33 and 34. Expressions analogous to Eq. 1 can be written for C_{cation} in the other TCOs (as well as for C_i and C_O in all three materials).

The chemical potential μ_{Zn} in Eq. (1) must satisfy the stability condition of the oxide in question; e.g., for ZnO:

$$\mu_{Zn} + \mu_O = \Delta H_f(ZnO), \quad (2)$$

where μ_O is the chemical potential of O, referenced to the energy per atom of an isolated O_2 molecule, and $\Delta H_f(ZnO) = -3.66$ eV is the calculated formation enthalpy of ZnO. The value of the O_2 reference energy is

calculated consistently with the HSE mixing parameter used for each individual compound, but the resulting O_2 binding energy varies by less than 0.15 eV over the range of mixing parameters used here. In principle μ_O can vary from 0 eV (extreme O-rich conditions) to –3.66 eV (extreme O-poor or Zn-rich conditions), which can strongly affect the stability of impurities and defects. In Ga_2O_3, which has a calculated enthalpy of formation of –10.40 eV, $\mu_O = -3.47$ eV under extreme O-poor conditions; and in In_2O_3, with a calculated enthalpy of formation of –8.59 eV, $\mu_O = -2.86$ eV under extreme O-poor conditions [35]. As we will discuss in Sec. III, not all of these conditions can necessarily be achieved during growth or processing.

III. RESULTS AND DISCUSSION

A. ZnO

In Fig. 1(a) we show the formation energy versus Fermi level for C_{Zn}, C_O, and C_i in ZnO under O-rich conditions. C substitution on the oxygen site in ZnO leads to highly localized, C $2p$-like states that are deep in the band gap. C_O^- causes small local lattice distortions: the Zn atoms nearest to C_O move outwards by only 2% of the bulk Zn-O bond length. For C_O^0, one C-Zn bond length increases by 6% of the Zn-O bond length, another increases by 7%, and the remaining two C-Zn bonds are only 1% larger than the Zn-O bond length. In the + charge state, all C-Zn bond lengths are larger than the bulk Zn-O bond, three by 9% and the fourth by 11%. Thorough testing of off-site displacements and distortions confirms that C_O occupies the O lattice site, accompanied only by breathing-mode relaxations. The $(0/-)$ transition level occurs 2.82 eV above the VBM, while the $(-/2-)$ level occurs 0.40 eV above the conduction-band minimum (CBM) (not shown). We also find a $(+/0)$ transition level at 1.72 eV above the VBM, and C_O^+ is the most stable charge-state configuration for E_F lower than 1.72 eV. However, in as-grown ZnO the Fermi level is likely to be near the CBM (since ZnO is most often n-type) indicating that C_O^- will be the most relevant charge state.

For interstitial C, C_i, we find the lowest-energy configuration to be of the split-interstitial type, in which C and O share occupation of an O lattice site and form a close bond with bond length 1.23 Å. This configuration is in agreement with a previously published report [21]. We also tested C occupation of the tetrahedral and octahedral interstitial sites, and found that C spontaneously moves off-site to form the split interstitial. As shown in Fig. 1(a), C_i acts as a donor in ZnO, with a $(2+/+)$ transition level at 1.63 eV and a $(+/0)$ level at 3.27 eV above the VBM.

For C_{Zn}, we find shallow double-donor behavior, as C_{Zn} is stable exclusively in the 2+ charge state for all E_F values within the band gap. We find no defect-induced
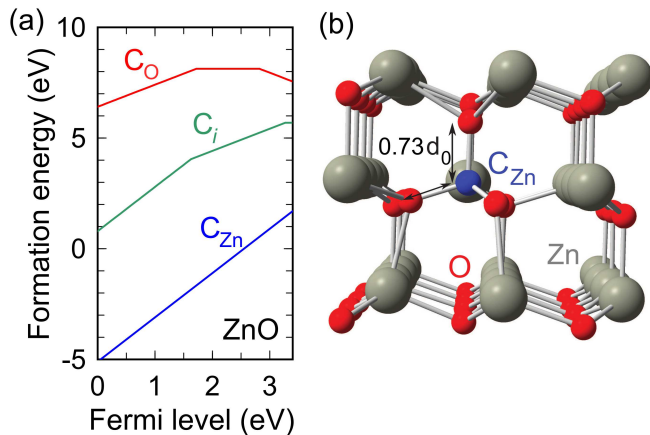
FIG. 1. (color online) (a) Formation energy versus Fermi level for C_{Zn}, C_O, and C_i in ZnO under O-rich conditions. (b) Atomic configuration of C_{Zn} in ZnO.
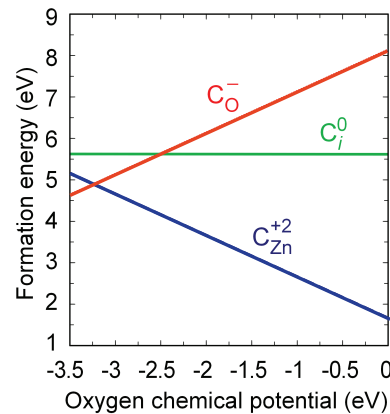

FIG. 2. (color online) Formation energy of C impurities in ZnO as a function of O chemical potential, when the Fermi level is at the CBM. Only the lowest-energy charge state of each configuration is plotted, i.e., C_{Zn}^{2+}, C_O^-, and C_i^0.

Kohn-Sham states in the band gap; adding electrons to the supercell in an attempt to simulate +, neutral, or negative charge states simply results in occupation of conduction-band states. These results are in contradiction with previous DFT+U calculations[24] which reported negative charge states for C_{Zn} becoming stable 2.5 eV above the VBM. Despite our attempts to stabilize such charge states, only the 2+ charge state of C_{Zn} has been found to be stable in our investigations. We suspect that the disagreement is due to the incorrect occupation of conduction-band states in the previous work [24]. As the band gap of ZnO in the DFT+U calculations was only 1.65 eV, the negative C_{Zn} states reported in Ref. 24 would lie 1 eV above the CBM and cannot actually be stabilized.

The double donor behavior of C_{Zn} is similar to that of Si_{Zn} and Ge_{Zn} in ZnO [17]. C_{Zn}^{2+} causes a large local lattice distortion of the ZnO lattice, as the nearest-neighbor O atoms are displaced inwards by 27% of the bulk bond length, resulting in C-O bond lengths of 1.44 Å [see Fig. 1(b)]. A large inward relaxation also occurred in the case of Si_{Zn}^{2+} and Ge_{Zn}^{2+} in ZnO [17], but for C_{Zn}^{2+} the relaxations are significantly larger due to the much smaller size of the C atom compared to Si and Ge. Tests of off-site displacements and symmetry-broken configurations confirm that only breathing relaxations occur, and that on-site occupation of the Zn lattice site is the most stable configuration for C_{Zn}.

Figure 1(a) shows that C_{Zn}^{2+} is the most stable configuration for the C impurity for almost all chemical potential conditions. This is also illustrated in the plot of formation energies of C_i^0, C_{Zn}^{2+}, and C_O^- as a function of μ_O in Fig. 2. These charge states were chosen because they correspond to the most stable states in n-type material; i.e., for E_F = 3.4 eV (at the CBM), which is the relevant situation for TCOs; however, our conclusions would hold at other E_F values as well. As shown in Fig. 2, C_{Zn}^{2+} is the most stable configuration down to μ_O = –3.3

eV, nearly at the O-poor limit. As we have discussed in previous work on oxide materials [36], such low oxygen chemical potentials are unlikely to occur during growth or processing.

These results suggest that C incorporation will occur almost exclusively on the Zn site, and also highlight the importance of considering all possible incorporation sites and their relevant charge states. Previous work, in which it was simply assumed that C_O would be the most stable C configuration in ZnO [20], should thus be re-examined in light of these results.

In order to aid in the experimental characterization of C impurities in ZnO, we also calculated the frequencies of the local vibrational modes (LVMs) of C_{Zn}. Due to the presence of strong C-O bonds, the local modes are expected to occur at frequencies higher than the highest phonon mode in ZnO, which is 600 cm^{-1} [37]. For C_{Zn}^{2+}, we find three LVMs in the range of 820–881 cm^{-1} (24.5-26.5 THz), indeed higher than the bulk phonon modes. Unfortunately, these frequencies lie in a range in which they may be difficult to detect due to free-carrier absorption in n-ZnO and due to two-phonon absorption processes. Still, recent experimental techniques have improved the sensitivity of defect-related LVM detection in frequency ranges where non-defect-related absorption may occur [38].

B. Ga$_2$O$_3$

The formation energy of carbon impurities in Ga$_2$O$_3$ under O-rich conditions is shown in Fig. 3(a). There are three distinct oxygen sites in Ga$_2$O$_3$,[39] and in Fig. 3(a) we plot only the results for the lowest-energy configuration for C_O, which we find to be the O_I site (as labeled in Ref. 39) for the 4+ charge state and the O_{II} site for the 0 and 1– charge states. Both the O_I and O_{II} sites are threefold coordinated by Ga atoms.
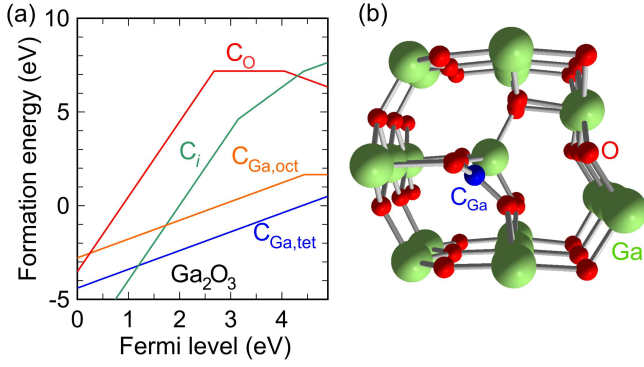
FIG. 3. (color online) (a) Formation energy versus Fermi level for C_{Ga}, C_O, and C_i in Ga_2O_3 under O-rich conditions. (b) Atomic configuration of $C_{Ga,tet}$ in Ga_2O_3.

For Fermi levels between 0 and 2.68 eV above the VBM, C_O is stable in the 4+ charge state. C_O^{4+} moves off the oxygen lattice site to form bonds with two O atoms with bond lengths of 1.30 Å . For E_F between 2.68 eV and 4.05 eV above the VBM, C_O^0 is the most stable charge state. At 4.05 eV above the VBM of Ga_2O_3, C_O transitions from the neutral to the − charge state. For both neutral and − configurations, only breathing-mode relaxations occur around C_O.

We find that C_i incorporates on a site close to three O atoms, forming C-O bonds 1.25-1.30 Å in length. As only positive charge states are stable over the entire band gap, C_i is a shallow donor in Ga_2O_3.

Turning now to C on the Ga site, we note that Ga_2O_3 has two distinct Ga sites, one octahedrally coordinated by O and one tetrahedrally coordinated. In Fig. 3(a), we plot results for C substituting on both sites. In each case, C_{Ga} does not remain on the Ga site, and displaces away from one O nearest neighbor. The three remaining O neighbors move inwards towards C, forming 1.27-1.30 Å C-O bonds. In Fig. 3(b) we show the configuration for C_{Ga} occupying the tetrahedral Ga site ($C_{Ga,tet}$). $C_{Ga,tet}$ is stable exclusively in the + charge state within the Ga_2O_3 band gap, indicating that it will be a shallow donor. When C occupies the octahedral Ga site ($C_{Ga,oct}$), on the other hand, it acts as a deep donor, with a (+/0) transition level 4.44 eV above the VBM (and 0.43 eV below the CBM). However, the $C_{Ga,tet}$ configuration is sufficiently more stable than $C_{Ga,oct}$ (by 1.30 eV, under n-type conditions) to ensure that C_{Ga} in Ga_2O_3 will always behave as a shallow donor.

As shown in Fig. 3(a), $C_{Ga,tet}$ is also the most stable site for incorporation of C impurities compared to other configurations, unless E_F is below 1.17 eV above the VBM—a condition which is unlikely to occur in this n-type TCO. With regard to chemical potentials, we find that under n-type conditions C_O^- would become more stable then $C_{Ga,tet}^+$ only when $\mu_O < -2.66$ eV, a condition which is, again, unlikely to occur during growth or processing. We conclude that the most likely form of C
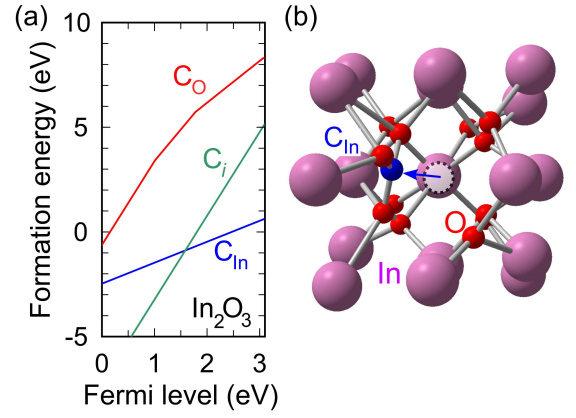

FIG. 4. (color online) (a) Formation energy versus Fermi level for C_{In}, C_O, and C_i in In_2O_3 under O-rich conditions. (b) Atomic configuration of C_{In} in In_2O_3. The position of the nominal substitutional site from which C_{In} moves away (in the direction of the arrow) is indicated by the dashed circle.

incorporating in Ga_2O_3 will be $C_{Ga,tet}$, which acts as a shallow donor.

C. In_2O_3

The formation energy of carbon impurities in In_2O_3 under O-rich conditions is shown in Fig. 4(a). C_O in In_2O_3 remains on the O site, again causing only breathing-mode relaxations of the In nearest neighbors (there is only one unique O site in the In_2O_3 crystal structure [16]). Unlike in ZnO and Ga_2O_3, C_O in In_2O_3 exhibits only positive charge states. From $E_F = 0$ to 1.01 eV above the VBM, C_O is stable in the 4+ charge state; from 1.01 eV to 1.78 eV, in the 3+ charge state; and from 1.78 eV up to the CBM, C_O is stable in the 2+ charge state. Interstitial C, just like in Ga_2O_3, incorporates at a site near three O atoms, and forms C-O bonds that are 1.28 Å in length. C_i is also a shallow donor in In_2O_3, stable only in the 4+ charge state across the entire band gap.

C on the In site, finally, moves away from the substitutional lattice site, similar to Ga_2O_3. In atoms in the bulk In_2O_3 crystal structure are normally six-fold O coordinated. However, the lowest energy position for C_{In} is to move off the In lattice site and become threefold coordinated to O atoms. In this configuration, C forms C-O bonds with bond lengths of 1.27 Å, 1.28 Å, and 1.31 Å. The three remaining O neighbors that do not bond with C become three-fold In-coordinated, with doubly occupied dangling bonds (lone pairs). This configuration is shown in Fig. 4(b). As was the case in Ga_2O_3, C_{In} is stable only in the + charge state within the In_2O_3 band gap, which indicates shallow-donor behavior. Although there are two distinct In positions in In_2O_3 [16], we find that both sites have very similar behavior when occupied by C: they exhibit nearly identical atomic configu-

rations, shallow donor behavior, and formation energies which differ by only 0.10 eV.

All forms of C in In_2O_3 are present only in positive charge states, meaning that C will act as a shallow donor regardless of the chemical potential conditions.

IV. DISCUSSION

A. Trends in behavior of C impurities in transparent conducting oxides

In each of the three TCOs studied here, our results indicate that C prefers cation-site occupation where it forms strong C-O bonds and acts as a shallow donor. In ZnO, C_{Zn} thus acts as a double donor, since it contributes four valence electrons and substitutes for Zn, which has two valence electrons. In the cases of In_2O_3 and Ga_2O_3, where the cations contribute three electrons, C_{Ga} and C_{In} are single donors.

While the behavior of the various configurations of C impurities is qualitatively similar in the three oxides, intriguing quantitative differences occur. In particular, in In_2O_3 C_O is exclusively a shallow donor, while in ZnO and Ga_2O_3 C_O is amphoteric and also exhibits negative charge states. For C_i, we only find the 4+ charge state stable in In_2O_3, while in ZnO and Ga_2O_3 C_O charge states lower than 4+ also occur. The difference can be explained by noting the band alignment between the materials studied here, which shows that In_2O_3 has the lowest-lying CBM [40]. Hence, the right-hand side of the formation-energy plot in Fig. 4 (where C_O would presumably become negatively charged, and other charge states of C_i would occur) is effectively "cut off."

B. Implications for applications in transparent conductors, transistors, and dilute magnetic semiconductors

The use of transparent conductors is still rising rapidly, and the demands on conductivity are becoming more stringent. In the expanding field of photovoltaics, lower-resistance contacts can beneficially affect efficiency.[41] TCO-based window coatings, for both active and passive control of reflection and absorption, are a crucial aspect of energy-efficient building design [42]. In_2O_3 (particularly, Sn-doped In_2O_3, or ITO), ZnO, and SnO_2 are currently the most widely used materials for these applications. (As noted in the Introduction, we did not include SnO_2 in our study because C is isoelectronic with the Sn cation and hence cannot act as a donor.) In active matrix displays, the higher mobility of TCOs compared to amorphous silicon[43] enables increased video rates. Amorphous oxide alloys composed of ZnO, In_2O_3 and Ga_2O_3 (InGaZnO$_x$ or IGZO for short) are already being used in commercial applications for this purpose.[43]

But for each of these applications, identifying suitable donor dopants that lead to increased conductivity without any side effects (such as instabilities) is still a concern. In ZnO, Ga and Al are common dopants, while in In_2O_3, Sn and Ge are frequently employed [41]. It has been noted that obtaining highly conductive Al-doped ZnO is difficult under oxidizing conditions[41]. For IGZO compounds, adjusting of O partial pressures has been used to influence conductivity, though this can lead to unwanted effects [44].

Our results indicate that carbon, which is already unintentionally present in many TCOs, is an attractive candidate for donor doping. A high solubility is required, and indeed we find that C_{cation} has modest formation energies under O-rich conditions, even in n-type material (where the formation energy of donors is highest). Under such conditions, C_{Zn} in ZnO has lower formation energies than donor impurities such as Si_{Zn} and Ge_{Zn} [17]. Similarly, in In_2O_3, C_{In} has a formation energy lower than the Sn_{In} donor under O-rich conditions [12], and also lower than H_i [35]. At the same time, the much higher formation energies of competing configurations such as interstitial C or C_O indicate that C_{cation} will be a robust shallow donor with little risk of self-compensation.

We also note that in both ZnO and In_2O_2, C_{cation} is significantly lower in energy than competing native defect donors under O-rich conditions. C_{Zn} is calculated to be more than 5 eV lower than previous HSE-calculated values for Zn_i in ZnO, and 2 eV more stable than the deep V_O donor when $\mu_O = 0$ eV [9]. In In_2O_3, the formation energy of C_{In} is 5 eV lower than previous LDA+U-calculated values of V_O and In_i [45].

Gallium oxide is currently not yet pursued as a TCO in its own right, although with its band gap of 4.87 eV it could be highly attractive for applications that require transparency in the ultraviolet (UV). The fact that it can be doped n-type at all [46] makes it fairly unique among semiconductors with such a large band gap, and it is being investigated for use in UV optoelectronic devices, such as deep-UV photodetectors [47, 48] and solar cells [49, 50]. Other applications include high-temperature gas sensors [51] and electroluminescent displays based on transition-metal doped Ga_2O_3 [52]. A recent surge of activity has focused on high-power electronics: high-voltage metal-semiconductor field-effect transistors [53], nanomembrane field-effect transistors [54], and Schottky barrier diodes [55, 56] have already been demonstrated. The availability of high-quality single-crystal substrates [46, 57, 58] raises the prospect of widespread use and commercialization. Control of n-type doping is still an issue for these applications; Sn has been the most widely used donor, but the highest achievable carrier concentrations (10^{19} cm^{-3} in Ref. 56) are lower than in other TCOs. Our results show that C_{Ga} in Ga_2O_2 has a lower formation energy than Sn, Si, and Ge dopants under O-rich conditions, and its formation energy is also lower than that of the interstitial hydrogen shallow donor, H_i [11, 35]. Again, C_{Ga} is so much more

stable than other configurations that self-compensation is not a problem. Furthermore, under O-rich conditions, we find that the shallow C_{Ga} is 4 eV lower in energy than the deep V_O donor [11].

Since C_{cation} exhibits shallow-donor behavior in all three oxides we propose that in oxide alloys composed of ZnO, In_2O_3 and Ga_2O_3, C impurities will also cause n-type conductivity. In such these IGZO alloys, achieving full control of electrical conductivity remains an issue, and no systematic studies of impurities have been performed [43]. An ongoing concern in IGZO-based transistors is the presence and generation of traps which can lead to threshold voltage instabilities [59]. An impurity such as carbon, which easily could be present unintentionally or can be used as an active donor, should therefore also be evaluated from the point of view of acting as a potential trapping center. This would especially be a risk if carbon would incorporate on the oxygen site (C_O) as has been posited previously [20]. However, our present results indicate that C will incorporate only on the cation site in all three constituents of IGZO, over a wide range of chemical potential and electronic conditions. We can thus rule out carbon as a source of carrier trapping in these oxides, a result that could not have been anticipated without the type of comprehensive first-principles study reported here.

Finally, ZnO:C has been proposed as a dilute magnetic semiconducting (DMS) system [20] due to the presence of C_O. Regardless of concerns [60] over whether such species could actually lead to ferromagnetism, the results presented here indicate that C_O is highly unlikely to incorporate into ZnO except under the most extreme chemical potential conditions. This suggests that previous results indicating DMS behavior in ZnO:C should be reconsidered. Furthermore, since our results indicate that C in In_2O_3 will also give rise to shallow donor behavior, with little likelihood of C_O incorporation, similar concerns apply to claims of DMS behavior in In_2O_3:C [23].

V. CONCLUSIONS

Employing hybrid density functional calculations, we have investigated the properties of carbon impurities in ZnO, Ga_2O_3, and In_2O_3 as a function of electronic Fermi level and chemical potential. By considering all relevant charge states of substitutional and interstitial C impurities, we are able to conclude that C impurities behave consistently as shallow donors within these TCOs, incorporating on a cation site. For applications of these oxides, it is important to be aware that unintentional incorporation of carbon (a ubiquitous impurity) may contribute to background n-type doping. But carbon also emerges as a robust n-type dopant with higher solubility than many of the currently used donors and no side effects such as self-compensation or trapping. Intentional carbon doping may thus be a pathway to achieving higher free-electron concentrations in this class of oxides.

ACKNOWLEDGMENTS

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