Electrically Benign Behavior of Grain Boundaries in Polycrystalline $CuInSe_2$ Films

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The classic grain-boundary (GB) model concludes that GBs in polycrystalline semiconductors create deep levels that are extremely harmful to optoelectronic applications. However, our first-principles density-functional theory calculations reveal that, surprisingly, GBs in $CuInSe_2$ (CIS) do not follow the classic GB model: GBs in CIS do not create deep levels due to the large atomic relaxation in GB regions. Thus, unlike the classic GB model, GBs in CIS are electrically benign, which explains the long-standing puzzling fact that polycrystalline CIS solar cells with remarkable efficiency can be achieved without deliberate GB passivation. This benign electrical character of GBs in CIS is confirmed by our scanning Kelvin probe microscopy measurements on $Cu(In, Ga)Se_2$ chalcopyrite films.

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Polycrystalline semiconductors generally exhibit poor optoelectronic properties compared to their single-crystal counterparts due to the existence of grain boundaries containing dislocation cores, which typically create deep levels and act as effective recombination centers, as the classic grain-boundary (GB) model concludes [1,2]. Thus, for polycrystalline solar cells, GB passivation is extremely important to suppress the harmful effects of GBs [3,4]. Surprisingly, however, without special GB passivation, the efficiency of polycrystalline $Cu(In, Ga)Se_2$ (CIGS)-based solar cells is now approaching 20% [5], surpassing their single-crystal counterparts (~13%) [6]. Therefore, understanding GB behaviors in $CuInSe_2$ (CIS) chalcopyrite films has attracted great attention for many years. Although extensive studies have been reported [7–16], to date, an unambiguous conclusion on the physics of GBs in CIS thin films is still lacking.

For a long time, GBs in polycrystalline CIS thin films have been explained by the classic electronic GB model because direct scanning Kelvin probe microscopy (SKPM) measurements have clearly shown that GBs in CIS and CIGS are charged [7–10]. However, the classic electronic GB model cannot explain the remarkable performance of polycrystalline CIS-based solar cells. A recent theoretical study has proposed that GBs in CIS could be significantly Cu poor, act as hole barriers, and are charge neutral [12]. A more recent study [16] argued that if the GB is Cu poor, then a type-II band alignment between the GB regions and grain-interior (GI) regions should form [17]. Thus, the GB not only behaves like a hole reflector, but also as an electron sink; therefore, it reduces the electron-hole recombination at the GB. However, these new theories are not yet definitively confirmed by experimental evidence.

Note that the new theories on GBs in CIS were not derived from real GB structures, but rather, are based on the characteristics of the CIS (112) polar surface, which is usually Cu poor. It is necessary to study the physics of realistic GB structures with dislocation cores in CIS to understand the role of GBs in the extraordinary performance of polycrystalline CIS-based solar cells.

In this Letter, we report on a first-principles density-functional theory study of GB structures with dislocation cores in CIS. We find that, contrary to the classic model, GBs in CIS do not create deep levels due to the large atomic relaxation in GB regions. Thus, they are electrically benign and not harmful to solar cell performance. We further find that Na segregates strongly into GBs in CIS and exhibits electrical potentials, which helps carrier separation. The electrically benign character of GBs in CIS and electrical potentials resulting from Na segregation are further confirmed by our SKPM measurements on polycrystalline CIGS chalcopyrite films grown on Na-free and Na-containing substrates. Thus, our results explain the long-standing puzzling fact of why polycrystalline CIS solar cells with remarkable efficiency can be achieved without deliberate GB passivation.

The first-principles total-energy calculations are based on the density-functional theory, using the Vienna *ab initio* simulation package (VASP) [18]. We used the local density approximation (LDA) and ultrasoft Vanderbilt-type pseudopotentials as supplied by Kresse and Hafner [19]. The cutoff energy for the plane-wave basis was 320 eV. The GBs were modeled using a 96-host-atom supercell. In all calculations, all atoms were allowed to relax to reach the minimum energies until the Hellmann-Feynman forces acting on them became less than 0.02 eV/Å.

Obtaining the atomic structures of GBs in polycrystalline films is a very difficult task. To date, no atomic GB structure with dislocation cores in CIS-related polycrystalline films has been determined. However, a realistic atomic GB structure can be adopted from other materials with similar structures. CIS possesses a chalcopyrite structure, which has the same fundamental structural characteristics of CdTe (zinc blende); i.e., they can be described as two interpenetrating face-centered cubic (FCC) cation and anion lattices [20]. Thus, the atomic structures of GBs determined in CdTe can be adopted for CIS. We have experimentally determined the atomic structure of GBs in CdTe [21]. These GBs comprise dislocation cores, containing dangling bonds, wrong bonds, and wrong bonding angles, which are the fundamental features of GBs responsible for deep levels. Thus, these GBs are well suited for studying GB physics in CIS.

Figures 1(a) and 1(b) show the atomic structures of two GBs in CIS adopted from CdTe [21]. The structures are fully relaxed by our density-functional total-energy calculations. These two GBs have the same geometry and dislocation core structure, but with different bonding configurations. For example, in Fig. 1(a), the Se atom marked by Se1 has one extra bond, but in Fig. 1(b), the cations marked by Cu1 and In1 have one extra bond. In Fig. 1(a), Se atoms marked by Se2 have dangling bonds, but in Fig. 1(b), the In atoms indicated by In2 have wrong bonds. Our previous study reveals that in CdTe these dangling bonds, wrong bonds, and extra bonds create deep levels [21,22]. Therefore, it is important to know if these principles would also apply to GBs in CIS.

Surprisingly, however, we find that the same GB structures in CIS behave dramatically different from those in CdTe. It is energetically unfavorable for Se atoms to form Se-Se wrong bonds. This leads to large atomic relaxation at the GB regions and results in significant GB expansion—about 1.3 Å for the structures shown in Figs. 1(a) and 1(b), respectively. As a result, the dangling bonds, wrong bonds, and extra bonds in the GBs in CIS do not create deep levels. Figure 2 shows calculated site projected density of states (PDOS) of Cu [Fig. 2(a)], In [Fig. 2(b)], and Se [Fig. 2(c)] atoms around the dislocation core shown in Fig. 1(a), which contain dangling bonds, wrong bonds, and extra bonds. For comparison, the sum of PDOS from one Cu, one In, and one Se atom in a perfect region is shown in the figure (marked by CIS), which serves as a guide when looking for possible deep levels created by atoms around the dislocation core. Cu1, In1, and Se2 atoms in Fig. 1(a) have a dangling bond, whereas Se1 has an extra bond. However, as seen in Fig. 2, these atoms do not create any deep levels. Similar results (not shown) are found for the GB structure shown in Fig. 1(b). Thus, the GB structures shown in Fig. 1 are expected to be electrically benign. Because dangling bonds, wrong bonds, and extra bonds represent the general features of dislocations and GBs, our results should be general and can be applied to all GB structures in CIS-based polycrystalline films. Hence, our results suggest that, unlike in typical polycrystalline semiconductors, GBs in CIS are not recombination centers, explaining the long-standing puzzling fact: polycrystalline CIS-based solar cells with remarkable efficiency can be achieved without deliberate GB passivation.

The absence of deep levels in GBs in CIS is truly an exception from the classic GB model. It also differs significantly from the recently proposed hole-barrier model. Our previous calculations showed that the same GBs in Si

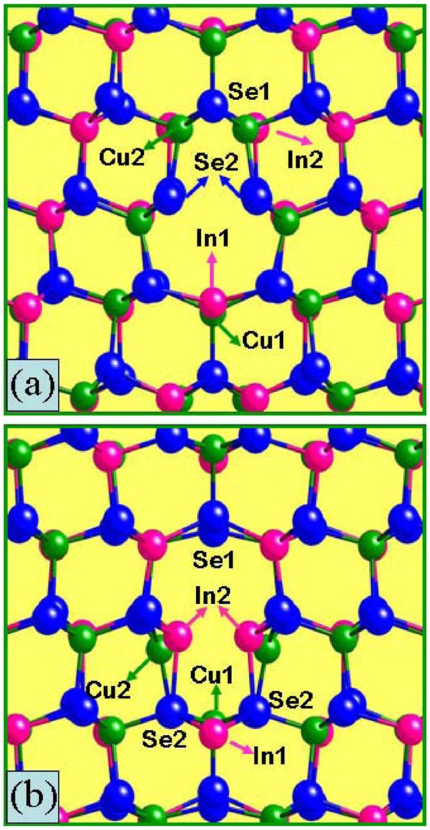

FIG. 1 (color online). Atomic structure of GBs containing dislocation cores adopted from GB structures determined in CdTe with (a) Se dangling bonds and (b) cation dangling bonds.

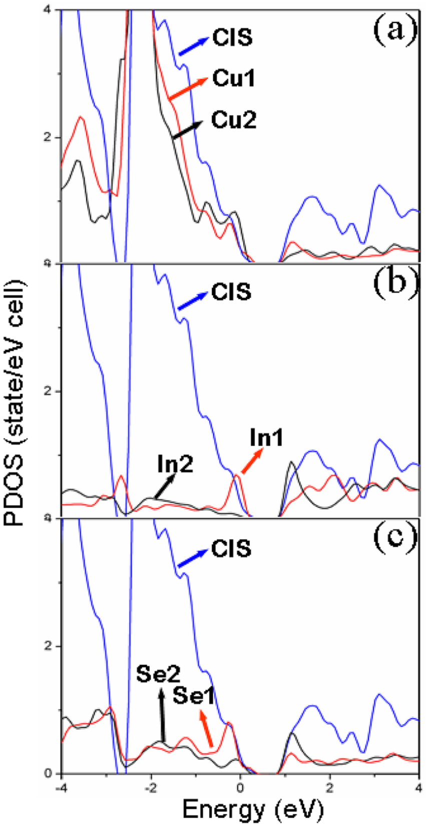

FIG. 2 (color online). Calculated PDOS of (a) Cu, (b) In, and (c) Se atoms around the dislocation core in the relaxed GB shown in Fig. 1(a).

and CdTe create deep levels. In CdTe, the deep levels can be passivated by Cl or I [22]. We find that the absence of deep levels in GBs in CIS is attributed to the large atomic relaxation in the GB regions. To confirm this, we have calculated PDOS of the same GBs without relaxation. Figure 3 shows the calculated PDOS for Cu, In, and Se atoms around the dislocation core shown in Fig. 1(a). It is clearly seen that the Cu, In, and Se atoms with dangling bonds, wrong bonds, and extra bonds create deep levels in the GB without atomic relaxation. We have also calculated PDOS (not shown) for the GB shown in Fig. 1(b) without atomic relaxation, and deep levels are also found. A comparison of Figs. 2 and 3 clearly shows that after the large atomic relaxation, the deep levels seen in Fig. 3 move into the valence bands and end with a clean band gap, as seen in Fig. 2. These results confirm that the absence of deep levels in GBs in CIS is attributed to the large atomic relaxation in the GB regions. We find that Se-Se wrong bonding is energetically very unfavorable, due to their large electronegativity. The strong repulsions between Se atoms result in the large atomic relaxation in the GB regions.

In a recent theoretical investigation [12], an extremely Cu-poor condition in GB regions is suggested. Therefore, we calculated the energy difference between a Cu vacancy located in the GB region and in the perfect region. We find that the formation energy is about 0.2 eV smaller for both GB structures in GB regions than in perfect regions, indicating that the concentration of Cu vacancies is slightly higher in the GB regions than in the perfect regions. Our results therefore suggest that GBs in CIS should not create significant neutral hole barriers, but only small barriers, which is consistent with the recent experimental results [14].

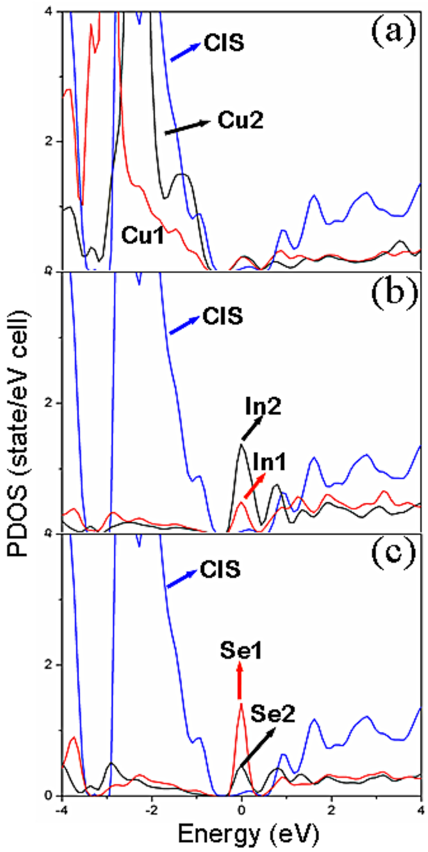

FIG. 3 (color online). Calculated PDOS of (a) Cu, (b) In, and (c) Se atoms around the dislocation core in the GB shown in Fig. 1(a) without atomic relaxation in the GB region.

It is known that to achieve high efficiency, CIS-based films must be grown on soda-lime glass substrates, where the diffusion of Na into CIGS films from the substrates improves the device performance [23–25]. We therefore study the segregation behavior of Na in GBs. Na atoms in CIS prefer interstitial sites and are shallow donors. We find that Na prefers an interstitial site in GBs and bond with two Se atoms with dangling bonds—namely, two Se2 atoms in the structure shown in Fig. 1(a) and two Se1 atoms in the structure shown in Fig. 1(b). We calculate the segregation energy of Na at GBs by

$$E_s = E_{\mathrm{tot}}(\mathrm{Na_{GB}}) - E_{\mathrm{tot}}(\mathrm{Na_{perf}}), \tag{1}$$

where $E_{\mathrm{tot}}(\mathrm{Na_{GB}})$ is the total energy of the supercell with a Na located in the GB, and $E_{\mathrm{tot}}(\mathrm{Na_{perf}})$ is the total energy of the supercell with a Na located in a perfect region. The calculated segregation energies are -2.2 and -2.4 eV/Na for GBs shown in Figs. 1(a) and 1(b), respectively. Thus, our results indicate that significant Na segregation in GBs in CIS films grown on soda-lime glass is expected. Indeed, Auger electron spectroscopy, photoelectron spectroscopy, and x-ray emission spectroscopy studies have clearly revealed that Na in CIGS does segregate into grain boundaries [26,27]. Na atoms in the GBs are also shallow donors. Consequently, in p-type CIS films, Na atoms in GBs are always positively charged, which should exhibit observable electrical potentials.

Our theoretical results conclude that unlike in typical semiconductors, GBs in CIS create no deep levels and are charge neutral; thus, they exhibit no electrical potentials. For CIS grown on soda-lime glass, Na segregates into GBs; as a result, GBs are positively charged and exhibit potentials. This distinct difference is directly confirmed by our SKPM study of polycrystalline CIGS films grown on Mo-coated soda-lime glass and Mo-coated borosilicate glass. The two films are grown side by side, so they have similar morphology. X-ray diffraction measurements reveal that both films have the [220]/[204]-preferred orientation. Figures 4(a) and 4(c) show the topography images of the surfaces of the CIGS films grown on Mo-coated soda-lime glass and Mo-coated borosilicate glass, respectively. It is seen that they are similar, confirming that the structures of these two films are similar. Their corresponding SKPM images with the same gray scale of 200 meV are shown in Figs. 4(b) and 4(d), respectively. Unlike the topography images, the SKPM images show distinctly different features. The GBs are clearly identified in Fig. 4(b), but Fig. 4(d) is almost featureless. The SKPM images are the

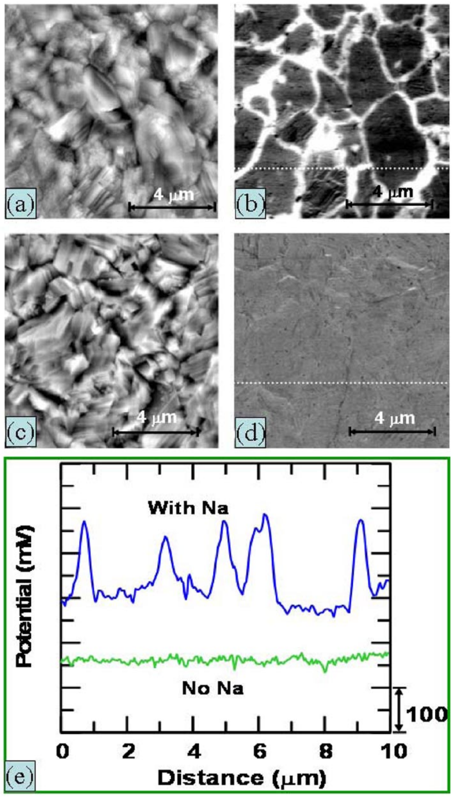

FIG. 4 (color online). Topography images of surfaces of the CIGS films grown on Mo-coated soda-lime glass (a) and Mo-coated boron silicate glass (c) and their corresponding SKPM images (b),(d) with the same gray scale of 200 meV. (e) Potential line profiles measured along the dotted lines shown in (b) (upper curve) and (d) (lower curve).

mapping of measured work functions across the surfaces. The brighter contrast along the GBs shown in Fig. 4(b) indicates higher electrical potentials and smaller work functions at GBs than in nearby surface regions.

The difference is seen even more clearly in the potential profiles [Fig. 4(e)] measured along the dotted lines shown in Fig. 4(b) (upper curve) and Fig. 4(d) (lower curve). We see that the potential profile of the film grown on the borosilicate glass (lower curve) is almost featureless, with only small potential variations ($<\sim 30$ meV), which may originate from a topographic effect. However, GBs in the film grown on soda-lime glass (upper curve) exhibit clear electrical potentials (150–200 meV). These results provide direct evidence confirming that GBs in pure CIGS are electrically benign and Na segregation into GBs in CIS is responsible for the measured electrical potentials. Note that interstitial Na atoms in GBs and perfect regions in CIS are shallow donors and not recombination centers. The electrical potentials created by Na segregation at GBs should repel holes and attract electrons, which should help carrier separation. Thus, Na-segregated GBs could be beneficial to performance in CIS-based solar cells, which is consistent with the fact that CIS-based solar cells must be grown on soda-lime glass substrates to achieve superior efficiency.

In conclusion, we have studied the atomic and electronic structure of GBs in CIS by density-functional theory calculations. We found that GBs in CIS are electrically benign and therefore are not very harmful to optoelectronic applications.

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[1] J. Y. W. Seto, J. Appl. Phys. **46**, 5247 (1975).
[2] A. P. Sutton and R. W. Balluffi, *Interfaces in Crystalline Materials* (Oxford Science Publications, New York, 1995).
[3] A. Rohatgi *et al.*, Appl. Phys. Lett. **84**, 145 (2004).
[4] X. Wu *et al.*, in *Proceedings of the 17th European Photovoltaic Solar Energy Conference, Munich, Germany, 2001* (ETA, Florence, 2002), p. 995.
[5] M. A. Contreras *et al.*, Prog. Photovoltaics **13**, 209 (2005).
[6] C. H. Champness, in *Proceedings of the 29th IEEE Photovoltaic Specialist Conference, New Orleans, 2002* (IEEE, Piscataway, NJ, 2002), p. 732.
[7] D. Fuertes Marrón *et al.*, Phys. Rev. B **71**, 033306 (2005).
[8] C. Leendertz *et al.*, Appl. Phys. Lett. **89**, 113120 (2006).
[9] C.-S. Jiang *et al.*, Appl. Phys. Lett. **84**, 3477 (2004).
[10] C.-S. Jiang *et al.*, Appl. Phys. Lett. **85**, 2625 (2004).
[11] M. J. Romero *et al.*, Appl. Phys. Lett. **87**, 172106 (2005).
[12] C. Persson and A. Zunger, Phys. Rev. Lett. **91**, 266401 (2003).
[13] Y. Yan, R. Noufi, and M. M. Al-Jassim, Phys. Rev. Lett. **96**, 205501 (2006).
[14] S. Siebentritt *et al.*, Phys. Rev. Lett. **97**, 146601 (2006).
[15] Y. Yan *et al.*, Appl. Phys. Lett. **81**, 1008 (2002).
[16] S.-H. Wei and S.-B. Zhang, J. Phys. Chem. Solids **66**, 1994 (2005).
[17] S. B. Zhang *et al.*, Phys. Rev. B **57**, 9642 (1998).
[18] G. Kresse and J. Hafner, Phys. Rev. B **47**, R558 (1993); **49**, 14251 (1994); and **54**, 11169 (1996).
[19] D. Vanderbilt, Phys. Rev. B **41**, R7892 (1990); G. Kresse and J. Hafner, J. Phys. Condens. Matter **6**, 8245 (1994).
[20] Y. Yan *et al.*, Physica (Amsterdam) **401–402B**, 25 (2007).
[21] Y. Yan, M. M. Al-Jassim, and K. M. Jones, J. Appl. Phys. **94**, 2976 (2003).
[22] Y. Yan, M. M. Al-Jassim, and K. M. Jones, J. Appl. Phys. **96**, 320 (2004).
[23] K. Granath, M. Bodegard, and L. Stolt, Solar Energy Mater. Sol. Cells **60**, 279 (2000).
[24] N. Kohara *et al.*, Appl. Phys. Lett. **71**, 835 (1997).
[25] S.-H. Wei, S. B. Zhang, and A. Zunger, J. Appl. Phys. **85**, 7214 (1999).
[26] D. W. Niles, M. Al-Jassim, and K. Ramanathan, J. Vac. Sci. Technol. A **17**, 291 (1999).
[27] C. Heske *et al.*, Surf. Interface Anal. **30**, 459 (2000).