AIP Applied Physics Letters

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Citation: Applied Physics Letters **87**, 211904 (2005); doi: 10.1063/1.2132537
View online: http://dx.doi.org/10.1063/1.2132537
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/87/21?ver=pdfcov
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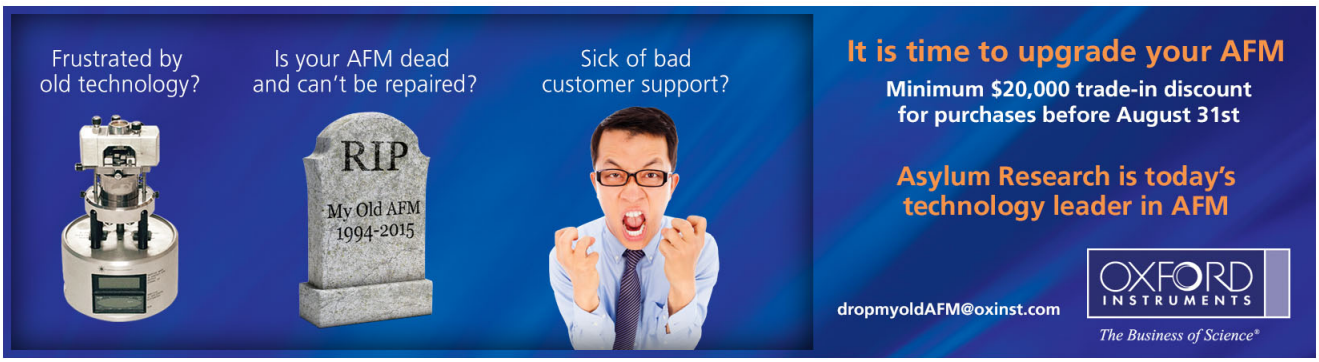

# Compositionally induced valence-band offset at the grain boundary of polycrystalline chalcopyrites creates a hole barrier

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(Received 15 June 2005; accepted 26 September 2005; published online 15 November 2005)

First-principles calculations of model grain boundaries (GBs) in $CuInSe_2$ and $CaGaSe_2$ show that cation-terminated GBs have a valence-band offset with respect to the grain interior (GI). This offset repels holes from the GBs, thus depriving electrons there from recombination at the GB defects. Anion-terminated GBs have no such valence offset. $CuGaSe_2$ has, in addition, a conduction-band offset at the GB/GI interface, attracting electrons to the GBs. These features explain how polycrystalline chalcopyrite solar cells could outperform their crystalline counterparts. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2132537]

Whereas the *polycrystalline* form of conventional semiconductors (Si, GaAs) has poor transport and electronic properties relative to their crystalline counterparts, surprisingly, polycrystalline alloys of $CuInSe_2$ (CIS; $E_g \approx 1.0$ eV) with $CuGaSe_2$ (CGS; $E_g \approx 1.7$ eV) has excellent properties, manifested, among others by nearly 20% solar cell conversion efficiency, outperforming even its crystalline counterpart.[1] This intriguing property of grain boundaries (GBs) in chalcopyrites has recently attracted much attention[1–7] both because of its relevance to solar cell performance and, more generally, because of the hope that understanding the underlying mechanism at play in polycrystalline chalcopyrites might help design benign GBs in conventional polycrystalline semiconductors (e.g., Si and GaAs) to the benefit of low-cost devices.

Recently,[1] 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 (Ref. 8) showed that in contrast with conventional semiconductors, such as GaAs, in CIS the polar surface is more stable than the nonpolar 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 $(\bar{1}\bar{1}2)$ face]. Unlike conventional bulk vacancies, this surface Cu vacancy is charge neutral because its negative (acceptorlike) charge has been used to cancel the electrostatic dipole. Furthermore, unlike GaAs, this reconstruction in CIS costs little energy because the creation of vacancies in the weakly bonded Cu sublattice is less costly than the creation of Ga vacancies in the strongly covalently bonded III-Vs. Thus, the interface between the GB and grain interior (GI) represents an interface between two materials of different 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 (VBM) at the Cu-poor GB [Fig 1(a)]. The calculated GB/GI conduction band offset $\Delta E_c$ in pure CIS was negligible. The reason that the Cu-poor material has a lower VBM is that it is deprived of Cu *d* orbitals, which when present, repel the Se *p*-based VBM upward.[9]

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. At the same time, recombination in the GI of solar cell quality $CuIn_xGa_{1-x}Se_2$ (CIGS) is rather weak, as most impurities and defects have migrated during growth into the GB, leaving the GI potentially more perfect and pristine than

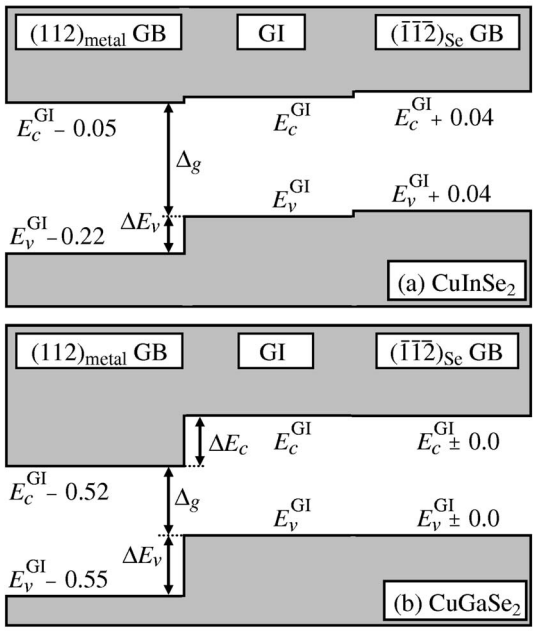


FIG. 1. Band offset energies (in units of eV) of $(112)_{metal}$ and $(\bar{1}\bar{1}2)_{Se}$ terminated CIS and CGS surfaces. The error bar is estimated to be <0.1 eV.

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conventional single-crystal CIS. This model[1] of *charge-neutral* hole reflector at the GB due to a compositional band offset is a new concept, which differs from the conventional model[3–7,10] of *charged* GBs. In the latter model, offered originally for Si (Ref. 10) and adopted later for II-VIs (Refs. 6 and 7) and chalcopyrites,[3–5] one assumes that the GB has a net concentration of a charged donors, which causes a downward bending of *both* valence and conduction bands. Recent detailed modeling[11] has shown, however, that even though positive (donor) electrostatic charges at the GB will repel holes, they will attract electrons sufficiently to raise the electron-hole $n \cdot p$ product, thus leading to enhanced recombination and reduced solar cell efficiency. Although charged defects and impurities may exist at the GB (leading to observable local changes of the work function),[3,4,9] these do not improve cell efficiencies, as was previously hoped.[4–7,10]

Our model of GB/GI charge-neutral band offset hole reflector was recently studied experimentally[2,3,12] and via device simulations.[11] Micro-Auger electron spectroscopy measurements[2] found a large (up to 50%) deficiency of Cu at the CIS GB, as predicted by the polar surface reconstruction model.[1] Pump-power dependent cathodoluminescence (CL) studies[3] 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[12] 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. Two-dimensional device simulations[11] of the model of neutral offset at the GB/GI interface indicate a strongly reduced recombination at the GB (due to a reduced $n \cdot p$ product), leading to a significant increase in solar cell efficiency relative to a cell having no band offset at the GB/GI interface.

What has not been studied so far is: (i) The effect of anion-terminated GB on the electronic properties, and (ii) a comparison between the electronic structure of CIS and CGS surfaces/GBs. Item (i) is important because nominally nonpolar surfaces of CIS facet spontaneously,[13] into a combination of metal-exposed (112) plus Se-exposed $(\bar{1}\bar{1}2)$ faces. Item (ii) is important because one desires to increase the open-circuit voltage, $V_{oc}$, of such solar cells by alloying the wider gap CGS into CIS. Disappointingly, such alloying does not produce better cells when the Ga composition increases above 30%,[14] prompting the supposition[4] that perhaps the GB of CGS does not have the same beneficial effect as the GB of CIS. These issues are addressed here.

Our calculation is based on a supercell model. The atomic position of the GB is fully optimized to lower the total energy and forces as calculated via the local density approximation (LDA) approach.[15] The differences between the current calculation and our previous[1] calculation are: (a) We use a larger unit cell of 56 atoms compared with 40 atoms previously. Finite size effects are small, as shown by the fact that our calculated band gap at the GI equals our bulk band gap; (b) we correct the LDA error by using the LDA+$U$ approach with $U_d$(Cu)=6 eV and $U_s$(Se)=−6 eV; (c) artificial charge-transfer between the top and bottom surfaces of the slab is inhibited by passivating the back surface via pseudo-hydrogen atoms with fractional charges, and by allowing dipole-compensating relaxation there. The residual dipole is expected to be negligible.

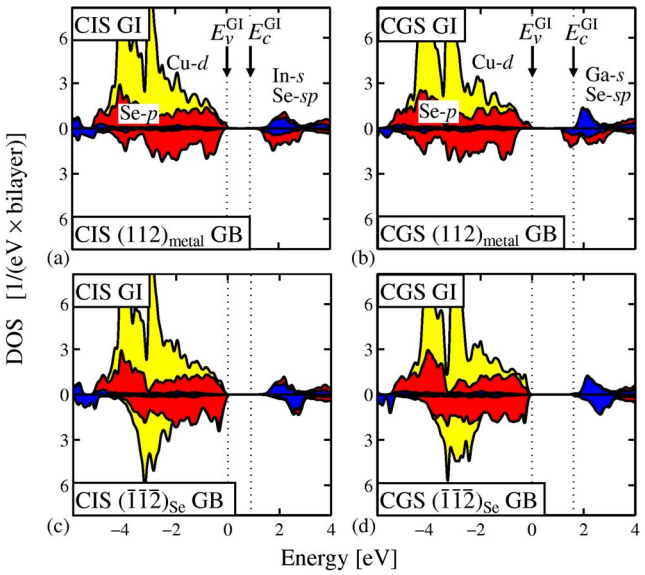


FIG. 2. (Color online). Atom- and orbital-resolved bilayer DOS of *bulk* CIS and CGS (top halves), and of $(112)_{metal}$ and $(\bar{1}\bar{1}2)_{Se}$ terminated *surfaces* (bottom halves). Dotted lines show bulk VBM $E_v^{bulk}$=0 and CBM $E_c^{bulk}$.

One can distinguish between two types of GBs, one type has an abrupt change in its crystallographic structure (or in the chemical composition), and the other has a growth-induced Cu-poor composition gradient over a larger distance. The former is expected to exist mainly deep inside the CIGS absorber,[4] and the latter more likely exists in the space-charge region near the CdS/CIGS interface[4] in a solar cell where actual samples often show an additional strong Cu-poor gradient. Both types of GBs involve Cu vacancies, and our calculations of reconstructed GBs/surfaces and of strongly Cu-poor dislocations[1] show similar band offsets in these cases. Figure 1 schematically represents the positions of the band edges at the surface/GB and GI. Figure 2 shows the atom- and orbital-resolved density of states (DOS) of bulk CIS and CGS (top halves of Fig. 2) and of the near-surface region (bottom halves). Results are shown separately for the metal-terminated (112) and the anion-terminated $(\bar{1}\bar{1}2)$ GB models. The main observations are as follows:

(i) *Anion-terminated GBs have negligible* $\Delta E_v$ *in CIS and CGS*: Whereas the metal-terminated (112) GB exhibits clear GB/GI *valence*-band offsets,[1] the anion-terminated $(\bar{1}\bar{1}2)$ GB in both CIS and CGS has a negligible valence-band offset. Thus, the anion-terminated GB does not repel holes and is therefore prone to recombination. Minimizing such GBs during growth is thus an advantage for solar cells. The absence of a valence-band offset at the anion-terminated interface and its presence in metal-terminated surface is due to the latter being stabilized by Cu vacancies[8] thus eliminating (along with Cu) its *d* orbitals, which have caused an upward repulsion of the VBM in the normal bulk. In contrast, the anion-terminated GB is stabilized by III-on-Cu antisite defects in the subsurface layer.[8] This replacement of one-half of the Cu atoms with III atoms creates a small outward relaxation of the surface Se layer. Whereas, the distance between the surface Se layer and the Cu+III layer is $\delta_z$=0.94 Å in CIS and 0.86Å in CGS (compared to $\delta_z$ =0.82 Å in bulk CIS and CGS). Such III-on-Cu defects disturb the VBM to a much lesser extent than the Cu vacancies at the metal-terminated surface, since the absence of all Cu

atoms implies a pronounced affect on the metal–Se bonds there; the distance between the surface III layer and the nearest Se layer ($\delta_z = -0.17$ Å in both CIS and CGS) represent a very strong inward relaxation of the metal terminated layer.

(ii) *Cation-terminated CGS has a larger GB*$\Delta E_v$ *compared to CIS*: We find (Fig. 1) that in $\Delta E_v(\mathrm{CGS}) = 0.5$ eV, whereas $\Delta E_v(\mathrm{CIS}) = (0.2-0.3)$ eV. This is a consequence of the shorter Cu–Se bond length in CGS relative to CIS, and is reflected by the greater energetic separation of the Cu *d* bands in CGS from its VBM than in CIS (i.e., larger *p-d* repulsion compared with CIS). As a result, the removal of Cu atoms upon the creation of a polar GB surface lowers the VBM of CGS more than it does in CIS. The different positions of the Cu *d* band in CIS and CGS are reflected also in the existence of a larger crystal-field splitting $\Delta_{\mathrm{CF}} = \epsilon(\Gamma_{5v}) - \epsilon(\Gamma_{4v}) = -0.10$ eV in CGS relative to 0.01eV in CIS. When the band structure of CGS is calculated using the atomic positions of CIS, we find $\Delta_{\mathrm{CF}} \sim 0$ and similar *d*-band separation from the VBM as in CIS, indicating that indeed the *d*-band energetic differences reflect a structural difference. In addition, the *carrier symmetry* affects tunneling, an effect which is absent in conventional *sp* semiconductors: Since the (112) GB VBM lacks electronic *d* states, the GI *d*-like hole states have no corresponding *d*-like states at the GB, and the GI $\rightarrow$ GB hole tunneling is impeded.

(iii) *The cation-terminated CGS has a larger GB* $\Delta E_c$ *than CIS*: Whereas the cation-terminated GB in CIS exhibits a negligible *conduction-band* offset with respect to the GI, in CGS the conduction-band minimum (CBM) at the GB is lower than that at the GI, thus manifesting $\Delta E_c = 0.5$ eV. The mechanism for a larger $\Delta E_c$ in CGS than in CIS is the energetic position of the (III-*s*)-(Se-*sp*) DOS peak relative to the CBM in CGS [Fig. 2] and CIS [Fig. 2]: In both materials, this state is energetically lowered at the GB, but in contrast to (In-*s*)-(Se-*sp*) in CIS, in bulk CGS the (Ga,*s*)-(Se,*sp*) peak is closer to the CBM, so it lowers the CBM more at the GB. The low CBM at the cation-terminated CGS GB also means that electrons will be drawn to this location from regions with a higher CBM, e.g., both from the CdS and the CGS layers. This means that while in both CIS and CGS the holes are reflected away from the GB, in CGS the electrons are attracted to the GB . This "type II" GB/GI band offset we find in CGS implies that photogenerated electron-hole pairs will dissociate at the interface (much like in organic solar cells)[16] with the electron being attracted to the GB, and the hole to the GI. This reduces recombination at the GB.

(iv) *Relative cell performance of CIS versus CGS:* Three factors are pertinent here. (1) We have recently shown[17] that an important reason for the lesser performance of Ga-rich (more than 30% Ga) CIGS solar cells is due to different behaviors of their GI not GB. Both materials exhibit pinning of the Fermi level at about $E_v + 0.8$ eV due to the spontaneous formation of electron-annihilating $V_{\mathrm{Cu}}$ acceptors; however, this energetic position is 0.9 eV below the CBM of CGS, whereas it is only 0.2 eV below the CBM of CIS. Thus, the maximum attainable voltage is more limited in Ga-rich material. (2) *At abrupt GI/GB interfaces*, the carrier transport can be limited by tunneling-assisted electron-hole recombinations (as in conventional *charged p-n* junctions.[10]) Whereas in CIS the energy difference $\Delta_g = E_c(\mathrm{GB}) - E_v(\mathrm{GI})$ at the charge-neutral GB/GI interface (Fig. 1) nearly equals the bulk CIS band gap, in CGS the smaller $\Delta_g = 0.6$ eV at the (112) GB/GI interface will increase recombination. (3) The larger $\Delta E_c$ in CGS can affect $V_{\mathrm{oc}}$: In the space-charge region near the CdS/CIGS interface, the band profile restricts $V_{\mathrm{oc}}$ and thus the cell performance. In CIS, $\Delta E_c = 0$ (Fig. 1) which does not limit $V_{\mathrm{oc}}$. However, in CGS, the strong downward band bending $\Delta E_c$ at the GB will affect $V_{\mathrm{oc}}$ adversely. Effects (1)–(3) lead to a lesser performance of CGS relative to CIS.

(v) *CIS and CGS have different electrostatic barriers*: Many Kelvin-probe studies[3–7] reveal the existence of a higher surface potential on the GB (downward movement of the VBM at the GB) indicating the existence of charges there. The effect is larger in CIS than CGS.[4] This is explained by our recent calculations,[17] which show that the III-on-Cu antisite double donor has a lower formation enthalpy in CIS than in CGS, leading to a rapid decline in donor concentration as Ga is added to CIS. Note that the electrostatically based Kelvin-probe experiment does not see directly the charge-neutral band offset and that CGS has a larger *neutral* offset than CIS (Fig. 1), yet a *smaller* electrostatic offset.

In conclusion, detailed atomistic modeling of the GB show that cation-terminated GBs have a beneficial effect on transport in that they deprive the GB electrons from holes with which they can annihilate. Anion-terminated GBs do not have a similar beneficial effect. The poor solar cell performance of Ga-rich CIGS is not related to hole repulsion at the GB, for CGS has more hole repulsion than CIS. The lesser performance of Ga-rich cells is related to differences in the respective GIs and $\Delta_g$. Device modeling, which includes the effects of our predicted *neutral* band offset model, are called for.

Work at NREL (for one of the authors, A.Z.) was supported by the U.S. DOE-EERE, under Contract No. DEAC36-98-GO10337. The Swedish Research Council supports work in Sweden (for the other author, C.P.).

[1] C. Persson and A. Zunger, Phys. Rev. Lett. **91**, 266401 (2003).
[2] M. J. Hetzer, Y. M. Strzhemechny, M. Gao, M. A. Contreras, A. Zunger, and L. J. Brillson, Appl. Phys. Lett. **86**, 162105 (2005).
[3] M. J. Romero, K. Ramanathan, M. A. Contreras, M. M. Al-Jassim, R. Noufi, and P. Sheldon, Appl. Phys. Lett. **83**, 4770 (2003).
[4] C.-S. Jiang, R. Noufi, J. A. AbuShama, K. Ramanathan, J. R. Moutinho, J. Pankow, and M. M. Al-Jassim, Appl. Phys. Lett. **84**, 3477 (2004).
[5] S. Schuler, S. Nishiwaki, J. Beckmann, N. Rega, S. Brehme, S. Siebentritt, and M. Ch. Lux-Steiner, *Proceedings of the 29th IEEE Photovoltaic Spec. Conf.*, New Orleans (2002), p. 504.
[6] I. Visoly-Fisher, S. R. Cohen, and D. Cahen, Appl. Phys. Lett. **82**, 556 (2003).
[7] I. Visoly-Fisher, S. R. Cohen, R. Ruzin, and D. Cahen, Adv. Mater. (Weinheim, Ger.) **16**, 879 (2004).
[8] J. E. Jaffe and A. Zunger, Phys. Rev. B **64**, 241304(R) (2001).
[9] J. E. Jaffe and A. Zunger, Phys. Rev. B **27**, 5176 (1983).
[10] J. Y. W. Seto, J. Appl. Phys. **46**, 5247 (1975).
[11] W. K. Metzger and M. Gloeckler, J. Appl. Phys. **98**, 063701 (2005).
[12] M. J. Romero, C.-S. Jiang, R. Noufi, and M. M. Al-Jassim, Appl. Phys. Lett. **86**, 143115 (2005).
[13] D. Liao and A. Rockett, Appl. Phys. Lett. **82**, 2829 (2003).
[14] W. N. Shafarman, R. Klenk, and B. E. McCandless, J. Appl. Phys. **79**, 7324 (1996).
[15] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993). We use the plane augmented wave method with energy cutoff of 300 eV and 76 **k** points in the irreducible Brillouin zone.
[16] P. Peumans, S. Uchida, and S. R. Forrest, Nature (London) **425**, 158 (2003).
[17] Y. J. Zhao, C. Persson, S. Lany, and A. Zunger, Appl. Phys. Lett. **85**, 5860 (2004).