Behavior of Σ 3 Grain Boundaries in CuInSe 2 and CuGaSe 2 Photovoltaic Absorbers Revealed by First-Principles Hybrid Functional Calculations

ARTICLE *in* PHYSICAL REVIEW APPLIED · JUNE 2015

DOI: 10.1103/PhysRevApplied.4.064005 · Source: arXiv

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The behavior of the Σ3 grain boundaries in the $CuInSe_2$ and $CuGaSe_2$ photovoltaic absorber as revealed by first-principles hybrid functional calculations

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The inconclusive results of the previous first-principles studies on the Σ3 grain boundaries (GBs) in $CuInSe_2$ reveal the importance of employing a method that can correctly describe the electronic structure of this solar-cell material. We have employed hybrid functional calculations to study the Σ3(112) and Σ3(114) GBs in $CuInSe_2$ and $CuGaSe_2$. The electronic structure changes introduced by the formation of GBs are threefold: creation of gap states, shift in band edges, and alteration of bandgap sizes. Gap states commonly behave as recombination centers, but the band alignment and the change in the bandgap size induced by GBs mitigate the destructive effect of these states in $CuInSe_2$. That means, Σ3 GBs are not detrimental for the carrier transport in $CuInSe_2$. Conversely, these GBs are destructive for the carrier transport in $CuGaSe_2$.

PACS numbers: 61.72.Mm, 71.15.Mb, 61.72.Bb

Thin-film solar cells based on Cu(In,Ga)Se_2 (CIGSe) are fabricated and deployed worldwide on an industrial scale due to their outstanding price/performance ratio [1, 2]. In contrast to silicon-based solar cells [3], the efficiency of CIGSe cells with polycrystalline light absorber exceeds the efficiency of their monocrystalline counterpart [4]. This is remarkable, because typically the performance of optoelectronic devices is considered to be worse for polycrystalline semiconductors due to the presence of grain boundaries (GBs). GBs are expected to create deep gap levels that act as recombination centers and are commonly regarded detrimental for the solar-cell performance. Despite the extensive studies carried out in the past decades to investigate the effects of GBs on the efficiency of CIGSe-based solar cells, their role remains a topic of intense debate.

In the literature, different atomic structures for symmetric GBs in $CuInSe_2$ and $CuGaSe_2$ have been reported. Abou-Ras *et al.* [5] identified and studied experimentally two types of Σ3(112) GBs in $CuInSe_2$: Se-Se-terminated {112} plane GBs and cation-Se-terminated {112} plane GBs. While the former showed Cu depletion and In enrichment, Cu depletion without In enrichment was detected for the latter. Yan *et al.* [6], on the other hand, reported no change in the atomic composition near the cation-Se-terminated {112} plane GBs. This discrepancy could be due to different methods employed to study the atomic composition [7, 8]. Another type of Σ3 GB, namely Σ3(114), has been studied in $CuInSe_2$ and $CuGaSe_2$ [9–12]. Although this type of GB is not experimentally identified in $CuInSe_2$ and $CuGaSe_2$, its structure is adopted from GBs in CdTe. A common feature of the Σ3 GBs is that high percentage of these GBs in $CuInSe_2$ and $CuGaSe_2$ are charge neutral [13–15].

The outcomes of the previous first-principles studies on GBs are not conclusive [6, 9–12, 16]. In their pioneering work, Persson and Zunger [16] employed LDA and LDA+U method to study the cation-terminated (112) surface of $CuInSe_2$ to explain the anomalous characteristics of the symmetric GBs. They proposed that the valence band maximum (VBM) of the surface is lower than the bulk VBM therefore the GBs act as a hole barrier. The Cu vacancy reconstruction at the surface, which lowers the surface VBM with respect to the bulk VBM, is in contrast to the results of Yan *et al.* [6]. Other authors employed different flavors of (local) LDA and (semi-local) GGA to study the Σ3(114) GBs in $CuInSe_2$ and $CuGaSe_2$. While some studies [9, 10] suggested that these GBs do not create any gap state, the other studies predicted the formation of deep gap states in the bandgap of the systems with GBs [11, 12].

The results achieved by (semi-) local methods remain doubtful, even if they are in agreement with experimental findings. This is because of the employed methods in the aforementioned studies that do not describe the semiconducting nature of $CuInSe_2$ and $CuGaSe_2$ adequately [17, 18]. Namely, for the defect-free $CuInSe_2$ and $CuGaSe_2$ bulk, the bandgaps predicted by PBE and PBE+U are severely underestimated [11]. This failure is partly due to the shortcomings of (semi-) local methods and partly due to underestimation of the anion displacement (u) of $CuInSe_2$ [19]. The size of the bandgap is of particular importance when the defect states, which might appear in the bandgap, are studied. In light of the shortcomings of the underlying methods, the inconsistencies between previous works are not surprising.

In this Letter we report on the first-principles hybrid functional study of two types of Σ3 GBs, namely Σ3(112) and Σ3(114), in $CuInSe_2$ and $CuGaSe_2$. Our results show that the formation of a GB can have three effects on the electronic structure of its system: it creates gap states, it shifts the VBM and conduction band minimum (CBM), and it changes the size of the bandgap. In $CuInSe_2$ and $CuGaSe_2$, none of the GBs can trap holes to become positively charged. Electrons, on the other hand, can be trapped in the gap states. For $CuInSe_2$, the GBs that create gap states act as a barrier for bulk carriers as well. Thus, the low concentration of electrons and holes near

these GBs prevents electron-hole recombination, making the formation of these GBs harmless for the carrier transport. The behavior of GBs in $CuGaSe_2$ is different from $CuInSe_2$. The conduction band offset increases the concentration of electrons at the GBs and these electrons can be trapped by the gap states. The valence band offset, on the other hand, is not large enough to prevent electron-hole recombination. The presence of these GBs (except one type of the GB that does not create defect levels) destroys the carrier transport in $CuGaSe_2$.

Hybrid functionals are known as a rather accurate method to study the electronic structure of semiconductors. In this approach a portion of the exact exchange calculated by Hartree-Fock method is incorporated into the exchange-correlation functional calculated by density functional theory (DFT). In the present work, we used HSE06 functional [20] with the fraction of the exact exchange set to 30 % [17, 21, 22]. Using this setup, the value of the anion displacement is calculated with an error smaller than 0.3 % and the computed bandgaps are 1.0 eV and 1.6 eV for $CuInSe_2$ and $CuGaSe_2$, respectively, in agreement with experimental values [23].

All calculations have been performed within the framework of DFT as implemented in Vienna Ab-initio Simulation Package (VASP) [24]. We used the projector augmented wave (PAW) [25, 26] method together with a plane-wave cutoff energy of 300 eV and a mesh of $(3 \times 3 \times 1)$ k-points. For density of stated (DOS) calculations a denser k-mesh has been used. The supercells consist of 128 and 180 atoms for the Σ3(112) and Σ3(114) GBs, respectively. To construct the supercells, the optimized lattice constants and atomic positions of the bulk have been used. The distance between periodic supercells separated by vacuum is about 30 Å. The surface dangling bonds were passivated with hydrogen-like pseudoatoms to quench the dipole moment of the slabs. The position of atoms in the outer four atomic layers were fixed to their bulk position to mimic the underlying bulk material. Other atoms were fully relaxed until the forces on each atom were below 0.01 eV/Å. Using the same methodology, a defect-free supercell with {112}-plane termination was constructed and considered as the reference. To calculate the relative shift of the VBM and CBM with respect to the bulk, the average electrostatic potentials of different systems were aligned [27].

The crystal structure of $Cu(In,Ga)Se_2$ and CdTe has the same fundamental characteristics and the GBs in $CuInSe_2$ and $CuGaSe_2$ can be modeled based on the observed GB structures in CdTe. In the present work, Σ3(112) and Σ3(114) correspond to lamellar and double-positioning twins in CdTe [28, 29]. In the Σ3(112) GBs, either a cation-containing plane is next to a Se-containing plane (Σ3(112)-I) or Se-containing planes are facing each other (Σ3(112)-II), see FIG. 1 (a) and (b). In the Σ3(114) GBs, either Se atoms have dangling bonds (Σ3(114)-I) or cations have dangling bonds (Σ3(114)-II), see FIG. 1 (c) and (d). The atomic structure of the Σ3(112) and Σ3(114) GBs are very different: while the Σ3(114) GBs contain dangling, wrong, and extra bonds the atomic structure of Σ3(112)-I is very similar to the bulk and the Σ3(112)-II GB contains Se dangling and Se-Se wrong bonds.

The atomic structures of GBs in $CuInSe_2$ after geometry optimization are presented in FIG. 1. While Σ3(112)-

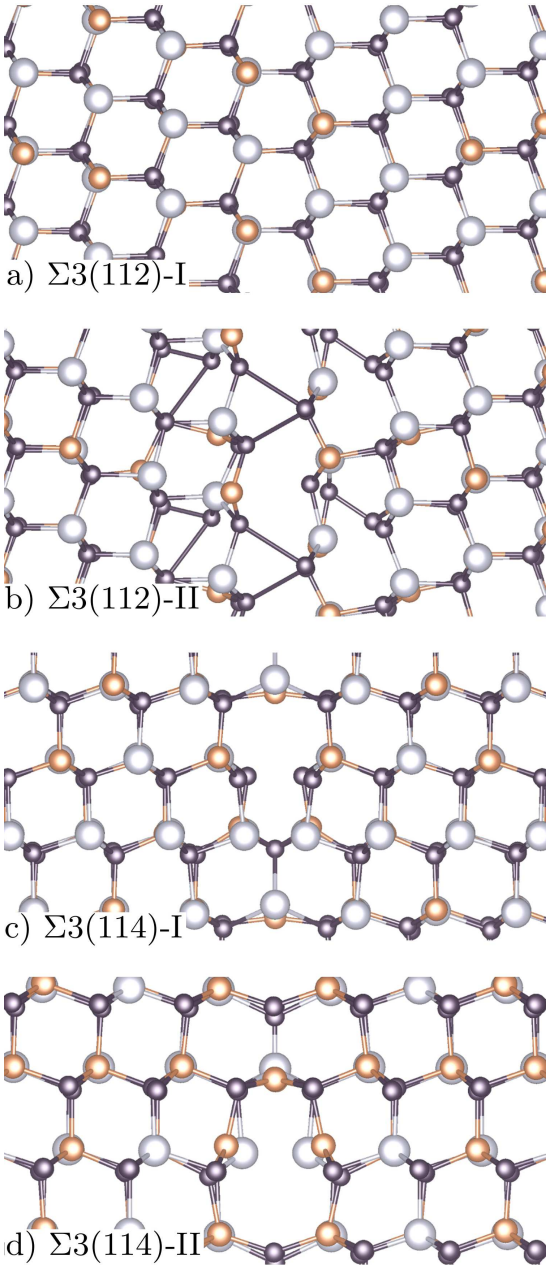

FIG. 1. (Color online) Atomic structure of the (a) cation-Se-terminated (type I) and (b) Se-Se-terminated (type II) Σ3(112) GB. (c) and (d) depict the atomic structure of the type I and type II of the Σ3(114) GB. The Cu, In, and Se atoms are shown as brown, large-light gray, and small-dark gray spheres, respectively.

I shows little changes in its structure, Σ3(112)-II undergoes dramatic structural relaxation. Compared to the bulk, Se atoms at the Σ3(112)-II GB are not surrounded by four cations. After optimization, the minimum distance between Se atoms increases from 3.11 Å to 3.52 Å. In contrast to $CuInSe_2$, Se atoms at the Σ3(112)-II GB of $CuGaSe_2$ (not shown here) are not located at the outermost layer of the GB: on one side of the GB, Se atoms migrate into the bulk and instead of Se-Se wrong bonds at the GBs, Se-cation bonds are formed. In a qualitatively agreement with the previous studies [9, 11], in the Σ3(114) GBs the atoms with dangling bonds show larger relaxation compared to the other atoms.

It has been discussed that dangling and wrong bonds in CdTe can create defect levels [30]. Since the Σ3(114) and Σ3(112)-II GBs contain these defects, one expects to see defect levels in the bandgap of the systems with these GBs as well. To study the effects of the GBs on the electronic structure, we calculated atom-projected partial DOS for the systems with GBs. The projected partial DOS for the Σ3(112) and Σ3(114) GBs in $CuInSe_2$ are shown in FIG. 2. All GBs (except Σ3(112)-I that creates no gap state) create unoccupied gap states close to the CBM which are in resonance with the conduction band states in agreement with the dI/dU simulations [31]. From the total energy of the charged (+1 and −1) GBs we have computed the thermodynamic charge transition levels. In $CuInSe_2$ and $CuGaSe_2$, the positively-charged GBs are not stable but the defect states can trap electrons to make the GBs negatively charged.

Our data show that the existence of GBs shifts the VBM and CBM with respect to the bulk VBM and CBM. This can lead to 'electron-free'/'hole-free' zone near the GBs where the concentration of electrons/holes is less than in the grain interior (GI). It has been discussed that the creation of such a barrier at the GBs for one type of the carrier (electron or hole) impedes electron-hole recombination at the GBs [16, 32, 33]. FIG. 3 schematically presents the computed band offsets between the GB and GI for $CuInSe_2$ and $CuGaSe_2$.

The other effect of the GBs on the electronic structure is to change the size of the bandgap. In the case of $CuInSe_2$, the systems containing Σ3(112)-I, Σ3(112)-II, Σ3(114)-I, and Σ3(114)-II have the bandgap size of 1.0 eV, 1.4 eV, 1.3 eV, and 1.3 eV, respectively. For the corresponding GBs in $CuGaSe_2$ the bandgaps are 1.6 eV, 1.6 eV, 1.8 eV, and 1.8 eV, respectively. In the following paragraphs, we give a detailed discussion of our findings for different types of GBs mentioned earlier.

Σ3(112)-I: in $CuInSe_2$ and $CuGaSe_2$, the Σ3(112)-I GBs do not create gap states but shift the VBM and CBM with respect to the bulk (FIG. 3). This band alignment draws electrons to the GB region but reflects holes away. The electron-hole recombination remains low because of insufficient holes at the GB. This GB forms easily in $Cu(In,Ga)Se_2$ due to its highly symmetric structure [34] and is harmless for the carrier transport.

Σ3(112)-II: the Σ3(112)-II GB in $CuInSe_2$ creates three gap states: one occupied state which is 0.1 eV above the VBM and two unoccupied states which are 0.3 eV and 0.4 eV below the CBM. The $\varepsilon(+/0)$ level is not in the bandgap, therefore holes are not trapped in the defect states. The $\varepsilon(0/-)$ level is in the bandgap, positioned 0.2 eV below the CBM. This defect level can be occupied by electrons only if $CuInSe_2$ is n-type. Our results are in agreement with the experimentally-observed charge-neutral Σ3(112) GBs in p-type $CuInSe_2$ [13]. In the system containing this type of GB, the VBM and CBM are 0.2 eV lower and higher than the bulk VBM and CBM, respectively (see FIG. 3, top panel). This

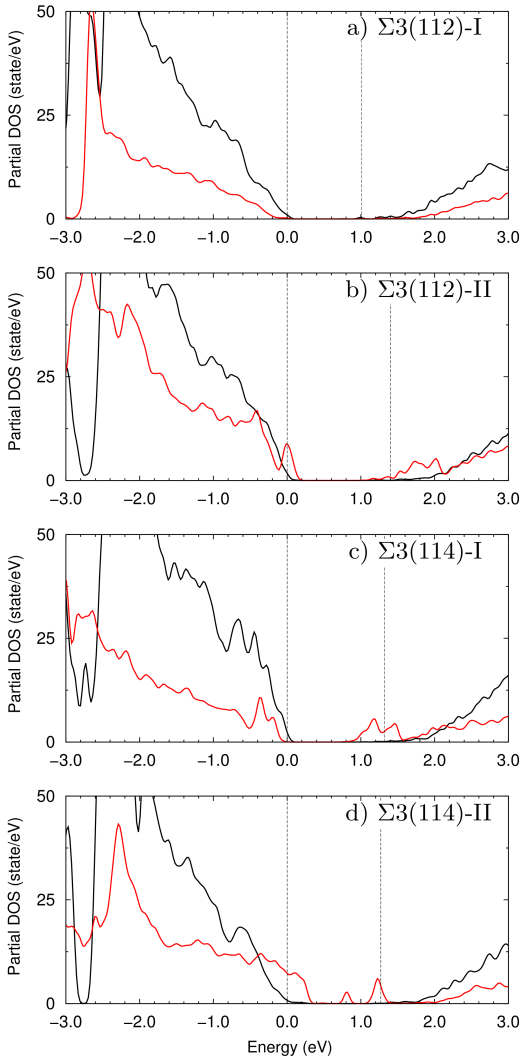

FIG. 2. (Color online) Partial DOS calculated for GBs in $CuInSe_2$. Black and red line show the projected DOS for the bulk atoms and the atoms close to the GBs, respectively. The zero of the energy is set at the bulk VBM. Vertical dashed lines show the VBM and CBM.

band alignment expels electrons and holes from the GB region. These electronic properties of the Σ3(112)-II GBs in $CuInSe_2$ explain why this type of GB is harmless for the carrier transport in p-type $CuInSe_2$.

In the case of $CuGaSe_2$, the $\varepsilon(+/0)$ level is not in the bandgap but the $\varepsilon(0/-)$ level is 1.5 eV below the CBM. Hence, electrons from the conduction band can be trapped in this level. Considering the band alignment (FIG. 3, bottom panel), both the VBM and CBM of this system are 0.2 eV lower than the VBM and CBM of the bulk. That is, while this GB creates an electrostatic barrier for holes, concentration of electrons close to this GB is higher than in the GI. The valence band offset, however, is not large enough to suppress the holes concentration at the GB [33] therefore the carrier lifetime is reduced if this type of the GB is formed in $CuGaSe_2$.

Σ3(114)-I: as it is shown in FIG. 2 (c), the dangling and wrong bonds of the Σ3(114)-I GB in $CuInSe_2$ cause unoccupied gap states to form. The deepest unoccupied state is 0.5 eV below the CBM. The $\varepsilon(0/-)$ and $\varepsilon(+/0)$ charge transition levels are 0.7 eV and 0.5 eV below the CBM and VBM, respectively. Thus, the positively-charged gap states are not stable but the defect levels can trap electrons and become negatively charged. The band offset of this system, however, screens this GB from bulk carriers and results in low probability of recombination.

Formation of the Σ3(114)-I GBs in $CuGaSe_2$ creates three unoccupied gap states. The $\varepsilon(0/-)$ level is 1.2 eV below the CBM, therefore the defect levels can trap electrons even for a p-type $CuGaSe_2$. Holes, on the other hand, cannot be trapped in the defect levels. The conduction band offset (FIG. 3, bottom panel) makes the region close to this GB electron rich. The motion of holes into the GB region, on the other hand, is impeded due to the valence band offset. The size of the valence band offset, however, is not large enough to mitigate the effect of the presence of this GB in the system [33].

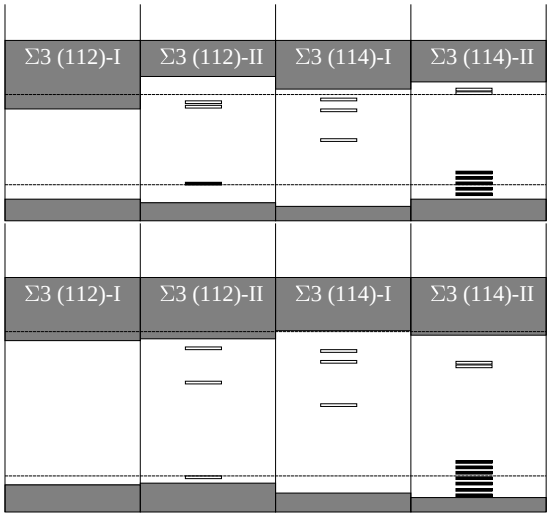

FIG. 3. Schematic band offset and gap states of GBs for $CuInSe_2$ (top panel) and $CuGaSe_2$ (bottom panel). The occupied and unoccupied gap states are represented as black and white rectangles. Horizontal dashed lines show the bandgap of the bulk $CuInSe_2$ ($E_g = 1.0$ eV) and $CuGaSe_2$ ($E_g = 1.6$ eV), respectively.

Σ3(114)-II: the cation dangling bonds create both occupied and unoccupied states in the bandgap of $CuInSe_2$ and $CuGaSe_2$. For $CuInSe_2$ (see FIG. 2 (d)), the occupied gap states are close to the VBM and the deepest state is 0.2 eV above the VBM. The deepest unoccupied gap state is 0.1 eV below the CBM. The $\varepsilon(+/0)$ level is not in the gap and the $\varepsilon(0/-)$ level is 0.5 eV below the CBM. This means, positively-charged gap states are not stable but if the chemical potential of the electrons is high, i. e. n-type $CuInSe_2$, then electrons can be trapped in the defect levels. Still, the electron- and hole-free zone near this GB make the probability of recombination low.

The VBM and CBM of this GB in $CuGaSe_2$ are 0.3 eV and 0.1 eV below the bulk VBM and CBM, respectively. The transition level $\varepsilon(+/0)$ is not in the gap and $\varepsilon(0/-)$ is 0.9 eV below the CBM. This GB remains neutral for p-type $CuGaSe_2$ but for high chemical potential of the electrons, the gap states can become negatively charged. The conduction band offset for this GB (FIG. 3, bottom panel) also leads to a high concentration of electrons close to the GB, meaning that the chance of electrons to be trapped in the gap state is high. Although the valence band offset repels holes from the GB, it cannot effectively screen the GB from holes and this GB is prone to recombination [33].

We note that in our study the electronic-structure changes are merely due to the existence of the GBs. To look into the influence of changing the chemical potential of the constituent atoms, we have studied the effect of the formation of a charge-neutral defect pair ($2V^{-}_{Cu} + In^{++}_{Cu}$) on the electronic structure of Σ3(112)-II in $CuInSe_2$. In agreement with previous results [16], the VBM is lower than the bulk VBM. In this system, the occupied gap state is removed from the bandgap but the unoccupied gap states are still present.

In summary, our results are the following: (i) to study GBs in $Cu(In,Ga)Se_2$, employing a method that can correctly describe the electronic structure of this material, hybrid functional for example, is essential. (ii) The formation of GBs can alter the electronic structure of their systems in three different ways: a) GB creates gap states, b) GB shifts the VBM and CBM with respect to the bulk, and c) GB changes the bandgap size. (iii) Although gap states can be detrimental for the carrier transport, the band offsets and the change in the bandgap sizes mitigate this destructive effect in $CuInSe_2$. (iv) The behavior of the Σ3 GBs in $CuGaSe_2$ is different from $CuInSe_2$. The conduction band offset draws electrons to the GB region and the valence band offset is not large enough to suppress the concentration of holes. This band offset makes the presence of the symmetric GBs in $CuGaSe_2$ destruc-

tive, except for the Σ3(112)-I GB that does not create defect levels.

We acknowledge the financial support from the *Bundesministerium für Wirtschaft und Energie (BMWi)* for the comCIGS II project (0325448C).

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[1] A. Chirila, P. Reinhard, F. Pianezzi, P. Bloesch, A. Uhl, C. Fella, L. Kranz, D. Keller, C. Gretener, H. Hagendorfer, D. Jaeger, R. Erni, S. Nishiwaki, S. Buecheler, and A. Tiwari, Nature Mater. **12**, 1107 (2013).
[2] P. Jackson, D. Hariskos, R. Wuerz, O. Kiowski, A. Bauer, T. M. Friedlmeier, and M. Powalla, physica status solidi (RRL) – Rapid Research Letters **9**, 28 (2015).
[3] C. H. Seager, G. E. Pike, and D. S. Ginley, Phys. Rev. Lett. **43**, 532 (1979).
[4] U. Rau, K. Taretto, and S. Siebentritt, Applied Physics A **96**, 221 (2009).
[5] D. Abou-Ras, B. Schaffer, M. Schaffer, S. S. Schmidt, R. Caballero, and T. Unold, Phys. Rev. Lett. **108**, 075502 (2012).
[6] Y. Yan, R. Noufi, and M. M. Al-Jassim, Phys. Rev. Lett. **96**, 205501 (2006).
[7] M. J. Hetzer, Y. M. Strzhemechny, M. Gao, M. A. Contreras, A. Zunger, and L. J. Brillson, Applied Physics Letters **86**, 162105 (2005).
[8] C. Lei, C. M. Li, A. Rockett, and I. M. Robertson, Journal of Applied Physics **101**, 024909 (2007).
[9] Y. Yan, C.-S. Jiang, R. Noufi, S.-H. Wei, H. R. Moutinho, and M. M. Al-Jassim, Phys. Rev. Lett. **99**, 235504 (2007).
[10] J. Li, D. B. Mitzi, and V. B. Vivek, ACS Nano **5**, 8613 (2011).
[11] W.-J. Yin, Y. Wu, R. Noufi, M. Al-Jassim, and Y. Yan, Applied Physics Letters **102**, 193905 (2013).
[12] C. Feng, M. Luo, B. Li, D. Li, J. Nie, and H. Dong, Physics Letters A **378**, 1956 (2014).
[13] R. Baier, D. Abou-Ras, T. Rissom, M. C. Lux-Steiner, and S. Sadewasser, Applied Physics Letters **99**, 172102 (2011).
[14] S. Siebentritt, S. Sadewasser, M. Wimmer, C. Leendertz, T. Eisenbarth, and M. C. Lux-Steiner, Phys. Rev. Lett. **97**, 146601 (2006).
[15] C.-S. Jiang, M. A. Contreras, I. Repins, H. R. Moutinho, Y. Yan, M. J. Romero, L. M. Mansfield, R. Noufi, and M. M. Al-Jassim, Applied Physics Letters **101**, 033903 (2012).
[16] C. Persson and A. Zunger, Phys. Rev. Lett. **91**, 266401 (2003).
[17] Y. Hinuma, F. Oba, Y. Kumagai, and I. Tanaka, Phys. Rev. B **88**, 035305 (2013).
[18] J. Pohl and K. Albe, Phys. Rev. B **87**, 245203 (2013).
[19] J. Vidal, S. Botti, P. Olsson, J.-F. m. c. Guillemoles, and L. Reining, Phys. Rev. Lett. **104**, 056401 (2010).
[20] J. Heyd, G. E. Scuseria, and M. Ernzerhof, The Journal of Chemical Physics **118**, 8207 (2003).
[21] J. Pohl, A. Klein, and K. Albe, Phys. Rev. B **84**, 121201 (2011).
[22] Y. Hinuma, F. Oba, Y. Kumagai, and I. Tanaka, Phys. Rev. B **86**, 245433 (2012).
[23] M. I. Alonso, K. Wakita, J. Pascual, M. Garriga, and N. Yamamoto, Phys. Rev. B **63**, 075203 (2001).
[24] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).
[25] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).
[26] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
[27] H.-P. Komsa, T. T. Rantala, and A. Pasquarello, Phys. Rev. B **86**, 045112 (2012).
[28] Y. Yan, M. M. Al-Jassim, and T. Demuth, Journal of Applied Physics **90**, 3952 (2001).
[29] Y. Yan, M. M. Al-Jassim, and K. M. Jones, Journal of Applied Physics **94**, 2976 (2003).
[30] L. Zhang, J. L. F. Da Silva, J. Li, Y. Yan, T. A. Gessert, and S.-H. Wei, Phys. Rev. Lett. **101**, 155501 (2008).
[31] H. Mönig, Y. Smith, R. Caballero, C. A. Kaufmann, I. Lauermann, M. C. Lux-Steiner, and S. Sadewasser, Phys. Rev. Lett. **105**, 116802 (2010).
[32] C. Persson and A. Zunger, Applied Physics Letters **87**, 211904 (2005).
[33] M. Gloeckler, J. R. Sites, and W. K. Metzger, Journal of Applied Physics **98**, 113704 (2005).
[34] R. Baier, *Electronic grain boundary properties in polycrystalline Cu(In,Ga)Se_2 semiconductors for thin film solar cells*, Ph.D. thesis, Helmholtz-Zentrum Berlin für Materialien und Energie (2012).