Limits to doping in oxides

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The chemical trends of limits to doping of many semiconducting metal oxides is analyzed in terms of the formation energies needed to form the compensating defects. The n-type oxides are found to have high electron affinities and charge neutrality levels that lie in midgap or the upper part of their gap, whereas p-type oxides have small photoionization potentials and charge neutrality levels lying in the lower gap. The doping-limit energy range is found to vary with the bulk free energy of the compound.

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I. INTRODUCTION

Metal oxides display a wide range of useful electronic functionality, such as magnetoresistive, superconducting, or multiferroic properties.1–4 The behavior of free carriers in SrTiO3 induced by polar surface doping has created widespread interest.2,3 At the same time, there is considerable effort to develop metal oxides such as ZnO as wide-band-gap light-emitting and high-mobility semiconductors,5,6 to use amorphous semiconducting oxides such as InGaZnO, as a higher-mobility channel material instead of amorphous silicon in thin-film transistors for large-area electronics,7,8 and to use the unusual properties of TiO2 in photoelectrochemistry for energy conversion and environmental cleanup.9–11 The latter applications require an ability to dope the oxide in a unipolar fashion and preferably in a bipolar fashion. The standard transparent conducting oxides can be heavily doped n-type, even in their amorphous phases, because of their ionic bonding,8,12 in contrast to covalently bonded a-Si, whose doping efficiency is severely impaired in the amorphous phase.13,14 Amorphous phases are particularly useful for large-area, low-cost electronics.8 On the other hand, p-type doping of oxides is rare, and there has been a significant effort to find practical p-type oxides.14–19 It is therefore useful to have guidance on the limits to doping of the various oxides in terms of their energy band alignments by using the pinning energy concepts introduced previously by Walukiewicz,20,21 Zhang et al.,22,23 and Zunger24 for the tetrahedrally bonded semiconductors.

Here we analyze the systematics of doping in oxide systems using the concept of pinning energy rule, and we derive their n-type pinning energy and p-type pinning energy. We find that the dopability of oxides can be viewed in terms of the valence band maximum and the conduction band minimum on an absolute energy scale or with respect to a common alignment energy such as the charge neutrality level derived from their band structures. The well-known n-type oxides (Zn, In2O3, and SnO2) are found to have conduction band edges deep below the vacuum level, while the known p-type oxides (NiO, Cu2O, CuAlO2, CuGaO2, and CuCrO2) have high-lying valence band edges. The analysis also predicts that TiO2 and SrTiO3 will be difficult to dope p-type.

Three factors can limit the ability to dope a material effectively: a lack of dopant solubility, the dopant level being too deep and unionizable, or the dopant being compensated by native defects. The key limitation is compensation by native defects. This occurs if moving the Fermi energy to a band edge causes the spontaneous formation of compensating defects because the formation energy of that defect has fallen to zero at that Fermi energy. This requires us to know the formation energies of the native defects of the various oxides.

II. METHOD

The defect-formation energies of the various oxides were calculated by the ab initio plane wave pseudopotential method. Generally, this would use the local density formalism (LDF) to approximate the electronic exchange-correlation energy. However, this leads to an underestimate of the band gap, which is a particularly severe problem for the transparent conducting oxides. To overcome this problem, we use hybrid density functionals to represent the exchange-correlation energy.25–29 These are accurate enough to give good band gaps while being efficient enough to be useful for calculations on supercells of up to 100 atoms. They have the advantage that they are true functionals, so that they can be used in energy minimizations.

We have used the screened exchange (sX) hybrid density functional.25,26 Screened exchange includes a short-range component of Hartree-Fock exchange. The sX functional replaces all the LDA exchange with a Thomas-Fermi screened Coulombic exchange potential, but retains the LDA version of correlation potential.26

\[ V_{\text{sX}}(r,r') = - \sum_i \frac{\psi_i(r) \psi^*_i(r')}{|r - r'|} + \delta_{\text{loc}}(\rho) \]

\[ - \int V_{\text{sX}}^\text{LDA}(\rho) F(\rho) \rho(r) dr, \]

where, i and j label the electronic bands, \( k_x \) is the inverse Thomas-Fermi screening length, \( \delta_{\text{loc}} \) is the exchange-correlation energy per electron as given by the LDA, and \( V_{\text{sX}} \) is the nonlocal exchange-correlation energy per electron evaluated in a homogeneous electron gas of density \( \rho \). \( k_x \) is evaluated from the valence electron density, as given in Ref. 26, omitting shallow d core electrons. This has recently been implemented for a plane wave basis set in the CASTEP code.30

Clark and Robertson26 have calculated the band gaps of a wide range of semiconductors and insulators by the sX method.
and it is found to give the minimum band gaps for the relevant oxides within 0.1 eV of their experimental values.

To extend the range of oxides covered, we also used defect-formation energy data from other groups who used the closely related Heyd, Scuseria, Ernzerhof (HSE) hybrid functional.27,28 HSE includes a fraction of the short-ranged component of the Hartree-Fock exchange, with a different screening length to sX. To date, the band gaps found by sX and HSE06 functionals for the various oxides are very similar, both being close to experiment, despite their different functional form. This is partly because the screening length in HSE06 was fitted to optimize the band gaps. Komsa et al.33 have discussed how the band-gap and defect-formation energies in practice vary relatively little with the functional.

This allows the defect-formation energies to be calculated.31–43 The sX method was used for defect-formation energies of ZnO,31 HfO2,32 TiO2,33 and Cu2O. Defect-formation energies from HSE are used for ZnO by Oba et al.,34 Agoston et al.,35 and Clark et al.,31 for TiO2 by Janotti et al.36 and Morgan and Watson,37 for Cu2O by Scanlon and Watson,38 and for CuAlO2 by Scanlon and Watson.39

The formation energy $H_\alpha$ of the defect of charge $q$ as a function of the Fermi energy ($\Delta E_F$) from the valence band edge $E_V$ and the relative chemical potential ($\Delta \mu$) of element $\alpha$ is expressed as

$$\Delta H_\alpha(\mu, E_F) = E_q - E_H + q(E_V + \Delta E_F) + \sum \mu_{\alpha,0} n_{\alpha}(\mu_{\alpha,0} + \Delta \mu_{\alpha}),$$  
(2)

where $\mu_{\alpha,0}$ is reference chemical potential of element $\alpha$ and $n_{\alpha}$ is the number of atoms of element $\alpha$. $\Delta E_F$ is the Fermi energy with respect to the valence band edge. The charge state and cell size corrections to the defect-formation energies are handled by the method of Lany and Zunger.44

The doping-limit energies are later displayed on a band alignment diagram. For this, the band edges of each oxide $(a,b)$ were aligned in either the Schottky or the Bardeen limit. In the Schottky limit, there is no charge transfer across the interface, and the conduction band offset $\phi_n$ is given by the difference in electron affinities of $a$ and $b$,

$$\phi_n = (\chi_a - \chi_b).$$  
(3)

as in the electron affinity rule. More usually, there is charge transfer at the interface. One model, which assumes that the interfaces bond on their nonpolar faces and neglects specific atomic models of the interfaces, proposes that the lineup is controlled by the line of charge neutrality levels,

$$\phi_n = (\chi_a - \Phi_{S,a}) - (\chi_b - \Phi_{S,b}) + S(\Phi_{S,a} - \Phi_{S,b})$$  
(4)

where $S$ is the Schottky barrier pinning factor, and $S = 0$ corresponds to the strongly pinned or Bardeen limit. $\chi_a$ is the electron affinity of oxide $a$, and $\Phi_{S,a}$ is the charge neutrality level of oxide $a$. This approximation holds for nonpolar interfaces.

III. RESULTS AND DISCUSSION

Figure 1 plots the formation energy of the most stable charge state of the most stable donor-type and acceptor-type native defects for various oxides as a function of the Fermi energy $E_F$, for both O-rich and metal-rich (O-poor) conditions. The slope of the lines is the stable charge state at that value of $E_F$. O-rich conditions correspond to the chemical potential ($\mu_O$) of O in the O$_2$ molecule, $\mu_O = 0$. The O-poor conditions correspond to $\mu_O$ equal to the metal/metal oxide equilibrium, or $\mu_O$ equaling the free energy per O of the bulk oxide.

We apply Eq. (2) to consider the native defects in the case of ZnO, in response to doping. Figure 1(a) shows the formation energies of defects in ZnO by the sX method.31 (Very similar values are found using HSE).34 If a donor (e.g., Al$_{Zn}$) is used to raise $E_F$ toward the conduction band edge $E_C$, we must consider the formation energy of possible negatively charged compensating acceptors such as Zn vacancies ($V_{Zn}$) or oxygen interstitials. Consider first the case of O-poor ZnO, with an O chemical potential $\mu_O = -3.37$ eV. Figure 1(a) shows that $V_{Zn}^-$ is the most stable of these two defects, but $V_{Zn}^{2-}$ still has...
a large positive formation energy (<3 eV) when \( E_F \) is at \( E_C \). \( E_F \) would have to be raised to 5.2 eV, 1.8 eV above \( E_C \), for Zn vacancies to form spontaneously. This energy is called the "n-type pinning energy" for donors.

On the other hand, if an acceptor dopant is used to lower \( E_F \) toward the valence band edge \( E_V \), we consider the formation energy of compensating donor defects such as O vacancies \( V_O \) or Zn interstitials. \( V_O \) is slightly the more stable of the two. Figure 1(a) shows that in the O-poor limit \( V_O \) has a negative formation energy if \( E_F \) drops below 1.8 eV above \( E_V \). Oxygen vacancies will spontaneously form if \( E_F \) moves toward \( E_V \) and opposes the p-type doping. The 1.8 eV is called the "p-type pinning energy." The energy range where we can shift \( E_F \) without spontaneously creating compensating defects is between these two limit energies, and equals 3.4 eV.

The same analysis applies to O-rich conditions. Figure 1(b) shows that the n- and p-type pinning energies both fall by 1.7 eV (this is the calculated free energy of bulk ZnO divided by 2, the charge of the defects). However, the energy range for which any native compensating defect does not form spontaneously is still 3.4 eV, from 0.2 to 3.6 eV. This is one reason that ZnO can only be doped n-type. As such, ZnO is representative of a number of conducting oxides such as SnO\(_2\) and In\(_2\)O\(_3\).

Figure 2(a) shows the free energy of various bulk oxides per O atom plotted against the work function (electron negativity) of the parent metal. Now consider HfO\(_2\), an oxide that is difficult to dope. It is a highly stable wide band-gap insulator used in electronics. Figure 1(c) shows that its most stable native defects are the O vacancy and the O interstitial. The data in Fig. 1(c) include the sX results of Xiong et al. for the O vacancy, and the generalised gradient approximation (GGA) results of Zheng et al. for the O interstitial. (Note that the O interstitial in HfO\(_2\) involves only occupied O valence states, which should be adequately handled by GGA.) In O-poor conditions, if we shift \( E_F \) toward \( E_C \) by n-type doping, then the O interstitial \( \text{I}^2 \) will spontaneously form for \( E_F \) lying above 5.1 eV, the n-type limit, where its formation energy goes negative. On the other hand, if we lower \( E_F \) toward \( E_V \), then O vacancies spontaneously form for \( E_F \) lying below 3.8 eV, the p-type pinning limit. The energy range over which no defects spontaneously form is now quite narrow, only 1.3 eV, from 3.8 to 5.1 eV. In the O-rich case in Fig. 1(d), the pinning limits shift to lower in the band gap, but its magnitude stays the same. HfO\(_2\) illustrates the case of a difficult-to-dope oxide, with a narrow doping range, impossibly far from the band edges.

Figures 1(e) and 1(f) show the case of TiO\(_2\), an important catalytic and electrochemically active oxide with a high bulk free energy. This uses data from the HSE06 results of Janotti et al., the LDA+U results of Morgan and Watson, and some sX results of Clark et al. TiO\(_2\) can also represent the energetics of doping in SrTiO\(_3\) in that this depends mainly on the TiO\(_2\) sublattice energies, TiO\(_2\) having a lower free energy per O than SrO [Fig. 2(a)]. Figure 1(e) shows the defect-formation energies, \( \mu_{\text{O}} = -4.07 \) eV. In O-poor conditions, if we shift \( E_F \) toward \( E_C \), then the possible compensating acceptors, O interstitials, still have a high formation energy. Thus, TiO\(_2\) is easily doped n-type. If we lower \( E_F \) toward \( E_V \), the formation energy of donors such as the O vacancy becomes negative for \( E_F \) below 2.1 eV above \( E_V \). The energy range between the n- and p-type pinning limits is 2.7 eV. In O-rich conditions, the pinning limits shift to lower energies, so that the p-type pinning limit falls to 0.3 eV above \( E_V \). The O-poor case is more relevant. However, as the p-type limit lies above the valence band edge in both the O-poor and the O-rich cases, Figs. 1(e) and 1(f) indicate that it will be very difficult to dope TiO\(_2\) or SrTiO\(_3\) p-type, without causing compensation, because the p-type pinning limit lies so high in its band gap. It is therefore unlikely that SrTiO\(_3\) can be made a bipolar semiconductor by electronic doping.

Figure 1(g) shows the case of Cu\(_2\)O, a less strongly bonded p-type oxide, using the HSE06 data of Scanlon and Watson and the GGA data of Raebinger et al. (Raebinger et al. applied correction methods to account for the band-gap error; Clark et al. finds similar vacancy formation energies for Cu\(_2\)O by the sX method.) We see that shifting \( E_F \) above 1.1 eV causes the formation energy of Cu vacancy acceptors to become negative. These states compensate any external donors. On the other hand, \( E_F \) can be shifted down to \( E_V \) by external acceptors without causing any native donor (O vacancy) to have a negative formation energy. Thus, they are uncompensated. The energy range between doping limits is 1.7 eV in Cu\(_2\)O. Thus, Fig. 1(g) shows that Cu\(_2\)O is possible to dope p-type.

FIG. 2. (Color online) (a) Bulk free energy of oxides per O atom versus the work function of the parent metal with data from Robertson et al. (Ref. 46). (b) Energy range between n-type and p-type doping limits vs bulk free energy/O atom, for the various oxides shown in Fig. 1.

075205-3
Figure 1(h) shows the equivalent doping limits for CuAlO$_2$ using the defect-formation energies calculated by Scanlon and Watson$^{40}$ by HSE. They find a band gap of 3.5 eV. The compensating defects are still the O vacancy and the Cu vacancy. The Cu vacancy compensates donors and has similar characteristics to that in Cu$_2$O, with its formation energy passing through zero at $E_F = 2.0$ eV. On the other hand, the O vacancy is much more stable, with a formation energy of $+4.6$ eV in its neutral state, compared to only $0.8$ eV in Cu$_2$O. Thus, the O vacancy formation energy only passes below zero for $E_F$ below $-1.5$ eV. This gives a doping energy range of 3.5 eV, similar to that in ZnO. The critical feature is that the strong Al-O bonds have formed a framework which anchors the O atoms into it. This makes O vacancies more costly and makes doping more difficult to compensate.

Previous analyses of doping limits have implicitly assumed that the doping energy range is approximately constant. Figure 2(b) shows the pinning energy range $\Delta E$ vs the oxide free energy per O atom of Fig. 2(a). We see that $\Delta E$ is not constant; it follows a chemical trend. $\Delta E$ first increases with the bulk free energy of the oxide. This is to be expected as the cost of an oxygen vacancy would increase for oxides with a higher free energy. Then, for the ionic oxides like TiO$_2$ and HfO$_2$, $\Delta E$ decreases, as O interstitial defects become the lower-cost donor than metal vacancies, and their presence curtails the possibility of $n$-type doping in the oxide. On the other hand, it is possible to obtain a more constant $\Delta E$ in a framework structure such as CuAlO$_2$ in which all O’s are below zero for their valence and conduction band energies plotted against the vacuum level.

The pinning-limit energies for the various oxides in the O-poor limit can be assembled into a band diagram, first for bands aligned according at the Schottky limit. This is shown in Fig. 3. We see that the $n$-pinning limit lies at a reasonably constant energy for ZnO, SnO$_2$, TiO$_2$, and CuAlO$_2$. Similarly, the $p$-limit energy also lies at a reasonably constant energy for these compounds. (Preliminary calculations suggest that the defect energetics of SnO$_2$ are similar to those of ZnO and TiO$_2$.) For Cu$_2$O and HfO$_2$ the pinning energies lie closer together.

It is useful to extend this to a wide range of oxides, to make predictions for oxides for which there are no explicit calculations of defect-formation energies. To do this, we assume that the pinning energies lie at constant energies, as in Walukiewicz,$^{21}$ taking the values given in ZnO and CuAlO$_2$ for their O-poor regime. They are plotted on global band diagrams in Fig. 4. Figure 4(a) shows the case where the band offsets of the oxides are shown in the “Schottky limit,” using electron affinities and ionization potentials as determined by photoemission or electrochemistry (Table I).$^{14,47-53}$ The data for the conducting oxides ZnO, In$_2$O$_3$, SnO$_2$, Cu$_2$O, CuAlO$_2$, CuInO$_2$, and SrCu$_2$O$_2$ are from Hosono,$^{48}$ those for the nitrides are from Ref. 50, and those for TiO$_2$ are from Gratzel.$^{11}$ The experimental data for SrTiO$_3$ and LaAlO$_3$ are from Chambers et al.$^{51}$ and Edge et al.$^{52}$ The SrTiO$_3$:LaAlO$_3$ interface has most of its 2.4-eV-wide band-gap mismatch taken up as a near 2-eV conduction band offset, with a small offset in the valence band, according to Chambers et al.$^{53}$ The data for CuCrO$_2$ is from Benko.$^{14}$ Its band gap is similar to that of CuAlO$_2$.$^{44}$ BiFeO$_3$ data is estimated.$^{35}$ The work function of (La,Sr)MnO$_3$ (LSMO) is from Ref. 56. Figure 4(b) shows band alignments in the “Bardeen limit,” in which screening causes the offsets to align their charge neutrality levels (CNLs). The CNL is the branch point of the complex band structure, where
the character of the gap states changes from valence band to conduction band like.\textsuperscript{57} Calculated and experimental CNL values are used.\textsuperscript{58–63} The chemical trends of band alignments are seen to be similar in both cases.

\(N\)-type and \(p\)-type pinning-limit energies are plotted in Fig. 4. It is convenient at first to treat the pinning limits as independent of the oxide. The explanation of Fig. 4 is as follows. The pinning-limit energies set the range over which \(E_F\) can be varied, without causing the formation of compensating defects that stop doping. If the \(n\)-type limit lies above \(E_C\) of that oxide, \(E_F\) can be shifted to \(E_C\) without defect formation and it can be doped \(n\)-type. If the \(p\)-type limit is below \(E_V\), then that oxide can be doped \(p\)-type without defect formation. Figure 4(a) says that the criterion for \(n\)-type dopability is that the electron affinity should be large (\(E_C\) well below the vacuum level), while \(p\)-type dopability requires the valence band ionization potential to be small (\(E_V\) not too far below the vacuum level). Figure 4(b) says that the criterion is that the CNL should lie in midgap or the upper gap for \(n\)-type dopability, or at midgap or in the lower gap for \(p\)-type dopability.

The \(n\)-type transparent conducting oxides stand out in having large electron affinities and also having CNLs that lie in their upper gap or indeed in the conduction bands. However, the corollary is that ZnO, In\(_2\)O\(_3\), and SnO\(_2\) have too-deep valence band edges to be doped \(p\)-type. TiO\(_2\) and SrTiO\(_3\) also fall into this category, their valence band edges are too deep below the vacuum level. The alloying of La with Sr in LSMO to achieve hole doping can be considered to be an interstitial doping of a framework structure. We see that the Fermi level lies within its doping limits so that we do not expect the hole doping to cause a compensation response in this compound.

For \(n\)-type oxides, these results largely confirm what is already known for ZnO from more detailed studies. \(P\)-type doping will be highly compensated and is favored by a high-O chemical potential. A way to avoid compensation is to avoid the defect concentrations reaching equilibrium. Also, as noted in Ref. 66, defects and dopants at grain boundaries have different formation energies, which might be exploited to obtain a \(p\)-doping response.

The overall model shows that the situation can be generalized to similar oxides such as SnO\(_2\), TiO\(_2\), and SrTiO\(_3\) even if there is not the same level of detailed calculations for these cases.

The \(p\)-type oxides Cu\(_2\)O, CuAlO\(_2\), CuCrO\(_2\), SrCu\(_2\)O\(_3\), and NiO all have low ionization potentials so that their valence band edge lies above the \(p\)-type limit in Fig. 4(a). This correlates with their \(p\)-like character. CuInO\(_3\) can be doped in both directions because its smaller gap allows its \(E_C\) to lie below the \(n\)-type pinning limit. It shows that the principle of Kawazoe\textsuperscript{15} to make \(p\)-type oxides, of using the Cu\(_{d^1}\):O \(2p\) hybridization to broaden the valence band and lower its effective mass, also works because it raises \(E_V\) toward the vacuum level. The prime example of this effect is in NiO caused by Ni\(_{3d}\):O \(2p\) hybridization. It also occurs in CuCrO\(_2\). The defect properties of the \(p\)-type oxides have only recently been studied. The benefit of the present work is that it applies a global model and shows that they behave in a manner expected from other systems.

The comparison of the greater doping ability of CuAlO\(_2\) than that of Cu\(_2\)O is valuable. It shows that the principle advantage of CuAlO\(_2\) is not just its wider band gap, making it transparent, but that its strongly bonded framework of Al-O bonds gives it much improved defect properties which inhibit dopant compensation. The same basic mechanism was proposed for amorphous InGaZnO\(_3\) semiconductors as used in thin-film transistors (TFTs).\textsuperscript{8} Ga is added to InZnO to increase the cost of O deficiency, to thereby reduce the background conductivity of the undoped material and the off-current of the TFT.

A further question is if wide-gap oxides like ZnO usually only show unipolar doping, why can nitrides (GaN) with the same band gap show bipolar doping?\textsuperscript{64} Figure 5 shows the formation energy diagram for the lowest energy defect for GaN. In Ga-rich GaN, the least costly defect turns out to be the N vacancy\textsuperscript{65} over the full range of \(E_F\) around the gap. This is due to its charge states. The lower slope for \(V^+\) in the formation energy diagram in Fig. 5 leads to a larger \(\Delta E\) range for GaN than for ZnO. Luckily, this range actually spans the band gap of GaN, rather than being asymmetrically disposed, so that the \(n\)- and \(p\)-type pinning limits fall just outside its band gap. It can therefore be doped both \(n\)- and \(p\)-type without compensation.

It is also useful to consider the second factor that limits doping, the deepness of the dopant level within the band gap.\textsuperscript{66–68} It has recently been noted that the substitutional N site is at least 1 eV deep in ZnO and consistent with ESR data\textsuperscript{69} which showed a localized hole state.\textsuperscript{66,67} On the other hand, substitutional N\(_2\) is well known to form a deep level in TiO\(_2\).\textsuperscript{70} Similarly, substitutional Mg in GaN is only a

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Data from Ref. 65. GaN, showing that its doping limits lie just outside its band gap. These cases show that systems which are difficult to dope in terms of compensation can also be difficult to dope in terms of the depth of the levels. Both factors follow the same basic chemical trends.

**IV. SUMMARY**

The limits to doping in metal oxides have been calculated from their defect-formation energies. The chemical trends of limits to doping of many metal oxides are plotted on a band lineup diagram, in terms of doping pinning energies. Oxides which can be doped $n$-type are found to have high electron affinities and charge neutrality levels that lie in midgap or the upper part of their gap. Oxides that can be doped $p$-type have small photoionization potentials and charge neutrality levels lying in the lower gap. TiO$_2$ and SrTiO$_3$ have low probability of being able to be doped $p$-type. There are advantages in using complex oxides such as CuAlO$_2$ to inhibit the formation of compensating defects.

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