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PAPER

Stability and electronic structure of the low-Σ grain boundaries in CdTe: a density functional study

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Abstract

Using first-principles density functional calculations, we investigate the relative stability and electronic structure of the grain boundaries (GBs) in zinc-blende CdTe. Among the low-Σ-value symmetric tilt $\Sigma3$ (111), $\Sigma3$ (112), $\Sigma5$ (120), and $\Sigma5$ (130) GBs, we show that the $\Sigma3$ (111) GB is always the most stable due to the absence of dangling bonds and wrong bonds. The $\Sigma5$ (120) GBs, however, are shown to be more stable than the $\Sigma3$ (112) GBs, even though the former has a higher Σ value, and the latter is often used as a model system to study GB effects in zinc-blende semiconductors. Moreover, we find that although containing wrong bonds, the $\Sigma5$ (120) GBs are electrically benign due to the short wrong bond lengths, and thus are not as harmful as the $\Sigma3$ (112) GBs also having wrong bonds but with longer bond lengths.

1. Introduction

Grain boundaries (GBs) are extended defects characterized by a common planar interface between two single crystals. They can exist in various forms and play important roles in determining material properties, and thus have been one of the most active research topics in materials science [1–6]. For example, segregation of impurities to the GBs is an effective way to purify materials, thus improving material quality for device applications [7–12]. GBs also increase phonon scattering, allowing the thermoelectric properties of a material to be improved by intentionally controlling its GB size [13, 14]. GBs in polycrystalline thin-film photovoltaic materials such as CdTe, $Cu(In,Ga)Se_2$ (CIGS), and $Cu_2ZnSn(S,Se)_4$ (CZTSSe) can greatly affect the performance of these solar cells. On one hand, GBs are detrimental to the performance of solar cells if they create defect levels that can act as effective recombination centers for photogenerated carriers, paths for forward current, or scattering centers for free carriers [15]. On the other hand, GBs can also be beneficial for solar cell performance if the GBs can act as a hole barrier and an electron sink, separating the photogenerated electrons from holes and thus increasing current collection by reducing carrier recombination [7, 8, 16–21].

Despite the importance of GBs in semiconductor device applications, the study of GBs is often hindered by their complicated atomic structures; the detailed atomic arrangement of the GB is not uniquely determined by the *coincidence site lattice* (CSL) theory [22]. The determination of the atomic structure of the GBs often requires combined efforts of high-resolution microscopy with atomistic theoretical simulation. Recently, there have been a series of studies on GBs in CdTe [23–26], which is one of the most promising thin-film solar cell absorbers. Most of the theoretical studies have been limited to the symmetric tilt $\Sigma3$ GBs, (111) and (112), whose atomic structures were clearly identified by experiments [23–26]. Because the symmetric tilt $\Sigma3$ GBs were experimentally observed in CdTe, it has been assumed that such a low-Σ-value GB has lower formation energy than other GBs with higher Σ values. However, there exist a variety of other GBs in CdTe [12, 20, 27], whose atomic structures, electronic structures, and optical properties have not been carefully studied. It is not clear whether the extensively studied $\Sigma3$ (111) or $\Sigma3$ (112) GBs are indeed the most stable GBs, and thus dominant in polycrystals.

Previous theoretical studies show that the formation of the wrong bonds will induce deep gap states [10, 12, 24]. Although some of the states can be passivated by doping, it is important to know which GBs are

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electrically less detrimental and whether their population can be controlled or not. To this perspective, stability and electronic structure of the GBs in zinc-blende materials such as CdTe need to be studied to establish a benchmark for future study of more complicated systems such as the zinc-blende-derived ternary (e.g., CIGS) and quaternary (e.g., CZTS) compounds. The GBs in zinc-blende materials have different structures and GB energy levels than in the well-studied diamond structures because they can form wrong cation–cation or anion–anion bonds, which do not exist in the diamond structure by definition. Because the defect levels of the different wrong bonds are different in energy, charge transfer between the defects commonly occurs, which affects to both the stability and the electronic structure of the GBs. The knowledge obtained from the study on CdTe can be easily extended to other zinc-blende or zinc-blende-derived systems [28].

In this work, using first-principles density functional calculations of the GBs in CdTe as an example, we investigate the stability and the electronic structure of low-Σ symmetric tilt GBs. We demonstrate that, as expected, the Σ3 (111) GB is the most stable one compared to other GBs considered in this study. However, we find that the Σ5 (120) GBs are more stable than the Σ3 (112) GBs, despite the former having a higher Σ value and the latter having been often used as a model system to study GB in zinc-blende semiconductors. The Σ5 (120) GBs are shown to be electrically benign in comparison to the Σ3 (112) GBs due to the short bond lengths of the wrong bonds in the Σ5 (120) GBs. Our results indicate that the GB electrical properties strongly depend on the materials, chemical potentials, and misorientation angles.

2. Methods of the calculations

The first-principles density functional calculations are performed using the Vienna *ab initio* Simulation Package (VASP) [29]. For the calculation of the formation energy of the GBs, we use the local density approximation (LDA) for the exchange correlation potential [30], and the projector-augmented wave (PAW) pseudo-potentials to describe the valence and core electron interactions [31]. The cutoff energy for the plane-wave basis is set to be 400 eV. The atomic structures are optimized until the residual forces are less than 0.02 eV Å^{-1}. The optimized lattice constant of CdTe is 6.42 Å, close to the experimental value of 6.48 Å, and the band gap is 0.64 eV, underestimated as compared to the experiment band gap of 1.60 eV at low temperature. The pure tilt GBs are modeled using slab geometry within the supercell method. To avoid possible charge transfer between two different GBs in the same supercell, we employ a slab geometry containing a single GB, in which the surface dangling bonds (DBs) are passivated by pseudo-hydrogens [10].

The GB formation energy (E_f) is given by $E_f = [\, E_{tot}(GB) - \Sigma_i n_i \mu_i \,]/S$, where $E_{tot}(GB)$ is the total energy of the slab which contains a GB, n_i is the number of i atoms (i = Cd, Te, pseudo hydrogens with fractional charges 2/4 e and 6/4 e to passivate Te DBs and Cd DBs, respectively) in the supercell, μ_i is the chemical potential of atom i, and S is the GB area in the supercell. Sum of the two chemical potentials, $\mu_{Cd} + \mu_{Te}$, should be equal to the total energy of bulk CdTe to keep the system in equilibrium. μ_{Cd} should be lower than that of bulk hexagonal Cd, and μ_{Te} should be lower than that of bulk trigonal Te to avoid clustering of the elements. Chemical potentials of pseudo-hydrogen atoms are determined by calculating the surface energies of the (111), (112), (120), and (130) surfaces. For the (112) surface, the procedure described in ref. [32] is used.

3. Results and discussions

Figure 1 shows the atomic structure of Σ3 GBs, including (111) and two different (112) GBs. These structures have been verified experimentally [23–26]. In the Σ3 (111) GB, which can be considered a stacking fault between the zinc-blende and wurtzite structures, there is no DB and wrong bond, and the maximum deviation of Cd–Te bond length from the ideal value of 2.78 Å is less than 0.01 Å. Because of the small deviation from the ideal structure, the formation energy and the change in the GB electronic structure are expected to be small. There are two different Σ3 (112) GBs. In figure 1(b), there are two Cd DBs (A, B), a Te DB (C), and a five-folded Cd atom (D) in the unit cell. In figure 1(c), however, there are two Te DBs (E, F), a Cd DB (G), and a five-folded Te atom (H) in the unit cell. The structure in figure 1(b) has more Cd DBs, and the structure in figure 1(c) has more Te DBs; thus, they are usually labeled as Cd-core and Te-core Σ3 (112) GBs, respectively. In the Cd-core, the two Cd atoms with DBs (denoted by A and B) repel each other due to lack of electrons and Coulomb interaction, resulting in a large Cd-Cd distance of 4.52 Å. However, in the Te-core, the two Te atoms (denoted by E and F) with occupied dangling bond states can interact with each other, forming a bonding state inside the valence band and an anti-bonding level above the valence-band maximum (VBM), consistent with previous studies [33, 34]. The calculated bond distance between the two Te atoms is 3.44 Å. Though they are called Cd-core or Te-core, the two types of Σ3 (112) GBs are stoichiometric, i.e., they have equal numbers of Cd and Te atoms; therefore, the GB formation energies do not depend on the Cd and Te chemical potentials.

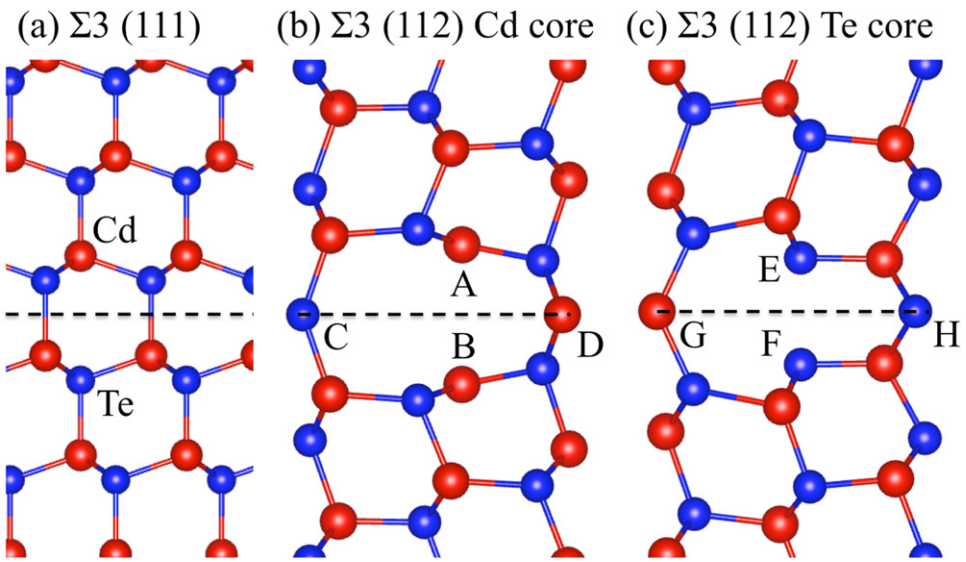

Figure 1. Atomic structures of Σ3 (111) and Σ3 (112) GBs. Dashed lines represent the GB.

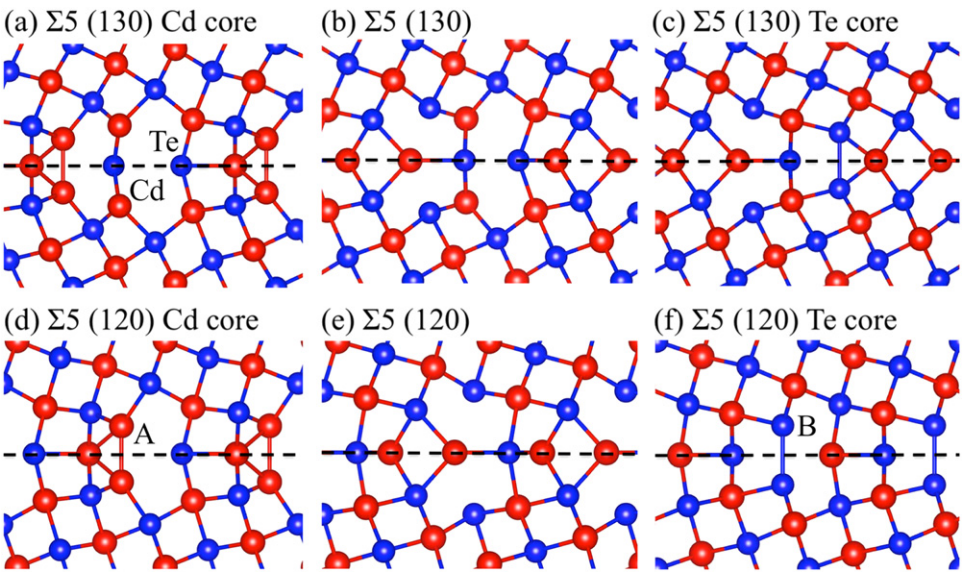

Figure 2. Atomic structures of Σ5 (130) and Σ5 (120) GBs. The structures in (a) and (d) have more Cd atoms, while the structures in (c) and (f) have more Te atoms. The structures in (b) and (e) are stoichiometric, i.e., they have an equal number of Cd and Te atoms. Dashed lines represent the GB.

To search for atomic structures of CdTe Σ5 GBs with low formation energy, we used the atomic structure of Si Σ5 GBs as the starting points because they have been well studied in the past [35, 36]. We studied only GBs with the mirror symmetry because fewer wrong bonds are formed for this symmetric structure compared to others. In our search, first, we made the initial GB structure based on the GBs in bulk Si. Next, we relaxed the structures and/or removed one or two elements from the wrong bonds to see if the energy could be reduced through this process. Figure 2 shows the atomic structures of several low-energy Σ5 (130) GBs [figures 2(a) to (c)], and Σ5 (120) GBs [figures 2(d) to (f)]. As shown in figure 2, there were two different kinds of wrong bonds: Three Cd atoms form a ring structure, and two Te atoms form wrong bonds, denoted as 'A' and 'B' in the figure, respectively. Note that the structures in (b) and (e) have an equal number of Cd and Te atoms at the GB; thus, there is no chemical potential dependence for their GB formation energies. In contrast, the GBs in (a) and (d) have more Cd atoms, and the structures in (c) and (f) contain more Te atoms. Hence, the formation energy of these GBs depends on the chemical potentials of Cd and Te. It is worth noting that although the atomic structure in the pure CdTe crystal is not changed after Cd and Te atoms are interchanged, such operation changes the

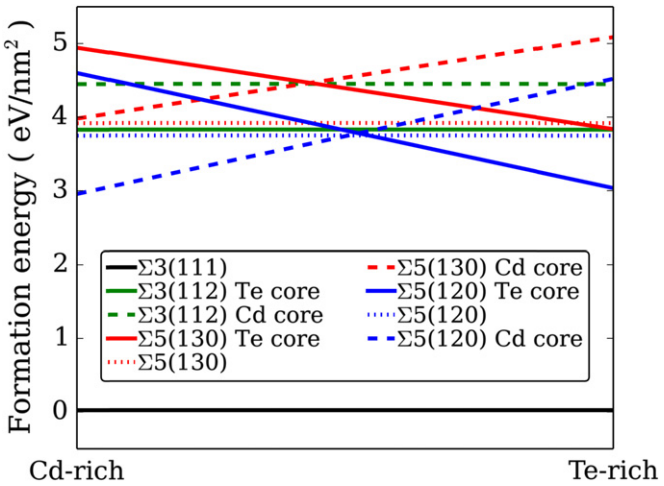

Figure 3. Formation energy of the GBs considered in this study as a function of atomic chemical potential.

structures in the Σ5 (120) GBs. However, our total energy calculations show that the Σ5 GBs obtained by exchanging Cd and Te atoms from the structures in figure 2 (not shown) all have higher formation energies.

As shown in figure 3, our results clearly show that the Σ3 (111) GB is the most stable one ($E_f = 0.03$ eV nm^{-2}) because there are no DBs or wrong bonds, and that the Σ5 (120) GBs have lower formation energy than Σ3 (112) GBs regardless of the chemical potential of Te, although the Σ3 (112) GBs have often been used as a model system to study GBs in II–VI semiconductors. The lowest-energy Σ5 (120) GB structure depends on the chemical potential of Te; the Cd-core GB [figure 2(d)] is formed under the Cd-rich condition, while the Te-core GB [figure 2(f)] becomes stable under the Te-rich condition. The stoichiometric Σ5 (120) GB with no wrong bonds [figure 2(e)] can also be formed in a limited range of the chemical potential. This indicates that we can control the atomic structure of GBs by changing the chemical potential. For the Σ3 (112) GBs in figure 1, we find that the Te-core GB is more stable than the Cd-core GB, which is consistent with both a previous theoretical calculation [33] and the fact that only the Te-core was found in most experiments [24]. Previous studies showed that the Te-core Σ3 (112) GB is more harmful than the Cd-core Σ3 (112) GB due to the deep gap states associated with the Te-core, although it can be more easily passivated [33, 34]. Also, the Σ5 (130) GBs have comparable formation energies as the Σ3 (112) GBs, whereas they are less stable than the Σ5 (120) GBs. We notice that the Σ5 (130) GB in Si is more stable than Σ5 (120) GBs [35], suggesting that the relative GB stability is determined by the material's ionicity and the ratio of the anion and cation sizes.

In compound semiconductors such as CdTe, CIGS, and CZTS, GB states inside the band gap are usually introduced by DBs and wrong bonds. Consequently, the lack of such defects makes the Σ3 (111) GB free of deep gap states and inactive for carrier recombination in CdTe compared to other GBs. Indeed, previous studies show that Σ3 (111) GB only weakly acts as a hole barrier because the VBM of the wurtzite-like GB region is a little higher than that of the ZB CdTe [23, 25]. In contrast, the atomic structure of the Σ5 GBs contains both DBs and wrong bonds. Because the Σ5 (120) GBs are the second most stable GBs in this study, we will discuss their electronic structures in more detail.

It is well known that the band gap is underestimated in the LDA. Consequently, the positions of defect levels derived from the wrong bonds, such as Cd–Cd and Te–Te, are not accurately determined. To correct the band gap error, we adopted hybrid functional calculations using the exchange correlation functional proposed by Heyd, Scuseria, and Ernzerhof (HSE06) [37]. The calculated band gap is 1.44 eV, close to the experimental value of 1.60 eV. The structure was relaxed in the HSE calculations by using Γ point only for the Brillouin zone integration. A denser $(3 \times 3 \times 1)$ k-point grid was used to obtain the projected density of states. The cutoff energy for the plane-wave basis is set to 205.8 eV because of the heavy computational cost of HSE. Using the HSE method, we calculate the electronic structures of the two Σ5 (120) GBs, which are stable in the Cd-rich and Te-rich conditions.

The Cd-core Σ5 (120) GB do not induce deep gap states, although some GB states appear at a position close to the VBM, as shown in figures 4(a). Figures 4(b) shows the charge density of the defect state, which is derived from the three Cd atoms forming a triangular ring and one Te DB in the unit cell. The bonds among the three Cd atoms are derived from the Cd 5s orbitals, and the level is pushed down to be close the VBM because of the short Cd–Cd bond lengths. Note that this state also couples weakly with the Te DB state, which is located at about 1.2 eV below the VBM. Since there is no empty gap state, this GB is not active in capturing electrons. Note that

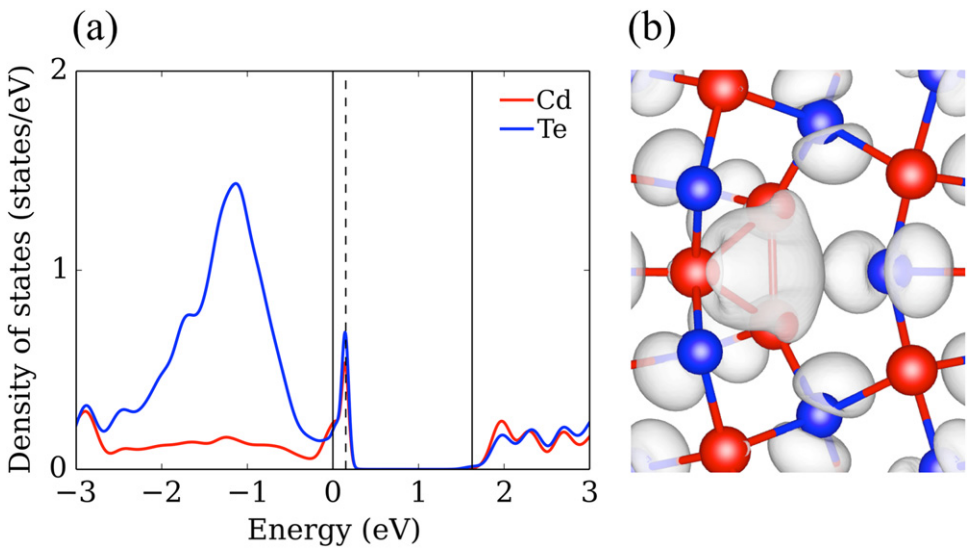

Figure 4. (a) Projected density of states of the Cd-core Σ5 (120) GB. The red line is the projected state on the three Cd atoms forming the triangular ring structure and the blue line is the projection on the Te atom with the dangling bond. Charge density of a defect state about 0.15 eV above the VBM at the Γ point is plotted in (b). In (a), the two thin vertical solid lines indicate the VBM and the CBM in the bulk region, and the vertical dashed line represents the Fermi energy. The energy zero is set at the VBM of bulk CdTe.

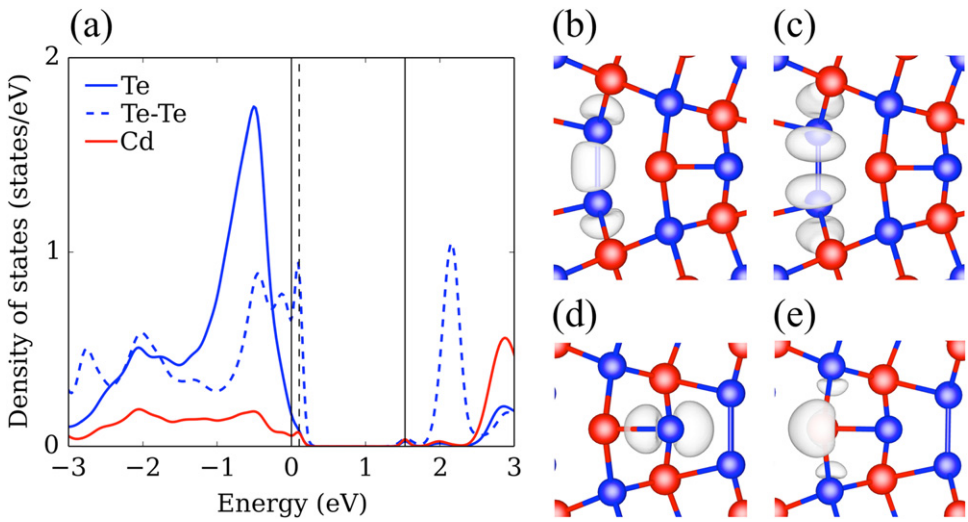

Figure 5. (a) Projected density of states of the Te-core Σ5 (120) GB. The dashed blue line is the projection on the Te–Te wrong bond. The solid blue (red) lines are projection on Te (Cd) atom with dangling bond. (b) and (c) plot the charge density of the Te–Te bonding and anti-bonding states at the Γ point; (d) and (e) plot the charge density of the Te and Cd dangling bond states. In (a), the two thin vertical solid lines indicate the VBM and CBM in the bulk region, and the vertical dashed line represents the Fermi energy. The energy zero is set at the VBM of bulk CdTe.

the capture and de-trapping of holes can easily occur because the GB state is close to the VBM. Consequently, we expect that this GB is not an active recombination center nor harmful to device performance.

In contrast to Cd atoms, Te atoms in the Te-core do not form the ring structure due to the difference of charge and size between the Cd and Te atoms. Therefore, there are one Te DB, one Te–Te wrong bond, and one Cd DB in the unit cell, resulting in different electronic structures. Also in this GB, there is no empty gap state, as shown by the PDOS in figure 5(a); only some fully occupied GB states appear above the VBM by 0.11 eV. The Cd DB level is higher than the conduction-band minimum (CBM) by about 1.5 eV, and the Te DBs are located below the VBM by about 0.7 eV. The occupied Te DB state is strongly hybridized with the valence band states, as is the Cd DB state with the conduction band. As the two Te DB levels interact, Te–Te σ bonding and anti-bonding states are located at about 3.2 eV below and 2 eV above the VBM, respectively. It is important to know that the Te–Te anti-bonding level depends strongly on the Te–Te bond length. In this Te-core Σ5 GB, the bond length is 2.76 Å, so the anti-bonding Te–Te σ wrong bond state is pushed above the CBM. However in the Te-

core Σ3 GB, the Te–Te wrong bond length is much longer at 3.51 Å [34]. Hence, the anti-bonding state of the Te-core Σ3 GB is located deep inside the band gap, and can trap electrons.

Because there is no partially occupied defect level deep inside the band gap, the Σ5 (120) GBs, which are energetically more favorable than the Σ3 (112) GBs, are electrically more benign than the Σ3 (112) GBs. Our calculations for Σ5 (130) GBs also show that the GBs are benign because the Cd–Cd and Te–Te wrong bonds have short distances in these GBs. The reason that the large Σ5 GBs have shorter Te–Te and Cd–Cd bond lengths could be because these GBs have sharp interface angles, and thus smaller space at the GBs; consequently, the wrong bonds are squeezed to have short lengths. We suggest that experimental studies should be done to verify our predicted Σ5 GB structures and our finding that despite the associated dangling bonds and wrong bonds, the Σ5 GBs in CdTe are electrically benign. More study on other high-Σ-value tilt GBs is also needed to see whether these GBs create deep GB levels inside the band gap or not.

4. Conclusions

In summary, using first-principle total energy calculations, we have systematically investigated the stability and electronic structure of symmetric tilt GBs in CdTe. Our results show that the Σ3 (111) GB is the most stable one among all the GBs considered in this study because of the absence of dangling bonds and wrong bonds. However, surprisingly, we find Σ5 (120) GBs are more stable than Σ3 (112) GBs despite the former having a high Σ number. The local structure of the Σ5 (120) GBs depends on the chemical potential of Cd and Te. Under the Cd-rich (Te-rich) condition, the Cd–Cd (Te–Te) wrong bonds are formed; therefore, the GBs can have different electronic structures depending on the chemical potentials. However, although wrong bonds, in general, are more detrimental to device performance compared to other defects because they usually introduce deep levels inside the band gap, we find that Σ5 (120) GBs are electronically benign compared to Σ3 (112) GBs because the wrong bonds in Σ5 (120) GBs are much shorter. The insights obtained in this study will help us to have a better understanding of the chemical trends of GB formation and the roles of GB in controlling material properties.

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