Origins of the *p*-type nature and cation deficiency in Cu_2O and related materials

Hannes Raebiger, Stephan Lany, and Alex Zunger
National Renewable Energy Laboratory, Golden, Colorado 80401, USA
(Received 20 February 2007; published 16 July 2007)

While most of crystalline wide gap oxides are both stoichiometric and insulating, a handful of them including ZnO and In_2O_3 are naturally anion-deficient and electron conductors. Even fewer of the oxides are naturally cation-deficient and hole conductors, the arch-type of which is Cu_2O. Based on first principles calculation of equilibrium nonstoichiometry and defect stability, we explain why the $Cu^{(I)}(d^{10})$ oxide-based materials are both *p*-type and naturally cation-deficient, and why cation vacancies lead to delocalized, conductive states, whereas in other oxides (e.g., ZnO and MgO), they lead to localized, nonconductive states.

DOI: 10.1103/PhysRevB.76.045209 PACS number(s): 71.55.−i, 71.20.−b, 72.20.Jv, 72.80.Jc

I. INTRODUCTION

Most crystalline wide gap oxides are both stoichiometric and electrically insulating.[1,2] Yet, a small group of oxides are naturally anion-deficient and electron conductors[3,4] (e.g., ZnO with $E_g=3.45$ and In_2O_3 with $E_g=3.5$ eV). Even a smaller group are naturally cation-deficient and hole conductors. The arch-type of the latter is cuprite Cu_2O ($E_g=2.1$ eV), and the group includes related $Cu^{(I)}(d^{10})$ oxide materials such as CuM_2O (delafossite with M=Al, Ga, In),[5] $SrCu_2O_2$,[6] and oxychalcogenide *Ln*CuO*X* (*Ln*=lanthanide, *X*=chalcogen).[7] Such *p*-type conductive oxides are interesting as some of them are transparent, and combined with known *n*-type transparent conductive oxides facilitate the design of transparent electronics. Standard structural inorganic chemistry[2] explains in broad terms that an oxide will naturally be cation-deficient if its cation is oxidizable, i.e., can have a more positive oxidation number. Indeed, the existence of an oxide compound with higher oxidation number of the metal cation indicates the propensity of the oxide to exist in a more cation-deficient composition (e.g., $Cu_2^{(I)}O$ and $Cu^{(II)}O$). In this work, we aim to explain quantitatively (i) how such conditions are accommodated microscopically, given that the cation deficiency could occur via metal vacancies, and/or oxygen interstitials, and/or oxygen antisites; (ii) what is the solubility limit of such defects in the host crystal, i.e., maximum concentration before they precipitate; and finally (iii) how the cation deficiency leads to *p*-type conductivity via free holes. Based on first principles calculation of equilibrium nonstoichiometry and defect stability, we address these questions here for Cu_2O. We find that in Cu_2O, (i) the cation deficiency is accommodated mostly by Cu vacancies (V_{Cu}) rather than oxygen interstitials (O_i), (ii) the stable concentration of V_{Cu} can reach $\sim 10^{20}$ cm^{-3}, and (iii) the V_{Cu} induces a host-derived acceptor level naturally making Cu_2O *p*-type, but the concentration of free holes at room temperature only reaches $\sim 10^{18}$ cm^{-3} as not all V_{Cu} are ionized to produce holes. Finally, we provide general design rules for *p*-type oxides.

Following the discovery of *p*-type nature in $Cu^{(I)}(d^{10})$ oxide compounds, it was speculated[5–8] that this *p*-type nature emerges from the introduction of covalency into the otherwise ionic metal-oxide network, thus avoiding localization of the holes around the negatively charged oxygen ions. However, the special feature of *p*-type oxides distinguishing them from conventional oxides is the existence of a stable and large concentration of holes; while introduction of covalency broadens the band and may lead to *lighter* effective masses and hence better carrier mobility, this property *does not enable* the creation of holes in the first place. Indeed, equilibrium creation of a substantial concentration of holes in a pure crystalline solid requires[9] (i) low formation energy of point defects that are *hole producers*, e.g., native acceptors such as cation vacancies; (ii) a small ionization energy for these defects so as to readily release holes (i.e., a shallow acceptor level with respect to the host valence band); and most crucially (iii) a high formation energy of native defects that are *hole killers* (e.g., native donors such as cation interstitials and anion vacancies). It turns out that the latter condition is rather difficult to meet in wide gap systems where the deliberate introduction of holes tends to spontaneously instigate the creation of structural hole killers. Additionally, for a *good p-type conductor*, the valence band should be highly disperse and delocalized, facilitating a low effective hole mass and thus high mobility. Here, we show that in $Cu^{(I)}(d^{10})$ oxide systems, (i) the Cu vacancy hole producer V_{Cu} has a low formation energy both in the cuprite structure with its linear O-Cu-O dumbbells and in the (hypothetical) antifluorite Cu_2O structure with tetrahedrally coordinated Cu. This ease of forming cation vacancies is in contrast to main group oxides with typically high cation-vacancy formation energies. The main reason for this low formation energy is the fact that the valence band maximum in copper oxides is an antibonding state mostly of $Cu^{(I)}(d^{10})$ orbitals and lies high in energy. (ii) The acceptor ionization energy $\varepsilon(0/-)$ of V_{Cu} at $E_v+0.28$ eV is relatively shallow as opposed to deep levels in, e.g., MgO, where cation vacancy causes optical absorption at 2.3 eV.[10] The reason for the shallow cation-vacancy level in Cu_2O is that the cation-vacancy levels (i.e., the anion dangling bond levels) are *below* the valence band minimum (VBM), whereas in other oxides, they are above the VBM. (iii) Even though the potential hole killer, i.e., the anion vacancy, has a rather low formation energy in Cu_2O, it has no donor level inside the band gap and thus cannot act as hole killer. Thus, the cation interstitial is the only native hole killer, but its formation energy is significantly higher than that of the hole producers, so it does not compensate holes. We conclude that Cu_2O and $Cu^{(I)}(d^{10})$ oxide systems in gen-

 ©2007 The American Physical Society

eral tend to be intrinsically p-type due to the ease of formation of cation vacancies as shallow hole producers and the lack of intrinsic potent hole killers.

II. METHODS

We calculate formation energies ΔH for various intrinsic defects and their ionization energies, as well as defect and carrier concentrations. The formation enthalpy ΔH for defect D in charge state q as a function of Fermi energy E_F is

$$\Delta H_{D,q}(E_F,\mu) = (E_{D,q} - E_H) + \sum_{\alpha} n_{\alpha}(\mu_{\alpha}^{\text{elem}} + \Delta\mu_{\alpha}) + q(E_v + \Delta E_F), \quad (1)$$

where E_H is the energy of the pure host and $E_{D,q}$ is that of defect-containing system, $\mu_\alpha=\mu_\alpha^{\text{elem}}+\Delta\mu_\alpha$ is the chemical potential of a reservoir of atoms α, and n_α is +1 or −1 if an atom is added to the reservoir or removed from it, respectively. The reference chemical potential μ_α^{elem} for metal elements is taken as that of the solid metal and for oxygen from the O_2 molecule. To maintain thermodynamic equilibrium with Cu_2O, the relation $2\mu_{\text{Cu}}+\mu_{\text{O}}=\mu_{\text{Cu}_2\text{O}}$, i.e., $2\Delta\mu_{\text{Cu}}+\Delta\mu_{\text{O}}=\Delta H_f(\text{Cu}_2\text{O})$, must hold, where $\Delta H_f(\text{Cu}_2\text{O}) = -1.26$ eV is the calculated formation energy for Cu_2O. The lower bound on μ_{O} (maximally Cu-rich/O-poor environment) is limited by Cu metal formation at $\Delta\mu_{\text{Cu}}=0$ and $\Delta\mu_{\text{O}}=-1.26$ eV. The upper bound on μ_{O} is limited by CuO formation, i.e., the condition $\Delta\mu_{\text{Cu}}+\Delta\mu_{\text{O}}\leq\Delta H_f(\text{CuO}) = -1.09$ eV yields the maximally Cu-poor/O-rich environment at $\Delta\mu_{\text{Cu}}=-0.16$ eV and $\Delta\mu_{\text{O}}=-0.93$ eV. The last term in Eq. (1) is the Fermi energy $E_F=E_v+\Delta E_F$, which ranges between VBM (or E_v) and conduction band minimum (CBM or E_c). The transition levels $\varepsilon(q/q')$ (to be distinguished from the *single-particle* eigenvalue, or orbital energy) for each defect are the value of E_F at which $\Delta H_{D,q}$ and $\Delta H_{D,q'}$ for defect D intersect. The calculated ΔH's and transition levels are then used in thermodynamic simulations to calculate the equilibrium defect concentration $c_{D,q}$ as a function of temperature as self-consistent solution to $c_{D,q}(E_F,\mu,T) = N\exp[-\Delta H_{D,q}(E_F,\mu)/kT]$, as described in Refs. 11 and 12.

The total energies E_H and $E_{D,q}$ of Eq. (1) are calculated from first principles. We employ the generalized gradient approximation (GGA-PBE) to density-functional theory using the projector augmented-wave method as implemented in the VASP code.[13] E_H and $E_{D,q}$ are calculated in supercells with 96 Cu_2O lattice sites, including a single lattice defect in various charge states q for $E_{D,q}$. We use the GGA calculated lattice constant for Cu_2O of 4.313 Å and allow all atomic positions to relax. Plane waves are included up to the cutoff energy of 400 eV together with a $4\times4\times4$ $\vec{k}$ mesh including the Γ point for total energies, while structural relaxations are performed using a $2\times2\times2$ $\vec{k}$ mesh.

The energy quantities from GGA-PBE supercell must be corrected due to a number of reasons. (1) The band gap $E_g^{\text{GGA}}=0.43$ eV is underestimated relative to the experimental gap of $E_g=2.1$ eV. The d orbitals in GGA (as in local density approximation) are typically underbound, and if the d orbitals are close to the VBM, this underbinding needs to be

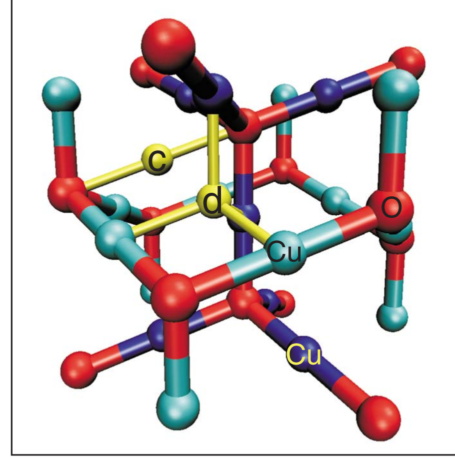

FIG. 1. (Color online) The cuprite structure of Cu_2O and possible interstitial positions. Cu and O atoms are given as blue and red spheres, respectively. The cuprite structure consists of two interpenetrating cristobalite lattices that are distinguished by using two different shades for Cu atoms in each of the lattices. Interstitial atoms are labeled "c" and "d" (yellow spheres) according to their Wyckoff positions (symmetries D_{3d} and D_{2d}, respectively).

corrected for in order to find the correct VBM energy. Therefore, we apply the GGA+U correction on the Cu(d) states to find the correct E_v; we choose U=6 and J=1 eV to reproduce photoemission experiment[14] and find that this selection pushes down E_v by 0.32 eV. Thus, we correct for the band gap error by shifting the VBM down by $\Delta E_v=0.32$ eV and the VBM up by $\Delta E_c=1.35$ eV, both shifts together correcting the total band gap error. The appropriate VBM or CBM shifts are then applied *a posteriori* to the total energies $E_{D,q}$ calculated within the GGA (without +U correction). Further corrections[15] are applied due to (2) potential alignment,[15] (3) the image charge effect[15] present in the finite supercell formalism, and (4) the band-filling effect[15] in the case of shallow defects.

Cu_2O crystallizes in the cuprite structure (space group $Pn3m$, No. 224), shown in Fig. 1. The copper and oxygen atoms have site symmetries D_{3d} and T_d, respectively. In addition to the copper vacancy V_{Cu}, we also consider the "split vacancy,"[16] which consists of two copper vacancies and a copper interstitial in site symmetry D_2 between the vacancies. There are a number of possible high symmetry interstitial positions; we consider the ones associated with largest empty volume around them, namely, those with site symmetries D_{3d} and D_{2d}, denoted with "c" and "d" (according to the Wyckoff notation), respectively, shown in Fig. 1.

III. DELOCALIZATION VS LOCALIZATION OF HOLE STATES IN OXIDES

While in many oxides, such as in MgO and ZnO, the cation vacancy introduces atomically localized, nonconductive gap levels with large ionization energies,[10,17] a few oxides, most notably, the Cu-containing oxides Cu_2O and $CuMO_2$,[5,8,18] show p-type conduction, presumably originating from Cu vacancies. Such p-type conductivity requires

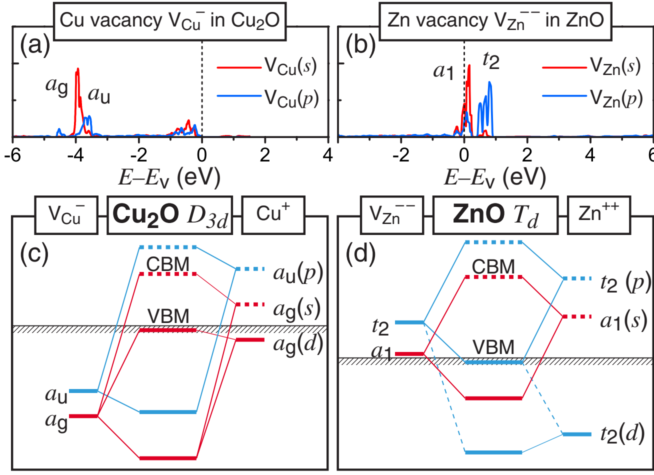

FIG. 2. (Color online) (a) The local density of states of the ideal Cu vacancy V_{Cu} in Cu_2O and (b) of V_{Zn} in ZnO, indicating the symmetric (a_g and a_1, red) and nonsymmetric (a_u and t_2, blue) representations according to the D_{3d} and the (local) T_d symmetries in the Cu_2O and ZnO lattices, respectively. (c) Schematic band diagram of bulk Cu_2O and (d) ZnO, constructed from the interaction of the symmetry-adapted cation-vacancy dangling bond levels with the atomic orbitals of the free metal ions.

that the holes introduced by V_{Cu} reside in delocalized, valence-band-like *perturbed-host states*[4] rather than occupying a *defect-localized state*[4] in the band gap. Indeed, as shown in Fig. 2(a), we find that in Cu_2O, the dangling bond states of the ideal (unrelaxed) Cu vacancy create a resonance 4 eV *below* the VBM, implying that the hole produced by V_{Cu} "float up" and occupy a *delocalized* perturbed-host state just above the VBM. In contrast, the O(p) dangling bond states of V_{Zn} in ZnO occur almost 1 eV *above* VBM deep inside the gap [Fig. 2(b)], leading to a partially occupied, *localized* defect level (which is subject to Jahn-Teller distortion that further deepens the level[17]). Notice that we consider dangling bond resonances of unrelaxed cation vacancies in order to construct the schematic model for band formation discussed below.

In order to illustrate the origin of these markedly different behaviors of cation vacancies in these two oxides, we construct in Figs. 2(c) and 2(d) schematic band structure diagram for bulk Cu_2O and ZnO, respectively, by considering the interaction of the symmetry-adapted dangling bond states of the ideal cation vacancy with the symmetry-adapted atomic levels of the free metal ion. In Cu_2O, the VBM is formed as the *antibonding* state of the "symmetric" (i.e., nodeless state, here, a_g) dangling bond level with the *occupied* atomic Cu(d) state a_g (d_{z^2} orbital along O-Cu-Cu dumbbell), leading to a VBM energy well above the dangling bond levels. In ZnO, the VBM is formed as the *bonding* state of the "nonsymmetric" (i.e., state that does have nodes, here, t_2) dangling bond level with the *unoccupied* atomic Zn(p) orbital, leading to a VBM energy below the ideal vacancy level.

IV. DOPING CONDITIONS

Conditions (i)—low formation energy of hole producers and (ii)—shallow acceptor levels. Figure 3(a) gives the calculated formation enthalpies of various intrinsic defects in different charge states for the Cu-rich/O-poor growth conditions. We see that even in these Cu-rich growth conditions, the copper vacancy V_{Cu} has the overall lowest formation enthalpy with $\Delta H(V_{Cu}^0)=0.7$ eV. The neutral split vacancy has a formation energy of $\Delta H(V_{split}^0)=1.0$ eV, slightly larger than that of V_{Cu}^0, while oxygen interstitials at positions d and c (Fig. 1) have formation energies of 1.3 and 1.8 eV, respectively. Going toward Cu-poor/O-rich conditions lowers $\Delta H(V_{Cu})$ and $\Delta H(O_i)$ formation enthalpies and increases those of V_O and Cu_i. This ensures that the V_{Cu} formation energy is low in any growth conditions and that the cation deficiency in Cu_2O is due to V_{Cu} rather than O_i.

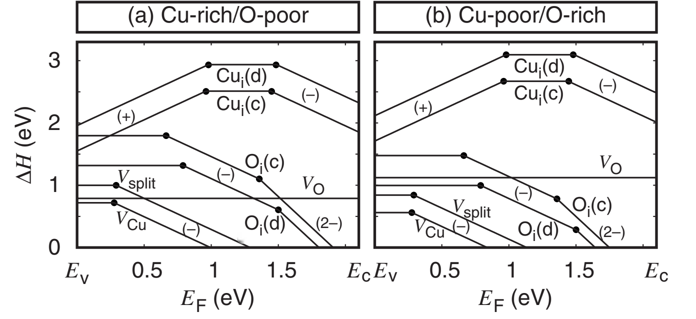

FIG. 3. Formation energies for intrinsic defects in Cu_2O in (a) Cu-rich/O-poor conditions and (b) Cu-poor/O-rich conditions. Only lowest energy charge states are shown; ionization levels are indicated with a dot.

Since the V_{Cu} single-particle levels lie far below VBM as shown in Fig. 2(a), the hole occupying this level inside the valence band would readily float to the VBM, yielding a host-derived acceptor level. Indeed, the $\varepsilon(0/-)$ ionization level for V_{Cu} calculated at $E_v+0.28$ eV is in agreement with the experimentally found[19] hole trap at $E_v+0.25$ eV and is consistent with the expected effective mass ionization energy [the dielectric constant $\epsilon=7.1\epsilon_0$ and the heavy hole mass $m_h^*=1.49m_e$ (Ref. 20) imply a single-band effective mass level at $E_a=0.40$ eV].

In contrast to the shallow V_{Cu} acceptor levels, we find deep levels for the oxygen interstitial, i.e., the $\varepsilon(0/-)$ transition levels are at $E_v+0.66$ and $E_v+0.78$, while the $\varepsilon(-/2-)$ levels are at $E_v+1.35$ and $E_v+1.50$ eV, respectively, for O_i(c) and O_i(d). Thus, while significant O_i concentrations may exist (Fig. 4), they are not a source of p-type conductivity. The deep hole trap levels reported in literature[19,21–23] could be explained by our calculated defect levels of interstitial oxygen.

Condition (iii): absence of hole killers. Potential hole killers in Cu_2O are the oxygen vacancy V_O and the Cu interstitials Cu_i. As shown in Fig. 3, the O vacancy has a relatively low formation energy under Cu-rich/O-poor conditions, but it is stable only in the charge-neutral state which does not compensate hole doping. Cu interstitials, on the other hand, do have a hole-eliminating positive charge state Cu_i^+ (Fig. 3),[24] but their formation energy is sufficiently high, so that no significant concentrations of this hole killer exist under equilibrium growth conditions (Fig. 4). Note that Cu_i is an amphoteric defect and has a deep, negatively charged accep-

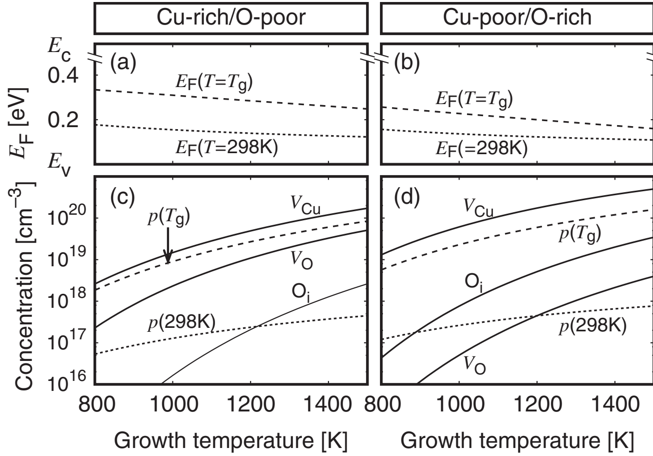

FIG. 4. Equilibrium Fermi level and defect concentrations calculated for [(a) and (c)] Cu-rich/O-poor conditions and [(b) and (d)] Cu-poor/O-rich conditions. The hole concentration and Fermi level are given both in equilibrium at growth temperature T_g and at room temperature (298 K).

tor state high in the gap (Fig. 3),[24] which originates from the atomic Cu(4*s*) orbital. Because the Fermi level generally lies close to the VBM (see below), this level is not occupied under equilibrium conditions.

V. EQUILIBRIUM CARRIER CONCENTRATION

In order to demonstrate the *p*-type nature, we need to show that hole producers indeed are the dominating defect and efficiently produce holes. Therefore, we evaluate equilibrium defect and carrier concentrations that are also quantities directly comparable with experiment. Figure 4 shows the defect concentrations and Fermi level E_F as function of growth temperature as calculated from thermodynamical simulations. The dominant defect in either Cu-rich or Cu-poor growth conditions is the V_{Cu} hole producer that forms in concentrations even above 10^{20} cm^{-3}. In O-poor (O-rich) growth conditions, the V_O concentration is about 1 order (2–3 orders) of magnitude less than that of V_{Cu}. Thus, Cu_2O is nonstoichiometric, and indeed the V_{Cu} concentrations are close to experimentally observed[18] copper deficiency ranging between 2×10^{18} and 2×10^{20} cm^{-3}. The concentration of O_i (sum of O atoms occupying sites c and d) is 1–2 orders (1 order) of magnitude *lower* than V_{Cu} concentration in O-poor (O-rich) conditions. The concentration of the only hole killer Cu_i remains below 10^{14} cm^{-3} throughout temperature range considered. Hence, in all growth conditions, the dominant defect is the hole producer V_{Cu} that also accounts for the experimentally observed off-stoichiometry.

The room temperature carrier concentrations are determined by recalculating the Fermi level at room temperature, while maintaining the equilibrium defect concentrations at a given, higher, growth temperature. The room temperature hole concentration (Fig. 4) is only a fraction of the V_{Cu} concentration, while the hole concentration at growth temperature T_g follows closely the concentration of V_{Cu}. The carrier concentration at room temperature drops by a few orders of magnitude from the carrier concentration at T_g because even though the V_{Cu} acceptor level is host derived, $\varepsilon(0/-)=0.28$ eV is so large that only a fraction of the V_{Cu} will release the hole to VBM. The host-derived acceptor level $\varepsilon(0/-)$ is rather high because of the relatively low dielectric constant $\epsilon=7.1\epsilon_0$.

VI. DESIGN RULES FOR *p*-TYPE OXIDE

The present study demonstrates that *p*-type doping of oxides is facilitated by the repulsive interaction between the atomic oxygen *p* orbitals with filled *d*-shell states of metal cations that have a high energy compared to the O(2*p*) atomic level. The *p*-type conductivity supporting effects are the following. (i) *Shallow levels*: Due to the ensuing high energy of the VBM with respect to the O(*p*) dangling bond levels, the cation vacancy creates a delocalized, conductive state close to the VBM. In the case of extrinsic acceptor doping, the high VBM energy makes it more unlikely that the impurities create deep levels inside the gap. (ii) *Increased solubility*: Since the formation energy of negatively charged hole producers (acceptors) decreases with the increasing VBM energy [viz., Eq. (1)], their solubility is enhanced. (iii) *Suppression of hole killers*: Since the formation energy of positively charged hole killers (donors) increases with increasing VBM energy [viz., Eq. (1)], their formation is suppressed. In the case of V_O in Cu_2O, the positive charge states become even unstable for all Fermi energies inside the band gap.

The above discussion for choosing a cation to design *p*-type conductive oxides is independent of structure or symmetries. Indeed, a model calculation of Cu_2O in the antifluorite structure verified that V_{Cu} single-particle levels in this tetrahedrally coordinated hypothetical material are also 4 eV below VBM, just like in the cuprite structure, ensuring a delocalized perturbed-host state for the defect level. Our guidelines also explain the *p*-type nature of the TCOs $SrCu_2O_2$, $CuMO_2$ delafossites, and *Ln*CuO*X*, where the band formation follows a similar scheme. The main difference of these *transparent* materials to Cu_2O is the fact that some of the Cu d^{10}-d^{10} interactions[25–28] that decrease the band gap and make Cu_2O colored have been eliminated by reducing dimensionality.[20]

VII. SUMMARY

We have shown from first principles calculations that Cu_2O is intrinsically copper-deficient due to formation of copper vacancies V_{Cu} that act as a shallow and efficient hole producer. Cu_2O is intrinsically *p*-type because (a) the potential hole killer V_O has no transition level in the gap and thus cannot annihilate holes, and (b) the possible hole killer Cu_i has both high formation energy and deep transition level and is thus incapable to efficiently destroy holes created by V_{Cu}. The rule for *p*-type oxide design is that the VBM should be formed by the interaction between a *filled* anion shell and a

filled cation shell that lie as high in energy as possible. Suitable cations apart from Cu(d^{10}) would thus be, e.g., Ag(d^{10}) and Au(d^{10}), as well as, e.g., elements from group VIII (Co, Rh, Ir) in d^6 low spin state.

ACKNOWLEDGMENT

This work was funded by DOE EERE under NREL Contract No. DE-AC36-99GO10337.

[1] A. F. Wells, *Structural Inorganic Chemistry* (Clarendon, Oxford, 1975).
[2] D. M. Smyth, *The Defect Chemistry of Metal Oxides* (Oxford University Press, Oxford, 2000).
[3] H. L. Hartnagel, A. L. Dawar, A. K. Jain, and C. Jagadish, *Semiconducting Transparent Thin Films* (IOP, Bristol, 1995).
[4] S. Lany and A. Zunger, Phys. Rev. Lett. **98**, 045501 (2007).
[5] H. Kawazoe, M. Yasukawa, H. Hyodo, M. Kurita, H. Yanagi, and H. Hosono, Nature (London) **389**, 939 (1997).
[6] A. Kudo, H. Yanagi, H. Hosono, and H. Kawazoe, Appl. Phys. Lett. **73**, 220 (1998).
[7] K. Ueda, H. Hiramatsu, H. Ohta, M. Hirano, T. Kamiya, and H. Hosono, Phys. Rev. B **69**, 155305 (2004).
[8] H. Kawazoe, H. Yanagi, K. Ueda, and H. Hosono, MRS Bull. **25**, 28 (2000).
[9] A. Zunger, Appl. Phys. Lett. **83**, 57 (2003).
[10] Y. Chen and M. M. Abraham, J. Phys. Chem. Solids **51**, 747 (1990).
[11] S. Lany, Y.-J. Zhao, C. Persson, and A. Zunger, Appl. Phys. Lett. **86**, 042109 (2005).
[12] J. Osorio-Guillén, S. Lany, S. V. Barabash, and A. Zunger, Phys. Rev. Lett. **96**, 107203 (2006).
[13] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996); G. Kresse and D. Joubert, *ibid.* **59**, 1758 (1999).
[14] J. Ghijsen, L. H. Tjeng, J. van Elp, H. Eskes, J. Westerink, G. A. Sawatzky, and M. T. Czyzyk, Phys. Rev. B **38**, 11322 (1988).
[15] C. Persson, Y. J. Zhao, S. Lany, and A. Zunger, Phys. Rev. B **72**, 035211 (2005).
[16] A. F. Wright and J. S. Nelson, J. Appl. Phys. **92**, 5849 (2002).
[17] L. S. Vlasenko and G. D. Watkins, Phys. Rev. B **72**, 035203 (2005).
[18] O. Porat and I. Riess, Solid State Ionics **74**, 229 (1994).
[19] G. K. Paul, Y. Nawa, H. Sato, T. Sakurai, and K. Akimoto, Appl. Phys. Lett. **88**, 141901 (2006).
[20] X. Nie, S.-H. Wei, and S. B. Zhang, Phys. Rev. B **65**, 075111 (2002).
[21] A. E. Rakhshani, Y. Makdisi, and X. Mathew, Thin Solid Films **288**, 69 (1996).
[22] G. P. Pollack and D. Trivich, J. Appl. Phys. **46**, 163 (1975).
[23] L. Papadimitrou, Solid-State Electron. **36**, 431 (1993).
[24] In LDA or GGA due to gap error, the Cu_i levels hybridize with CBM and appear shallow. To uncloak the correct ionization levels, CBM was artificially pushed up by $+U$ correction on O(s) states with $U=-8$ eV.
[25] E. Ruiz, S. Alvarez, P. Alemany, and R. A. Evarestov, Phys. Rev. B **56**, 7189 (1997).
[26] J. M. Zuo, M. Kim, M. O'Keefe, and J. C. H. Spence, Nature (London) **401**, 49 (1999).
[27] R. Laskowski, P. Blaha, and K. Schwarz, Phys. Rev. B **67**, 075102 (2003).
[28] A. Filippetti and V. Fiorentini, Phys. Rev. B **72**, 035128 (2005).