



New insights on chalcopyrites from solid-state theory

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I describe here new insights, gleaned from recent quantum-mechanical electronic structure calculations on dopability, metastability and carrier reflection at grain boundaries for CuInSe₂ and CuGaSe₂ chalcopyrites.

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1. Introduction

In this paper I summarize recent insights on the remarkable properties of chalcopyrite CuInSe₂ (CIS) and CuGaSe₂ (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. Dopability of chalcopyrites and other semiconductors

Our main insight on the dopability of chalcopyrites and other semiconductors were recently summarized in an article entitled, “*Dopability of Semiconductors*” [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 killer”), whereas p-type doping will be enhanced in materials with $E_{\text{VBM}} < E_{\text{F}}^{(n)}$, whereas p-type doping will be enhanced in materials with $E_{\text{VBM}} > E_{\text{F}}^{(p)}$.

The important difference between CuInSe₂ (CIS) and CuGaSe₂ (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 (Cu) (Cu vacancy) is easy to form and becomes exothermic when the Fermi energy approaches $E_{\text{VBM}} + 0.8$ 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) *First-principles total-energy calculations* [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) *Chemical trends with Cd vs. Zn vs. Mg* were unraveled [6].
- (iii) *First-principles total-energy calculation for hydrogen impurities* in CuInSe₂ and CuGaSe₂ shows that H⁺ takes up the Cu–Se bond center position, whereas H⁰

enhanced in materials with $E_{\text{VBM}} > E_{\text{F}}^{(n)}$. Conduction band (CBM) energies

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and H^- take up tetrahedral interstitial site next to In (in CIS)

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 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