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New insights on chalcopyrites from solid-state theory

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Abstract

I describe here new insights, gleaned from recent quantum-mechanical electronic structure calculations on dopability, metastability and carrier reflection at grain boundaries for $CuInSe_2$ and $CuGaSe_2$ chalcopyrites.

1. Introduction

In this paper I summarize recent insights on the remarkable properties of chalcopyrite $CuInSe_2$ (CIS) and $CuGaSe_2$ (CGS) gained from quantum-mechanical theory. In particular, I discuss the questions: (i) Is dopability encoded in the "genetics" of a material, or, does it depend mostly on growth circumstances?; (ii) The peculiar properties of anion vacancies in chalcopyrites and the way they lead to light-induced and to voltage-induced metastability and persistent photoconductivity; (iii) The way grain boundaries result in good materials — a new, "charge-neutral" model and its ramifications.

2. Doping chalcopyrites: universal behavior

Our main insight on the dopability of chalcopyrites and other semiconductors were recently summarized in an article entitled, "*Practical Doping Principles*" [1]. What we emphasized was that dopability depends not only on the dopant (because of its potentially low-solubility or too deep energy level), but more notably on the properties of the pure host material. Indeed, each host material has a natural propensity to oppose disrupting its bonding via either n-type and p-type doping. Thus, each material spontaneously develops "antibodies" in response to attempts to dope it. For attempts to dope n type, such antibodies can take the form of spontaneously created cation vacancies (= "electron killer"), whereas for attempts to dope p type the antibodies can take the form of anion-vacancy or cation-interstitial (= "hole killers"), etc. Since the formation energy of each such intrinsic defect depends on the Fermi energy, we could define $E_F^{(n)}$ and $E_F^{(p)}$ as the values of the Fermi energies where the formation enthalpy of electron-killer and hole-killer defects, respectively, becomes exothermic. The values of such pinning energies were obtained from theory [2] and from experiment [3], and represent demarcation energies. This leads to the formulation of "Doping Rules" [1]. For example, n-type doping will be enhanced in materials with *low* Conduction Band Minimum (CBM) energies $E_{CBM} < E_F^{(n)}$, whereas p-type doping will be enhanced in materials with *high* Valence-Band Maximum (VBM) energies $E_{VBM} > E_F^{(p)}$.

The important difference between $CuInSe_2$ (CIS) and $CuGaSe_2$ (CGS) is that E_{CBM} is much higher in the latter material than in the former one. Thus, n-type doping of CGS at equilibrium is difficult, if not impossible. The high E_{CBM} in CGS reflects the fact that the electron killer V(Cu) (Cu vacancy) is easy to form and becomes exothermic when the Fermi energy approaches E_{VBM} +0.8 eV, i.e., well below E_{CBM}.

The above noted dopant-independent distinction between CIS and CGS was borne by a number of recent specific calculations:

(i) *Doping by halogens* [4,5]: CIS can be doped n type, but CGS cannot. The factor that makes CIS dopable is the choice of growth conditions that are rich in In-on-Cu antisite.
(ii) *Doping by divalent cations Cd, Zn, Mg* [5,6]: CIS can be doped n type, but CGS cannot. Chemical trends with Cd vs. Zn vs. Mg were unraveled [6].
(iii) *Doping by hydrogen* [7,8]: CIS can be doped n type but CGS cannot. First-principles total-energy calculation for hydrogen impurities in $CuInSe_2$ and $CuGaSe_2$ shows that H^+ takes up the Cu–Se bond center position, whereas H^0

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and H^- take up tetrahedral interstitial site next to In (in CIS) or Ga (in CGS). Hydrogen creates a negative-U center (i.e., H^0 is never stable), with a (+/−) transition level at $E_c - 0.39$ eV in CIS and $E_c - 0.57$ eV in CGS. However, once combined with the $2V_{Cu}^- + III_{Cu}^{2+}$ complex, hydrogen forms shallower centers with transition levels at $E_c - 0.15$ eV in CIS, and $E_c - 0.39$ eV in CGS. We conclude that hydrogen could convert CIS to n type but not CGS.

(iv) *Generalization* [9]: The above results suggest that in some materials hydrogen is a dopant (e.g. in ZnO), whereas in others it creates gap levels (e.g. in MgO), thus does not lead to conductivity. How can we guess how a given material behaves here? First-principles total-energy calculations suggest that interstitial hydrogen impurity forms a shallow donor in SnO_2, CdO and ZnO, but a deep donor in MgO. We generalize this result to other oxides by recognizing that there exists a “hydrogen pinning level” at about 3.0 ± 0.4 eV below vacuum. Materials such as Ag_2O, HgO, CuO, PbO, PtO, IrO_2, PbO_2, TiO_2, WO_3, Bi_2O_3, Cr_2O_3, Fe_2O_3, Sb_2O_3, Nb_2O_5, Ta_2O_5, $FeTiO_3$ and $PbTiO_3$, whose CBM lie below this level (i.e., electron affinity $> 3.0 \pm 0.4$ eV) will become conductive once hydrogen is incorporated into the lattice, without reducing the host. Conversely, materials such as BaO, NiO, SrO, HfO_2 and Al_2O_3, whose CBM lie above this level (i.e., electron affinity $< 3.0 \pm 0.4$ eV) will remain nonconductive since hydrogen forms a deep impurity.

3. Anion vacancy in chalcopyrites: source of light- or voltage-induced metastability?

For a long time we were unable to calculate accurately the energetics of anion vacancies in chalcopyrites [10,11]. The reason was the unexpected dual behavior of such vacancies. However, recent first-principles total energy calculations [12,13] reveal a novel local atomic reconstruction mode around anion vacancies in II–VI and chalcopyrite compounds resulting from the formation of metal dimers. As a consequence, the neutral Se vacancy has an unexpected low symmetry in ZnSe and becomes a deep donor in both ZnSe and $CuGaSe_2$, contrary to the common belief regarding chalcopyrites. The calculated optical transition energies explain the hitherto puzzling absorption band observed in the classic experiment of the color center in ZnS.

Specifically, we predict persistent *electron* photoconductivity (n-type PPC) caused by the oxygen vacancy V_O in n-ZnO, originating from a metastable shallow donor state of V_O. In contrast, we predict persistent *hole* photoconductivity (p-type PPC) caused by the Se vacancy V_{Se} in p-$CuInSe_2$ and p-$CuGaSe_2$. We find that V_{Se} in the chalcopyrite materials is amphoteric with two transitions: a double donor transition $\varepsilon(2+/0)$ close to the valence band, and a double-acceptor transition $\varepsilon(0/2-)$ closer to the conduction band. Further, we investigated theoretically light- and bias-induced metastability in Cu(In,Ga)Se_2 (CIGS) based solar cells, suggesting the Se–Cu divacancy complex (V_{Se}–V_{Cu}) as the source of this hitherto puzzling phenomenon. Due to its amphoteric nature, the (V_{Se}–V_{Cu}) complex is able to convert by persistent carrier capture or emission from a shallow donor – into a shallow acceptor – configuration and vice versa, thereby changing in a metastable fashion the local net acceptor density inside the CIGS absorber of the solar cell, e.g., a CdS/CIGS heterojunction. In order to establish a comprehensive picture of metastability caused by the (V_{Se}–V_{Cu}) complex, we determine defect formation energies from first-principles calculations, employ numerical simulations of equilibrium defect thermodynamics and develop a model for the transition dynamics after creation of a metastable non-equilibrium state. We find that the (V_{Se}–V_{Cu}) complex can account for the light-induced metastabilities, i.e., the “red” and “blue” illumination effects, as well as for the reverse-bias effect. [14]. Thus, our (V_{Se}–V_{Cu}) model implies that the different metastabilities observed in CIGS share a common origin. A defect state in the band gap caused by (V_{Se}–V_{Cu}) in the acceptor-configuration creates a potentially detrimental recombination center, and may contribute to the saturation of the open circuit voltage in larger-gap Cu(In,Ga)Se_2 alloys with higher Ga-content. Therefore, the presence of metastable defects should be regarded as a concern for solar cell performance.

4. The effect of grain boundaries

For a long time, it was assumed that the existence of *charged* defects at grain boundaries has beneficial effects. We have recently predicted [15] that “although charged defects and impurities may exist at the GB (leading to observable local changes of the work function), these do not improve cell efficiencies, as was previously hoped” [16–19].

Many recent papers, including at this conference [20], have reported the existence of charged defects at GB. As noted above, this is neither novel, not in dispute. The interesting question is whether charge-neutral defects exist and affect beneficially solar cell performance.

Recently [15] we have explained theoretically why, despite the existence of many defects and impurities at the GBs of $CuInSe_2$, there appears to be negligible recombination of electrons and holes there. Our conclusion was based on the analogy between the structure of GB “internal surfaces” and the surface structure of CIS films. Total-energy minimization of the surface structure of CIS [21] showed that in contrast with conventional semiconductors, such as GaAs, in CIS the polar surface is more stable that the non-polar surface. As in GaAs, polar CIS surfaces must reconstruct to remove the electrostatic dipole created by the alternation of pure cation and pure anion planes along the polar axis. This reconstruction involves creating rows of either Cu vacancies [in the metal-exposed (112) surface] or In-on-Cu antisites [at the subsurface of the anion-exposed $(\bar{1}\bar{1}\bar{2})$ face]. Unlike conventional bulk vacancies, this surface Cu vacancy is charge neutral because its negative (acceptor like) charge has been used to cancel the electrostatic dipole. Thus, the interface between the GB and Grain Interior (GI) represents an interface between two materials of difference chemical compositions — one strongly Cu poor and one more closely Cu stoichiometric. This leads to a band offset between the GB and GI involving a (112) lowering of the Valence-Band Maximum at the Cu-poor GB. The predicted existence of a low VBM on the GB side causes photogenerated holes to repel from the GB into the GI. Although, the GB has numerous defect recombination centers, the electrons there have no holes with which to recombine.

Recent developments: Recent experimental studies [21–23] have examined the model of neutral band offset. Micro-Auger electron spectroscopy measurements [22] found a large (up to 50%) deficiency of Cu at the CIS GB, as predicted by the polar surface reconstruction model. Pump-power dependent cathodoluminescence (CL) studies [23] showed strongly reduced recombination at the GB and rapid saturation of the CL energy with power at the GB, indicating the limited supply of one type of carrier there. Scanning tunneling microscopy scans at low voltage, (when only electrons are injected from the tip into the GB) revealed [24] a decrease in photon emission intensity at the GB when compared to GI, demonstrating a reduced hole density at the GB as predicted by the model.

At this conference, S. Siebentritt [25] reported a first successful growth of an artificial GB in this system, finding a notable neutral band offset (albeit, smaller than the one predicted for an ideal GB [15]). Device simulations show that *charged* GB [26,27] invariables reduce device efficiency (unless an unphysically very large electrostatic field exists). On the other hand, a charge-neutral band offset can effectively block holes from the GB region and allow efficiencies comparable to a single-crystal material [28]. In fact, in our charge-neutral band offset model, *any* value of band offset contributes to improved V_{oc} and efficiency (Fig. 11, Ref. [28]). The electrostatically-charged GB model leads, instead to a deterioration of the cell performance, except for extremely high electrostatic potentials.

A recent microscopy study [29] observed *twin* boundaries/stacking faults in highly thinned CIGS samples, failing to observe the Cu-poor regions predicted theoretically [14,15] for surface-like *grain* boundaries. However, the predicted Cu-deficiency pertains to grain boundaries representing surface-like structures, not to twin boundaries where the composition and structure are continuous through the boundary. Thus, this experiment is largely irrelevant to the issue of GB band offsets raised in Ref. [15]. Furthermore, Yan et al. [29] have not investigated the statistical significance of the microstructure they report on (i.e., is the twin/stacking fault imaged frequent or rare?). Thus, as interesting as this observation is, its relevance to the issue of GB-induced offsets is doubtful.

Yan et al. [29] have noted interesting spatial homogeneities in their sample. This led them to speculate that (i) these are related to Cu vacancies, forming Cu-rich and Cu-poor domains which would (ii) conspire to produce 3D, spatially interconnected, percolating network, leading to (iii) a type-II band offset and thus to charge separation of the sort predicted in Ref. [15] for GB's (electrons in Cu-poor side, holes in Cu-stoichiometric side). Unfortunately, at this time, none of these postulates is anchored in experimental observation.

Spatial fluctuations in CIGS alloys can result from multiple sources. For example: (a) being a Ga/In alloy, the CIGS sample may have random alloy fluctuation, i.e. local deviations from the nominal Ga/In ratio, just as seen in InGaN. Also, (b) there can be phase-diagram induced fluctuations, i.e. phase-coexistence regions in the phase-diagram that will create precipitates that lead to an inhomogeneous microstructure (just like Al–Zn alloys in metallurgy). (c) There may also be growth-induced fluctuations due to spatial composition gradients. Finally, (d) since the sample has various charged defects, one expects also electrostatically-induced fluctuations. At this time, the origin of the observed fluctuation is not known, and perhaps all sources contribute. Clearly, it will be highly coincidental if such complex system of inhomogeneity will lead to percolation. While we predicted theoretically in 1995 that there is a type-II band offset between Cu-poor "ODC" and Cu-stoichiometric CIS (Fig. 12 in Ref. [10]), it remains to be seen if this prediction of charge separation is realized by the peculiar fluctuations seen by Ref. [29], as suggested by the authors.

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