Passivation of deep electronic states of partial dislocations in GaAs: A theoretical study

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The structure and electronic properties of reconstructed cores of 90° partial dislocations in GaAs are studied using first-principles methods. We find that a double-period reconstruction is most stable for an As-core whereas a single-period reconstruction is most stable for a Ga-core. We show that As and Ga dimers induce detrimental deep electronic states. These deep levels can be partially removed by introducing passivating dopants that break dimers in the dislocation core. © *2010 American Institute of Physics*. [doi:10.1063/1.3364140]

Dislocations in covalent semiconductors often act as recombination centers for carriers, degrading the performance of electronic and optoelectronic devices.[1] Reducing the density of these dislocations adds to the complexity and cost of these devices. For example, multijunction solar cells based on III–V zincblende semiconductors[2,3] have achieved efficiencies exceeding 40%, but only after extensive device development programs focused on reducing the dislocation densities in these devices. An intriguing alternative would be to eliminate the negative effects of the dislocations by passivating the associated deep states with appropriate dopants that can lower the occupied states to the valence band maximum (VBM) and raise the unoccupied states to the conduction band minimum (CBM).[4,5] To determine whether or not deep states in III–V semiconductors such as GaAs can be effectively passivated, it is crucial to understand (a) the origin of dislocation-induced deep recombination center states, and (b) how they are affected by the introduction of dopants. Even if these deep states cannot be effectively passivated, a better understanding of the atomic structure of dislocations in these materials contributes to our ability to reduce the densities of dislocations in a device.

GaAs is a prototype III–V zincblende semiconductor whose bulk and surface properties have been extensively studied in the past. It has been experimentally shown that a dislocation with a ⟨110⟩ line direction in GaAs will split into two partial dislocations.[6,7] However, due to the complexity of the dislocation system, the electronic properties, especially the passivation effects of various dopants, have not yet been thoroughly studied theoretically.[8] In this paper, using first-principles total energy and band structure methods, we will study both the dislocation core structure and the passivation effects of various dopants for 90° partial dislocations.

Our calculations are based on the density functional theory as implemented in the VASP code.[9] We use the projector-augmented wave method with local-density approximation potentials.[10] The atomic structure of the GaAs 90° partial dislocations are modeled by a super-cell of size $10\times6\times2$, which means that the supercell contains 10, 6, and 2 unit cells of GaAs along the $[11\bar{2}]$, [111], and $[1\bar{1}0]$ directions as shown in Fig. 1 (in which the dislocation line direction is $[1\bar{1}0]$). The super-cell contains one Ga core and one As core. One of the cores is selectively studied by fully passivating the other core with pseudohydrogen atoms. The cut-off energy used for the plane-wave basis set is set to the recommended value of 210 eV.[9] Our tests show that this is sufficient for a system with s and p electrons. The integration in the Brillouin zone is done with a $1\times1\times2$ k-point mesh. The lattice is fully relaxed until the forces on all the atoms are less than 0.02 eV/Å.

In zincblende semiconductors like GaAs, a full 60° dislocation always dissociates into a 90° partial dislocation and a 30° partial dislocation linked by a strip of stacking fault. Because there are two types of polar (111) glide planes, there are also two types of 90° and 30° partial dislocation cores. One type is called As-core (α dislocation) and the other is called Ga-core (β dislocation). Unreconstructed 90° partial dislocations contain two parallel lines of partially bonded anion or cation atoms. Two possible reconstructions have been widely studied for a variety of semiconductors: a single-period (SP) reconstruction and a double-period (DP) reconstruction. In Fig. 1 a DP-reconstructed As-core and a SP-reconstructed Ga-core dislocation are shown. In the SP reconstruction [Figs. 1(b) and 1(d)], the unit cell along the dislocation line is one lattice unit long and the reconstruction is characterized by buckled like-atom dimers. In the DP re-

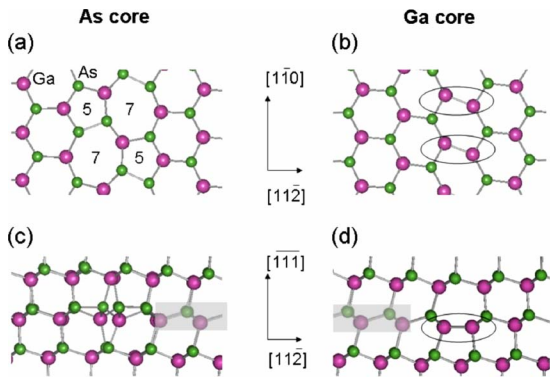

FIG. 1. (Color online) Reconstructed 90° partial dislocations in GaAs. (a) Top and (c) side views of a DP reconstruction for an As-core (α) dislocation. (b) Top and (d) side views of a SP reconstruction for a Ga-core (β) dislocation. The shaded areas are the stacking faults accompanying the partial dislocations.

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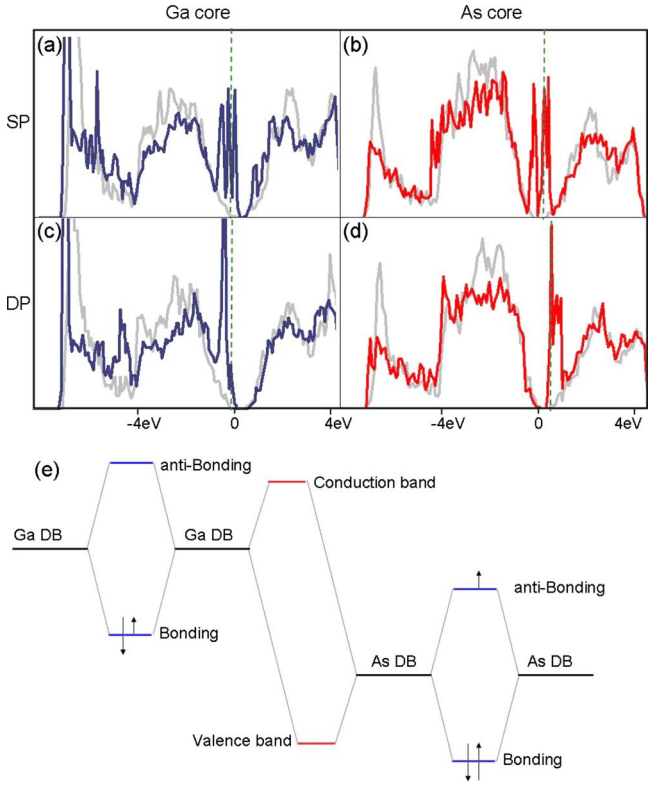

FIG. 2. (Color online) LDOSs for (a) a Ga atom in the SP Ga-core, (b) an As atom in the SP As-core, (c) a Ga atom in the DP Ga-core and (d) an As atom in the DP As-core reconstructions. The light (gray) curves in the background are for the same type of atom (Ga or As) in the bulk. The energy levels are aligned with respect to the 1s core levels of Ga and As in bulk GaAs. Zero energy indicates the middle of the calculated GaAs band gap. The dotted (green) lines indicate the highest occupied levels. (e) A schematic plot of the energy levels involved in the reconstruction.

construction [Figs. 1(a) and 1(c)], the unit cell along the dislocation line is two lattice units long and the reconstruction is characterized by the 5- and 7-atom rings shown in Fig. 1(a).

The core structure of a 30° partial dislocation (not shown) consists of a single line of partially bonded anion or cation atoms lying along the dislocation line. The reconstruction is characterized by dimerization of these atoms with dimer bonds parallel to the dislocation line. A SP 90° partial and a 30° partial are structurally related in that they both reconstruct via a simple dimerization of neighboring dangling bonds. Here we will discuss only the 90° partial dislocation.

Our total energy calculations show that the As-core has a lower energy (0.25 eV/As-pair) in DP than in SP reconstruction, whereas the Ga-core has a lower energy (0.30 eV/Ga-pair) in SP than in DP reconstruction. The local density of states (LDOS) of the characteristic atoms for the two types of cores in the two reconstructions are shown in Figs. 2(a)–2(d), respectively. We find that for the As-core, the DP reconstruction lowers the energy of occupied dislocation states from mid-gap to below the VBM, stabilizing the DP reconstruction. In contrast, a DP reconstruction of the Ga-core raises the energy of unoccupied dislocation states from mid-gap to above the CBM, which does little to stabilize the DP reconstruction. It is interesting to note that in our previous study of dislocations in III–V nitrides, no dimer is formed in the dislocation cores.[11] This is attributed to the large ionicity of III–V nitride semiconductors.

The schematic plot of the energy levels in Fig. 2(e) shows that for the As-core, the partially occupied deep states are the antibonding As dangling bond (DB) states, whereas for the Ga-core, the partially occupied deep states are the bonding Ga DB states. This can be understood as follows: In bulk GaAs, Ga and As are both fourfold coordinated. In the dislocation cores, before reconstruction, both the Ga in Ga-core and the As in As-core are threefold coordinated and there is one DB on each atom. On each Ga DB there are nominally 3/4 electrons, and on each As DB there are 5/4 electrons. After reconstruction, the (Ga–Ga dimer) bonding state of Ga DBs is partially filled with 1.5 electrons and the anti-bonding state is totally empty. In As-core under the same condition the (As–As dimer) bonding state of As DBs is fully occupied and the antibonding state is partially filled with 0.5 electrons. These analyses indicate that both dislocation cores are electronically active and can strongly interact with other point defects and impurities.

Our analyses above show that the deep dislocation states originate from the dimerization of identical atoms in the dislocation cores. So to eliminate these deep states, one might try to break the dimers by adding electrons to the antibonding state or removing electrons from the bonding state of the dimers using various point defects or impurities. Because Ga-core and As-core have different electron occupations, different types of dopants may be needed to passivate the different dislocation states. We will first consider *p*-type dopants such as a substitutional Zn atom on a Ga site (Zn_{Ga}), or a Ga vacancy (V_{Ga}). Then we will study the effect of an *n*-type dopant, substitutional Se on an As site (Se_{As}). All of these studies will be performed for the SP reconstruction. For the DP reconstruction, the results are expected to be similar due to the similar electronic properties.

Zn_{Ga} is a *p*-type dopant in GaAs with an acceptor level near the VBM. Therefore, it can be used to passivate the Ga-core by removing electrons from the Ga-core bonding state. We find that the formation energy for placing a Zn atom within the Ga-core structure is 0.5 eV lower than for placing the Zn atom in the bulk, away from the dislocation core. In the resulting structure [Figs. 3(a) and 3(b)], every-other Ga–Ga dimer has been broken and replaced by an unbonded Zn_{Ga}-Ga_d pair. The unbonded Ga atom (Ga_d) donates 1/4 electron to the unbonded Zn atom (Zn_{Ga}) and 1/2 electron to the remaining Ga–Ga dimer. In this configuration, both the Zn_{Ga} and Ga_d atoms have empty dangling bonds and can relax back toward more favorable positions, and the remaining Ga–Ga dimer bond is fully occupied.

The calculated LDOS for Ga_d [Fig. 3(c)] shows no significant deep states in the band gap. The absence of deep states associated with the Ga_d site is due to a combination of charge transfer and relaxation of the Ga_d atom. Unfortunately, the remaining dimer still supports a deep state. Its bond length decreases by ~3.5%, but its deep electronic states do not shift significantly except for becoming more localized. The stronger bonding of this dimer is mostly a result of the 0.5 electron charge transfer from the unbonded Ga_d atom.

A Ga vacancy (V_{Ga}) is another *p*-type defect. Surprisingly, the formation energy of a V_{Ga} in the Ga-core is favored by about 1.8 eV with respect to a V_{Ga} in the bulk. The

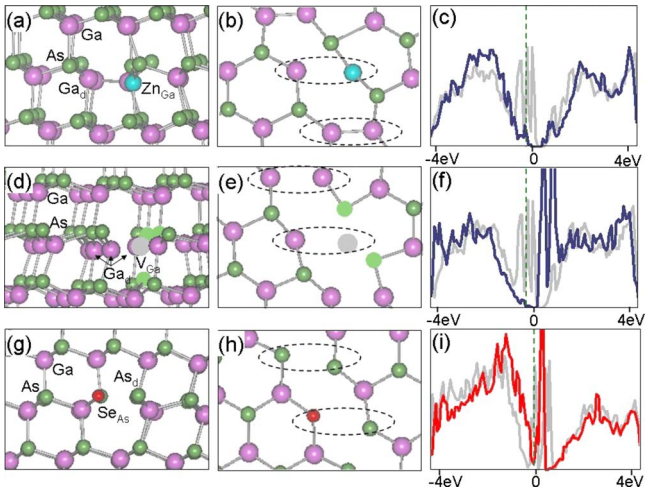

FIG. 3. (Color online) [(a)–(c)] A Ga-core reconstruction containing a Zn_{Ga} defect. (a) Side view. (b) Top view. (c) The dark (blue) line shows the LDOS of Ga atom (Ga_d) in the broken dimer. The light (gray) curve shows the LDOS of a dimerized Ga atom in the original SP structure for comparison. [(d)–(f)] A Ga-core reconstruction containing a V_{Ga} defect. (d) Side view. (e) Top view. The light (gray) ball stands for V_{Ga} and the highlighted (green) balls are the three nearest neighboring As atoms of V_{Ga}. (f) The dark (blue) line shows the LDOS of the Ga atom (Ga_d) in the broken dimer. The light (gray) curve shows the LDOS of a dimerized Ga atom in the original SP structure for comparison. [(g)–(i)] An As-core reconstruction containing a Se_{As} defect. (g) Side view. (h) Top view. The dashed ellipses indicate the original dimers. (i) The dark (red) line shows the LDOS of As in the partially broken As-dimer (As_d). The light (gray) curve shows the LDOS of a dimerized As atom in the original SP structure for comparison.

resulting structure is shown in Figs. 3(d) and 3(e). Notice that all of the Ga–Ga bonds are broken in this structure, and every-other Ga–Ga dimer has been replaced with an unbonded Ga-V_{Ga} pair. Before charge transfer, there are $(3/4 \times 3)=9/4$ electrons on the three Ga atoms and $(5/4\times 3)=15/4$ electrons on the three As DBs. Charge transfer can therefore empty all of the Ga DBs and fill all of the As DBs, satisfying the electron counting rule and stabilizing the reconstruction.[12,13] Our calculations indeed confirm this result. The LDOS of one of these Ga atoms [Fig. 3(f)] shows that the deep states are now shifted about 1 eV toward the CBM. However, there are shallow states associated with the resulting As DBs. Therefore, the formation of one Ga vacancy removes two Ga-dimer induced deep states and creates three As DB induced shallow states.

Finally, we will consider Se substitution on an As site, an *n*-type dopant which creates shallow donor levels near the CBM. In principle it could therefore passivate an As-core partial dislocation by adding electrons to the As-core antibonding state. The formation energy of Se_{As} in the As-core is favored by 0.61 eV with respect to Se_{As} in the bulk. The resulting structure is shown in Figs. 3(g) and 3(h). One As–As dimer has been replaced by a partially bonded Se_{As}-As pair, and the remaining As–As dimer is partially broken. The As–As distance in the remaining As–As dimer has increased to 2.91 Å, compared to 2.66 Å for an SP reconstruction (without Se). The LDOSs of the three As atoms are similar and one of them is shown in Fig. 3(i). Compared with the LDOS of an As atom in the original dimer, the deep states are more localized and closer to the VBM. Although the dimers are partially broken, none of the deep states is effectively removed. This can be understood as follows: Before the Se substitution, in a two-dimer unit cell, there are $5/4\times 4=5$ electrons. With the substitution, there are $5+1=6$ electrons. But these electrons are not enough to fill all the DBs on the three As atoms and Se_{As} sites (two more electrons are needed). Instead, our calculations indicate partial occupancy of all three As DBs and the Se_{As} DB.

In summary, we have studied the stability and electronic structure of the reconstructed cores of 90° partial dislocations in GaAs. We find that the DP reconstruction is most stable for the As-core partial dislocation, whereas the SP reconstruction is most stable for the Ga-core partial dislocation. In addition, stable structures were identified for dislocations containing both *p* and *n* type dopants. These dopants partially passivate the partial dislocations by breaking dimer bonds in the cores. More specifically, *p*-type dopants such as Zn_{Ga} can fully remove some deep states in a Ga-core partial dislocation, whereas *n*-type dopants such as Se_{As} can only partially remove deep states in an As-core partial dislocation. In general, we find that passivation of dislocation or grain boundary induced states in more covalent III–V compounds is much more difficult than in more ionic II–VI and chalcogenide compounds.[4,5]

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