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# GRAIN-BOUNDARY PHYSICS IN POLYCRYSTALLINE PHOTOVOLTAIC MATERIALS

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## ABSTRACT

We use the combination of high-resolution electron microscopy and density-functional theory to study the atomic structure and electronic effects of grain boundaries in polycrystalline photovoltaic materials such as Si, CdTe, $CuInSe_2$, and $CuGaSe_2$. We find that grain boundaries containing dislocation cores create deep levels in Si, CdTe, and $CuGaSe_2$. Surprisingly, however, they do not create deep levels in $CuInSe_2$. We further find that the presence of Ga in grain boundaries in $CuInSe_2$ generates deep levels. These results may explain the fact that Si and CdTe solar cells usually require special passivation, whereas $CuInSe_2$ solar cells do not. The passivation of grain boundaries in Si and CdTe is also studied. We find that grain boundaries in CdTe can be passivated very well by Cl, Br, and I.

## INTRODUCTION

Polycrystalline semiconductor materials, such as Si, CdTe, and $CuInSe_2$ (CIS), hold great promise for producing low-cost, high-efficiency, and large-area solar cells [1–3]. However, polycrystalline materials are typically expected to exhibit poor performance compared to their single-crystalline counterparts [4], because of grain boundaries, which are usually effective recombination centers for photon-generated electrons and holes, as well as scattering centers of free carriers. Therefore, passivation is usually required for making high-efficiency Si and CdTe solar cells [1,2]. However, CIS is an exception. Without special grain-boundary (GB) passivation, the efficiency of the polycrystalline Cu(In,Ga)Se$_2$ (CIGS)-based device is now approaching 20% [3], significantly surpassing the best corresponding single-crystal devices (~13%) [5]. CuGaSe$_2$ (CGS) has the same structure as CIS. However, CGS solar cells have much lower performance than CIS cells. The classic "electronic" GB model concludes that GBs in polycrystalline semiconductors usually contain charged intrinsic defects that trap an excess number of majority carriers and form electrical potentials [6]. In the past, several scenarios were also presented to explain the behavior of GBs in CIS, but they are still under debate [7,8]. Therefore, there is still a need to understand the GB physics in photovoltaic materials.

Here, we use the combination of high-resolution electron microscopy and first-principles calculations to determine the atomic structure of grain boundaries and calculate the electronic properties of the following photovoltaic materials: Si, CdTe, CIS, and CGS. We found

that GBs in Si, CdTe, and CGS create deep levels and belong to the conventional GB model—the "electronic model." However, GBs in CIS do not create deep levels and are electrically benign [10]. Our results explain why CIS solar cells do not require a special passivation process, and we propose that high Ga concentration of Ga in CIGS grain boundaries are not desired. Our results also indicate that GBs in Si can only be partially passivated. However, GBs in polycrystalline CdTe are well passivated by Cl and I impurities.

## METHOD

Transmission electron microscopy (TEM) specimens were prepared by mechanical polishing to a thickness of ~100 μm, then dimpling the central portion of the specimens down to ~5 μm. The samples were subsequently thinned to electron transparency using a 4-kV Ar ion beam at 14° inclination, then cleaned at a lower voltage (1.5 kV). A liquid $N_2$ cooling stage was used to minimize milling damage. High-resolution TEM (HRTEM) images were taken on a Philips CM30 microscope with a Cs=2.0 mm, operating at 300 kV. The image simulations were carried out using the MacTempas program packages.

The first-principles total-energy calculations are based on the density-functional theory, using the Vienna ab-initio Simulation Package (VASP) [11]. We used the local density approximation (LDA) and ultrasoft Vanderbilt-type pseudopotentials [12] as supplied by Kresse and Hafner [13]. The cutoff energy for the plane-wave basis was 380 eV. The GBs were modeled using a 144-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.

## RESULTS AND DISCUSSION

We first determined the atomic structure of GBs in Si, CdTe, CIS, and CGS. It is usually very difficult to determine atomic structure of GBs in polycrystalline thin films. However, Si, CdTe, CIS, and CIGS have similar cubic crystal structures that can be described from the basic diamond structure. Si has a diamond structure that can be described by stacking Si layers along the [111] direction. CdTe can be described in the same manner, but with alternating Cd and Te layers. CIS can be described by alternately stacking a Se layer and a mixed Cu and In layer. Thus, it is reasonable to assume that GBs with the same characteristics should have the same atomic structure. We were only able to determine experimentally

the atomic structure GBs in polycrystalline CdTe thin films. We will adopt the structure for the defects in Si, CIS, and CGS for density-functional theory calculations.
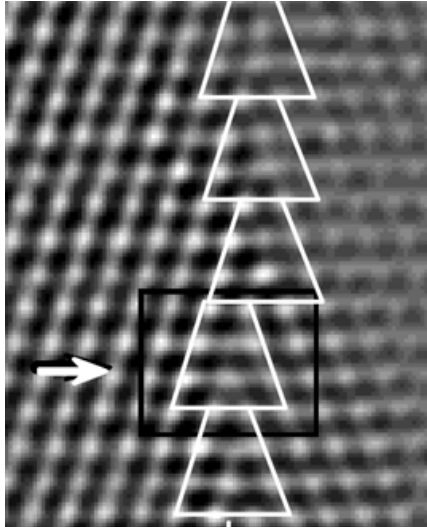


Fig. 1. HRTEM image of a GB in CdTe.

Figure 1 shows a HRTEM image of a GB obtained in a polycrystalline CdTe thin film. The GB consists of dislocation cores, as indicated by the white trapezoids. The GB is on the (11-2) plane. Based on the HRTEM image, eight possible structural models for the DP twin boundary are constructed with the guidance of the HRTEM image. These structure models are then relaxed using first-principles density-functional total-energy calculations. We find that there are only two structures that remain stable after the relaxation. Their optimized structures are shown in Figs. 2(a) and 2(b). The blue (dark color) balls indicate Cd atoms, whereas the gray (light color) balls indicate Te atoms. These two structures, called GB1 and GB2, respectively, look similar, but have different details. For example, in GB1, in Fig. 2(a), the atom numbered by 3 has four bonds and Te numbered by 2 has a dangling bond. But in GB2, the atom numbered by 3 has four bonds and Te numbered by 2 has a dangling bond.

Our first-principles density-functional total-energy calculations indicate that both structures could exist. It is not clear which of the two structures should fit the HRTEM image of the DP twin shown in Fig. 1. Thus, the two structurally optimized models are used for HRTEM image simulations. The experimental parameters are obtained by through-focus and through-thickness simulations of the HRTEM image of the perfect regions near the boundary. We find that the defocus value is about -65 nm and thickness is about 55 nm. Figures 2(c) and 2(d) are the simulated images using the structural models of Figs. 2(a) and 2(b), respectively. For these simulations, the defocus value of -65 nm and thickness of 55 nm are used. It is seen that Fig. 2(c) fits with Fig. 1 much better than Fig. 2(d). Thus, the combination of first-principles density-

functional total-energy calculations and HRTEM image indicates that the GB1 structure shown in Fig. 2(a) is a convincing model for the GB that we have observed experimentally. However, it is noted that the GB2 structure may also be observed in CdTe. Thus, theoretically, we will consider both structures.
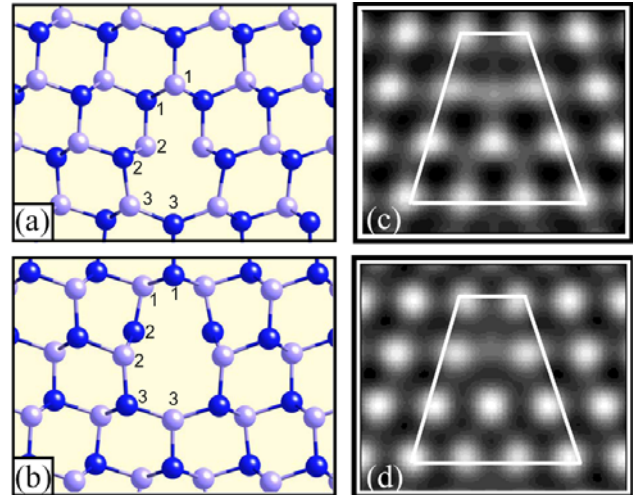


Fig. 2. (a) and (b) Determined atomic structure of GB1 and GB2. (c) and (d) Simulated HRTEM images of GB1 and GB2.
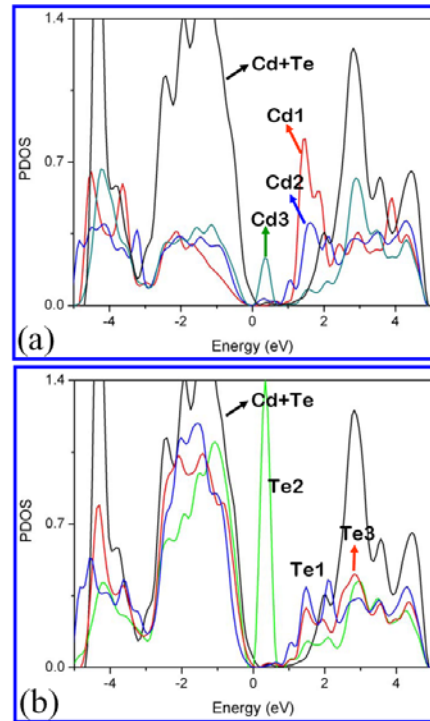


Fig. 3. Calculated PDOS of Cd and Te atoms around GB1.

To study the possible effects of the DP twin structures on the electronic property of CdTe, we calculate site-

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projected density of states (PDOS) of individual atoms around the boundaries and compare them with the PDOS of a Cd and Te pair in the perfect regions. Figure 3(a) shows the comparison of PDOS of the three Cd atoms on the GB1 shown in Fig. 2(a). The black solid line marked by Cd+Te is the PDOS of the Cd and Te pair in the perfect region. The PDOS of the Cd atoms marked by number 1, 2, and 3 in Fig. 2(a) are indicated by Cd1, Cd2, and Cd3, respectively. We see that the Cd3 atom produces a peak in the gap of CdTe. This is likely due to the fact that the Cd3 atom has a dangling bond. The rest of the Cd atoms are all four-fold and have no dangling bonds; thus, they do not produce deep levels in the gap.

Figure 3(b) shows the PDOS of the three Te atoms on the DP(1) boundary shown in Fig. 7(b) and a Cd and Te pair in a perfect region. The black solid line is the PDOS of the Cd and Te pair in the perfect region. The PDOS of the three Te atoms marked by numbers 1, 2, and 3 in Fig. 2(a) are indicated by Te1, Te2, and Te3, respectively. We see that the Te2 atom produces a very large peak in the gap region. This is because the Te2 atom has weak interaction with another Te atom.
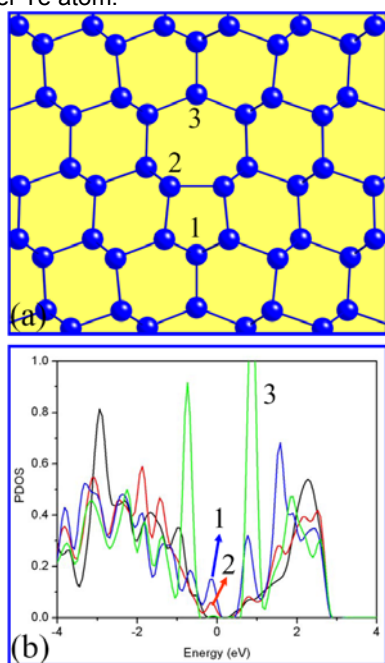


Fig. 4. (a) Atomic structure of GB in Si. (b) Calculated PDOS of Si atoms around the GB.

Figure 4(a) shows the GB structure in Si relaxed by density-functional theory. Compared to Si in perfect regions, Si1 has one extra bond, Si2 has wrong bonding angles, and Si3 has a dangling bond. Typically, the dangling bonds create deep-level states. However, our calculations revealed different results. Figure 4(b) shows the PDOS of the three Si atoms on the DP boundary and a Si atom in a perfect region. The black solid line is the PDOS of the Si in the perfect region. The PDOS of the three Si atoms marked by numbers 1, 2, and 3 in Fig. 4(a) are indicated by 1, 2, and 3, respectively. Our results

reveal that Si3 does not create deep levels. Instead, Si1 and Si2 create deep levels, as indicated by the arrows.
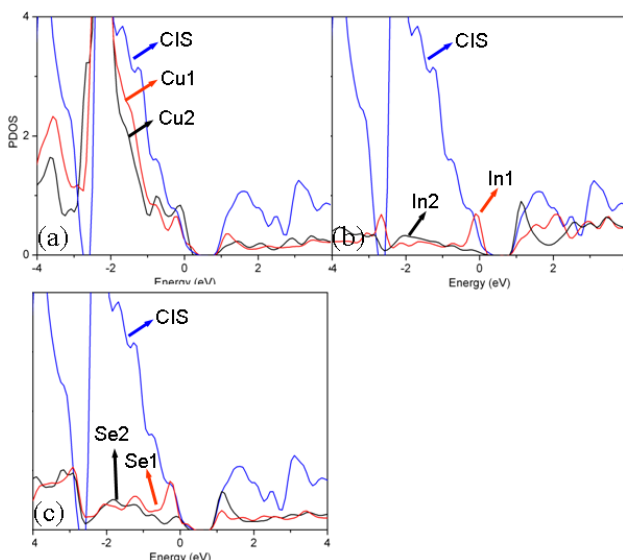


Fig. 5. Calculated PDOS of (a) Cu, (b) In, and (c) Se atoms around GB1 in CIS.

We have also adopted the GB structure for CIS. Surprisingly, however, they do not create deep levels in $CuInSe_2$. Figure 5 shows the calculated PDOS of (a) Cu, (b) In, and (c) Se atoms around GB1 in CIS. It is seen that unlike the GBs in Si and CdTe, the GBs in CIS exhibit no deep levels. We found that the reason for this unusual behavior in CIS is due to the huge expansion around the boundary. Our results thus explain why Si and CdTe solar cells usually require special passivation, whereas CIS solar cells do not.
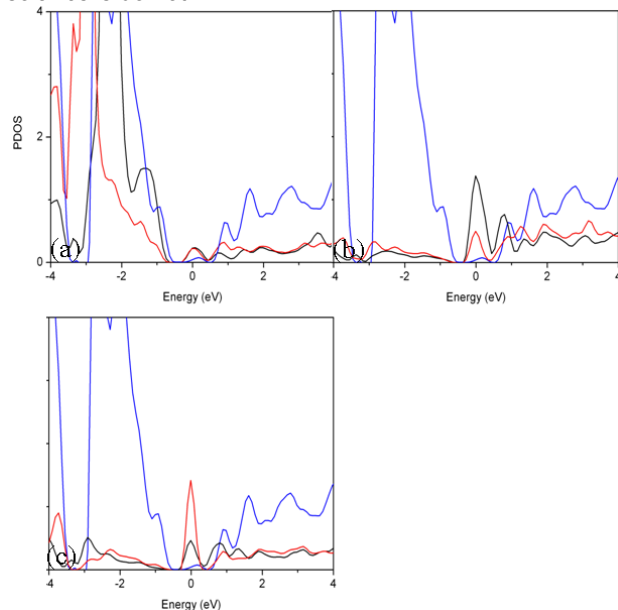


Fig. 6. Calculated PDOS of (a) Cu, (b) In, and (c) Se atoms around GB1 in CIS without expansion.

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To demonstrate our explanation, we have calculated the PDOS of (a) Cu, (b) In, and (c) Se of GB1 without expansion (Fig. 6). It is seen that without expansion, the very same GB showed deep levels.

We further find that the presence of Ga can affect the behavior of GBs in CIS. Ga at some In sites are found to present deep levels. In addition, the Se atoms bonding to these Ga atoms are also affected.
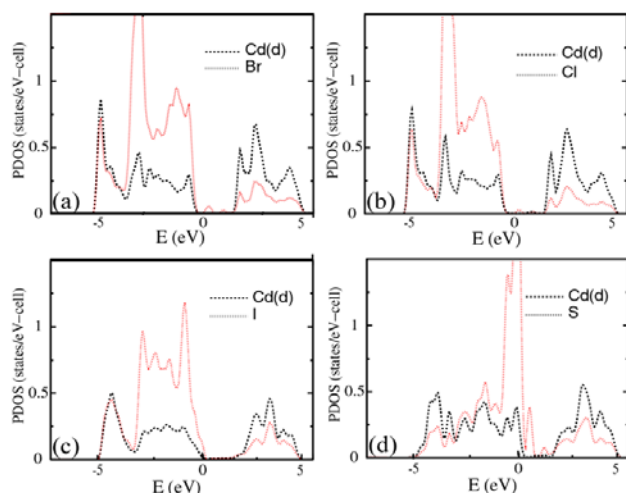


Fig. 7. Calculated PDOS of GB1 passivated by (a) Br, (b) Cl, (c) I, and (d) S.

We now discuss how the GBs in Si and CdTe can be passivated. We find that hydrogen can passivate the dangling bond of Si3 in Fig. 4(a). However, this passivation does not affect Si2 and Si 3 atoms. It interacts strongly with Si3.

It is believed that one of the effects of CdCl treatment is the passivation of defects by Cl. In our calculations, in addition to Cl, we also considered S and two other group-V elements, Br and I. Our total-energy calculations reveal that all these atoms are more favorable to bond with two Cd(1) atoms with dangling bonds, rather than to bond with Te atoms. To study the passivation effects of the GB1 by Br, Cl, I, and S, we calculate PDOS of individual atoms around the boundaries. Figure 7 shows the PDOS of a Cd(1) atom in the GB1 boundary after it is bonded with a Br, Cl, I, or S atom (dashed line) and the PDOS of the Br, Cl, I, and S atoms (dotted line). We see that the Cd(1) atom is no longer producing significant energy levels in the gap when Cd(1) atoms are bonded by the Br, Cl, I, and S atoms. The Br, Cl, and I atoms themselves also do not produce significant peaks in the gap. These indicate that Br, Cl, I, and S atoms can passivate well the Cd dangling bonds in the DP(1) twin boundaries. However, unlike Br, Cl, and I atoms, the S atom does not effectively passivate the Cd dangling bonds, as seen in Fig. 7(d), though the S atom bonds with the Cd atoms with dangling bonds. The S atom itself, as well as the Cd atom bonded by the S atom, produces high densities of energy levels in the bandgap.

## CONCLUSIONS

We studied the atomic structure and electronic properties of GBs in polycrystalline photovoltaic materials such as Si, CdTe, CIS, and CGS, using a combination of high-resolution electron microscopy and first-principles calculations. We found that GBs in Si, CdTe, and CGS create deep levels, and belong to the conventional GB model (the "electronic model"). However, GBs in CIS do not create deep levels and therefore are electrically benign and do not exactly belong to the conventional GB model. Our study of GB passivation indicates that GBs in Si can only be partially passivated by H. GBs in polycrystalline CdTe can be passivated well by Cl and I impurities.

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