

Effect of Copassivation of Cl and Cu on CdTe Grain Boundaries

Lixin Zhang,¹ Juarez L. F. Da Silva,¹ Jingbo Li,² Yanfa Yan,¹ T. A. Gessert,¹ and Su-Huai Wei¹

¹National Renewable Energy Laboratory, Golden, Colorado 80401, USA

²State Key Laboratory for Superlattices and Microstructures, Institute of Semiconductors, Chinese Academy of Sciences, P.O. Box 912, Beijing 100083, People's Republic of China

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Using a first-principles method, we investigate the structural and electronic properties of grain boundaries (GBs) in polycrystalline CdTe and the effects of copassivation of elements with far distinct electronegativities. Of the two types of GBs studied in this Letter, we find that the Cd core is less harmful to the carrier transport, but is difficult to passivate with impurities such as Cl and Cu, whereas the Te core creates a high defect density below the conduction band minimum, but all these levels can be removed by copassivation of Cl and Cu. Our analysis indicates that for most polycrystalline systems copassivation or multipassivation is required to passivate the GBs.

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Grain boundaries (GBs) and dislocations are generally viewed as detrimental to device applications, because they usually contain a high density of deep defect levels that act as recombination centers for charge carriers [1]. Surprisingly, two leading polycrystalline thin-film solar cells based on CuInSe₂ (CIS) and CdTe have produced very high efficiencies of 20% [2] and 16.5% [3], respectively, despite the fact that these materials contain significant amounts of GBs. Because these polycrystalline materials can be produced at relatively low cost and their efficiencies are higher than their single-crystalline counterparts [4], polycrystalline thin films have become one of the most important solar energy materials. However, the role of the GB in these systems is still unclear [5,6]. Therefore, understanding the behavior of the GB is not only important to further increasing the efficiencies in CIS- and CdTe-based solar cells, but also to the exploration of other polycrystalline materials such as Si and GaAs. A recent study on CIS has revealed that unlike in other materials, the GBs in CIS do not create deep levels because of the large relaxation in the GB region [4]. For CdTe, previous studies show that this is not the case; thus, careful passivation is needed to eliminate the effects of deep levels in CdTe GBs [7].

During the fabrication and processing of CdTe-based solar cells, many impurities are introduced intentionally or unintentionally. Among them, Cl and Cu are believed to be the two most important impurities. It has been observed from experiments that two treatments during the fabrication of CdTe-based solar cells are the most relevant in enhancing the energy conversion efficiency. One is post-deposition CdCl₂ heat treatment [8] and the other is to include Cu in the back contact of the solar module [9]. To date, there is no consensus about the exact role that the CdCl₂ heat treatment plays. It has been suggested that Cl can accumulate at the GBs, which can enhance grain growth, help grain recrystallization [8], and improve *p*

doping, possibly by creating a shallow acceptor complex, V_{Cd}-Cl_{Te} [10]. It has also been proposed that Cl may have a passivation effect on the GBs, thus improving the electric properties of the polycrystalline material [7]. For the Cu atoms in the back contact, it is believed that they can easily diffuse into CdTe due to the small diffusion barriers. Based on Cu being a *p*-type dopant in CdTe, it is natural to think that Cu impurities may improve the *p*-type conductivity and thus increase the efficiency of the solar cell. However, calculations have shown that the Cu_{Cd} defect level is relatively deep compared to V_{Cd}, the most abundant acceptor, thus adding Cu may reduce *p*-type conductivity than enhance it [10]. Experiments also suggested that Cu and Cl may have higher diffusivity in GBs than in the bulk and they may prefer to accumulate at the GBs [11]. There is also evidence that diffusion and accumulation of Cu and Cl may be correlated, in the form of a Cu_{Cd}-Cl_{Te} complex [12]. Therefore, it is important to perform a microscopic study to understand the roles of Cl, Cu, and the GBs.

In this Letter, we study the interaction of Cl and Cu with the GBs in CdTe. The well-established double-positioning twin boundaries [13] are taken as the prototype GB for polycrystalline CdTe. Two types of GBs exist within this model, and are referred to as the Te core and Cd core. First-principles electronic-structure calculations reveal that the Cd core is less harmful than the Te core in terms of density of deep levels in the band gap of CdTe. Energetic studies show that Cl favors substituting Te (Cl_{Te}) and Cu favors substituting Cd (Cu_{Cd}), both in the Te core. Each substitution can remove part of the deep levels, but to completely passivate the Te core GB, both Cl and Cu are needed. On the other hand, neither Cl nor Cu can passivate the deep levels in the Cd core. The results indicate that for CdTe polycrystalline solar cells, it is preferable to have only one type of core (i.e., Te core), because this type of core can be completely passivated by Cl and Cu, so the GBs do not reduce the electric and optical performance of the solar

cell. The results also indicate that for other polycrystalline systems, to passivate the deep levels of the GBs, copassivation or multipassivation may be needed.

The calculations are based on the density functional theory as implemented in the VASP code [14]. We used the projector-augmented wave (PAW) method with PBE potential [15]. The GBs have been incorporated in a $10 \times 2 \times 3$ unit cell of 120 atoms as shown in Fig. 1. The cutoff energy used for the plane-wave basis set is 280 eV, and the k points sampling in the Brillouin zone is done with a $1 \times 4 \times 2$ mesh. The calculated equilibrium lattice constant for bulk CdTe is 6.57 Å (experiment: 6.48 Å). Band alignment of the different structures is done by comparing calculated core levels. The GB and defect formation energies are calculated using

$$E_f = E_{\text{tot}} - (E_s + n_{\text{Cd}}\mu_{\text{Cd}} + n_{\text{Te}}\mu_{\text{Te}} + n_{\text{Cl}}\mu_{\text{Cl}} + n_{\text{Cu}}\mu_{\text{Cu}}), \quad (1)$$

where E_{tot} is the total energy of a specific structure; E_s is the total energy of a reference structure; $n_{\text{Cd}}(n_{\text{Te}}, n_{\text{Cl}}, n_{\text{Cu}})$ is the number of added Cd (Te, Cl, Cu) atoms from a reservoir to the reference structure in order to form the specific structure, and $\mu_{\text{Cd}}(\mu_{\text{Te}}, \mu_{\text{Cl}}, \mu_{\text{Cu}})$ is the chemical potential of the reservoir. Under equilibrium growth condition, the chemical potentials are restricted [16] by $\mu_{\text{Cd}} + \mu_{\text{Te}} = \Delta H_{\text{CdTe}}$; $\mu_{\text{Cl}} \leq \min(0, (\Delta H_{\text{CdCl}_2} - \mu_{\text{Cd}})/2)$ and $\mu_{\text{Cu}} \leq \min(0, (\Delta H_{\text{Cu}_7\text{Te}_4} - 4\mu_{\text{Te}})/7)$ [17], where the calculated values are $\Delta H_{\text{CdTe}} = -0.94$ eV (experiments: -0.73 to -0.96 eV), $\Delta H_{\text{CdCl}_2} = -3.65$ eV and $\Delta H_{\text{Cu}_7\text{Te}_4} = -0.81$ eV.

The GBs are formed by joining two identical (111) surfaces at an angle of $\sim 39^\circ$. Because there are two types of (111) surfaces in binary compounds, there are also two types of GB cores for CdTe as shown in Fig. 1(a). One is formed by Cd-terminated (111) surfaces and thereafter

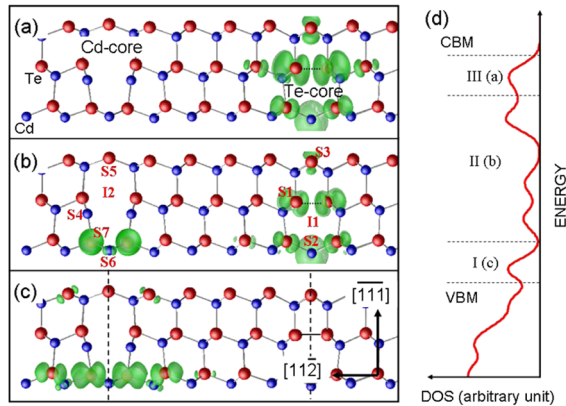


FIG. 1 (color online). Atomic structure of the GBs and charge density contours at density of $5 \times 10^{-3} e/\text{\AA}^3$ of defect states belong to three regions: (a) the shallow levels below CBM, (b) the deep levels, and (c) the shallow levels above VBM. The corresponding DOS is shown in (d).

referred to as Cd core; the other is formed by Te-terminated ($\bar{1}\bar{1}\bar{1}$) surfaces and referred to as Te core. Each core has mirror symmetry; the mirror planes are shown as dashed lines in Fig. 1(c). The cores are periodic along [111] direction and the periodicity is three double layers of CdTe. There are three configurations for the atoms in the GBs. The first is the five-coordinated Te (Cd) at S3 (S6) in Te core (Cd core). These atoms are shared by the two forming surfaces. The second is the three-coordinated Te (Cd) at S1 (S4) in Te core (Cd core). These atoms are just on the forming surfaces and assume a sp^3 configuration before relaxation. After relaxation, the Cd will assume a sp^2 configuration and the Te will form dimers with the mirror Te on the other forming surface. The third is the three-coordinated Te (Cd) at S2 (S5). These atoms are the bridging atoms that connect the two forming surfaces. They assume a sp^2 configuration before relaxation. After the relaxation, the Cd atoms prefer to form dimers but not Te.

In Fig. 1(d) the density of states (DOS) for the unit cell containing the two types of cores is shown. We see that the electronic levels of the GBs span the whole range of the band gap of CdTe. We divide the gap into three regions. Region I is from the valence band maximum (VBM) to 0.15 eV above; the states within this region are shallow levels above VBM. Region III is from the conduction band minimum (CBM) to 0.15 eV below; the states within this region are shallow levels below CBM. The remaining part is region II; the states within this region are deep levels and are the most detrimental to the carrier transport. From the contour plots of the partial charge density for the states within the three regions (Fig. 1), it is obvious that the electronic properties of the two cores are contrasting. In region III and upper part of region II, the GB levels are localized in the Te core. This is because in the Te core the Te atoms at S1 form dimers with Te on the mirror site. The antibonding Te dimer state with charge centered at S1 has energy in region III and behaves as a donor. The Cd atoms at S2 also form dimers along the $[1\bar{1}0]$ direction. The bonding dimer state with charge located between the two Cd atoms in a dimer has energy in the upper part of region II and accepts electrons from the Te dimer antibonding state. On the other hand, the states in region I and the lower part of region II are mainly centered at the fivefold-coordinated Cd atoms at S6 in Cd core. This is because in the Cd core, the Cd at S4 prefers to donate electrons and move away from its mirror image, so it does not form Cd dimers. The dangling bond state of the threefold-coordinated Te atoms at S5 falls inside the valence band. Therefore, only the fivefold-coordinated Cd at S6 behaves like surface Te with dangling bond states near the VBM.

It is believed that Cl and Cu may play important roles in passivating the GB states. To understand the effects, we have first calculated the formation energies of the two impurities at all the possible configurations in the GBs as

well as in the bulk. The results for maximum Cl or Cu chemical potential are shown in Fig. 2. We find that the most favorable site for Cl is Cl_{Te} at S1, and for Cu is Cu_{Cd} at S2, both in the Te core. In the Cd core, both substitutional and interstitial Cl or Cu have higher energies than in the Te core, but still have lower energies than in the bulk. So during the diffusion, Cl and Cu will tend to accumulate at the GBs.

The above conclusion is independent of the Te (Cd) chemical potentials. On the other hand, the second-lowest energy positions are mostly in the Cd core and depend on the growth conditions. For example, the substitutional Cl_{Te} at S7 site ($\text{Cl}_{\text{Te}}^{\text{S7}}$) is preferred only under Te-poor condition; the interstitial Cl_i at I2 site (Cl_i^{I2}) is preferred only under Te-rich condition; the substitutional Cu_{Cd} at S4 site ($\text{Cu}_{\text{Cd}}^{\text{S4}}$) is preferred only under Te-rich condition, whereas under Te-poor condition, Cu becomes more stable at an interstitial I1 site (Cu_i^{I1}) in the Te core. It is interesting to note that Cu_{Cd} at the S6 site ($\text{Cu}_{\text{Cd}}^{\text{S6}}$) has rather high energy.

As discussed above, the Te dimers at S1 site in Te core are one of the main sources for the deep levels in CdTe GBs and Cl prefers to occupy the S1 site. We find that after Cl substitutes one of the Te atoms in the dimer, the deep levels on the two Te atoms are removed. This can be understood by a simple electron counting rule [18]. The substitutional Cl has three Cd neighbors, each donating $2/4$ electrons. So the Cl has $(7 + 6/4 = 8.5)$ electrons, which is 0.5 electrons more than the 8 that are needed for Cl^- . The dimer will break and the other Te atom in the dimer will relax back; it has one dangling bond that can accept $(2 - 6/4 = 0.5)$ electrons to get fully filled. So if half of all the S1 site Te atoms are substituted by Cl, all the deep levels derived by the Te dimers in the GB can be completely passivated. In Fig. 3(a), the DOS of the GBs after half of the Te atoms are substituted by Cl is shown. First we see that the shallow

levels below CBM are totally cleared. The DOS of the deep levels in region II is reduced compared to the DOS in Fig. 1(d). The partial charge density contour plot in Fig. 3(d) for the deep levels further shows that the deep levels on the S1 Te atoms in the Te core are completely passivated. The deep levels on the Cd atoms at S2 site in the Te core and around Cd atoms at S6 site in Cd core are not affected. So we see that the passivation is essentially a localized effect.

Cl may also occupy the next favorable sites, i.e., $\text{Cl}_{\text{Te}}^{\text{S7}}$ and Cl_i^{I2} , especially in the process of diffusion, before global equilibrium is reached. In Fig. 3(b), the effect of Cl_i^{I2} on the DOS is shown. We see that Cl_i^{I2} forms acceptor states inside the gap; the contour plot in Fig. 3(e) shows that the charge density of the deep levels in the Cd core is increased. In Fig. 3(c), the effect of $\text{Cl}_{\text{Te}}^{\text{S7}}$ is shown. In this case, the coupling between the GB states and the more electronegative Cl states moves the shallow states in region I into the valence band, but it also creates more antibonding gap states near the CBM [Fig. 3(f)]. So we find that Cl is not effective in passivating GB states derived from the Cd core.

As we see in Figs. 3(a) and 3(d), the passivation of the Te core GB states is not completed by Cl. To accomplish that, we also need to passivate the GB states derived from the Cd at S2. We see in Fig. 2 that Cu at $\text{Cu}_{\text{Cd}}^{\text{S2}}$ is the most stable configuration; thus, we naturally expect Cu can passivate the derived states at S2 in the Te core because Cu is less electronegative than Cd, so the substitution can move these GB states inside the CBM. Indeed, after we replace all the Cd atoms at S2 with Cu, the DOS and the partial charge contour for the deep levels shown in Figs. 4(a) and 4(c) indicate that this is what happened. We see that the DOS in region II is dramatically reduced compared with the DOS in Fig. 3(a), although some shallow levels near VBM are

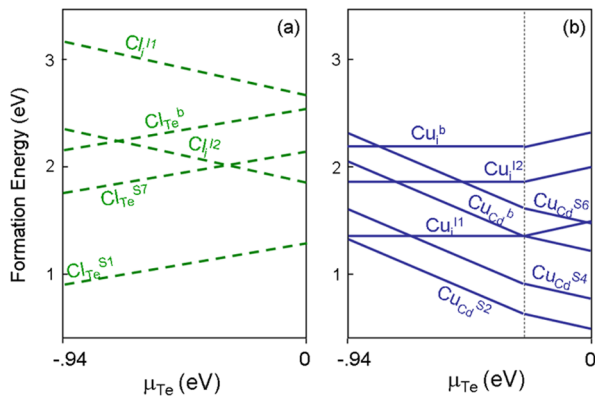


FIG. 2 (color online). Formation energies of (a) Cl and (b) Cu impurities in the GBs and in the bulk. Subscript i indicates interstitial. Subscripts Te and Cd indicate substitutional on the Te and Cd site. Superscript b indicates in the bulk. Other superscripts indicate at sites assigned in Fig. 1(b).

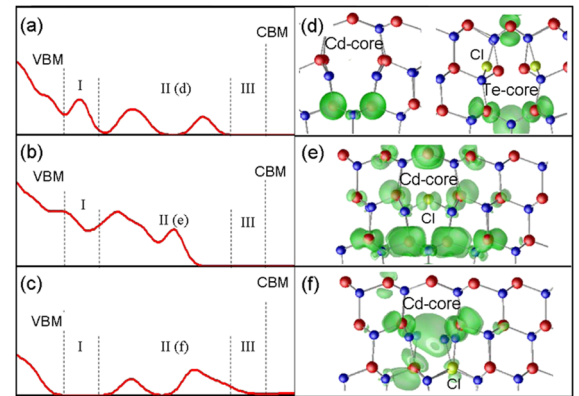


FIG. 3 (color online). DOS of the Cl-passivated GBs and the distribution of the deep-level electrons. (a) Cl substitutes half of the Te at S1 in Te core; (b) Cl at the interstitial site I2 in Cd core; (c) Cl substitutes Te at S7 in Cd core. The partial charge density contours of the deep levels are plotted in (d)–(f), respectively. In (e) and (f), only the Cd core is shown.

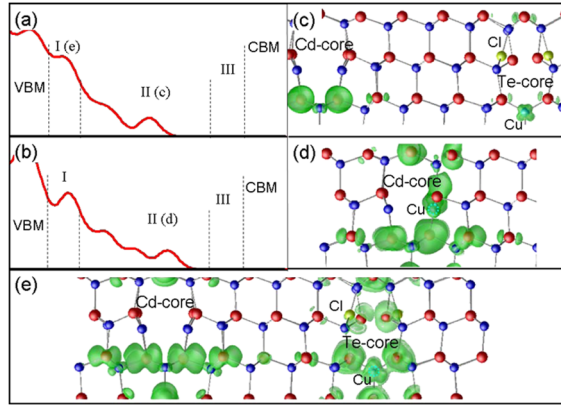


FIG. 4 (color online). DOS of the Cu-passivated GBs and the distribution of the deep-level electrons. (a) Substitutional Cu at the S2 site in the Te core. (b) Substitutional Cu at the S4 site in the Cd core. The partial charge contours of the deep levels are plotted in (c) and (d), respectively. (e) The partial charge contour of the shallow levels above VBM for the DOS in (a).

created due to coupling between Cu d and neighboring Te p states. From the partial charge contour plot in Fig. 4(c), we see that the charge density of the deep levels in Te core is nearly zero. These results indicate that with half Cl at S1 sites and Cu at all S2 sites, the deep levels in the Te core can be completely passivated. The remaining deep levels are only in the Cd core with charge density around the Cd atom at S6 site.

The next favorable configuration for Cu is $\text{Cu}_{\text{Cd}}^{\text{S4}}$ in Cd core. After the substitution, the DOS and partial charge contour for the deep states are shown in Figs. 4(b) and 4(d). It is clear that such substitution will increase the DOS in region II. Combining the results of Cl and Cu, we can conclude that neither impurity can effectively passivate the Cd core GB. The accumulation of the two types of defects in the Cd core GB will increase the density of the deep levels and worsen the optoelectronic properties. On the contrary, Cl and Cu can completely passivate all the deep levels in the Te core through $\text{Cl}_{\text{Te}}^{\text{S1}}$ and $\text{Cu}_{\text{Cd}}^{\text{S2}}$ copassivation; after the complete passivation, only shallow levels above the VBM, which is similar to Cu_{Cd} level in bulk CdTe, remain. In the Te core, the acceptor level of Cu is about 0.05 eV lower than in the bulk, indicating that holes could be more easily activated in the well-passivated polycrystalline CdTe than in single crystal.

Our study indicates that if we can control the growth in a manner that only Te core GB exists (e.g., under Te-rich growth conditions), the detrimental GB effects can be removed by introducing an appropriate amount of Cl and Cu into the system. Experimental studies indeed show that in high-efficiency CdTe solar cell samples, the observed GB prefers to be Te core [13]. It is important to emphasize

that due to the GB structure, copassivation is required to completely remove the GB deep-level states.

In summary, we studied the structural and electronic properties of GBs in CdTe and the passivation effect of Cl and Cu in polycrystalline CdTe. Of the two types of cores in the GBs, the Cd core is less harmful to the carrier transport but difficult to be passivated by impurities such as Cl and Cu, whereas the Te core creates high defect density below the CBM, but these levels can be removed by copassivation of Cl and Cu. No impurity by itself can completely passivate the Te core. We expect that the concept of copassivation revealed in this study can be applied to other polycrystalline semiconductors, which to date are difficult to passivate successfully.

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