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Ab initio prediction of the structure of glide set dislocation cores in GaAs

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Abstract

The structures of the glide set partial dislocations in GaAs are predicted using an *ab initio* electronic structure total energy method employing ultrasoft pseudopotentials. The single- and double-period reconstructions of the 90° partial dislocations are found to be nearly degenerate in energy. The structure of the 30° β-dislocation is found to agree qualitatively with an experimentally determined structure.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The structure of dislocation cores in semiconductors has been subject of ongoing scrutiny [1–4]. Their study is motivated by the fact that dislocation cores may be electro-optically active, and consequently have an impact on device performance. Since the optoelectronic properties are linked intimately to the dislocation core structure, the first step in predicting the electronic properties of a dislocation is, in fact, the prediction of the dislocation core structure. In addition to prediction of the optoelectronic properties, knowledge of the dislocation core structures may allow for an atomic scale theory of the mobility of the dislocations, a quantity having an impact on the mechanical properties of these materials.

Most efforts focus on the prediction of dislocation cores within homopolar, diamond cubic semiconductors. It appears that a consensus concerning the structure of the 30° partial dislocation has formed [5, 6]. These dislocations are thought to be reconstructed along the core direction through a dimerization that saturates the dangling bonds that would otherwise

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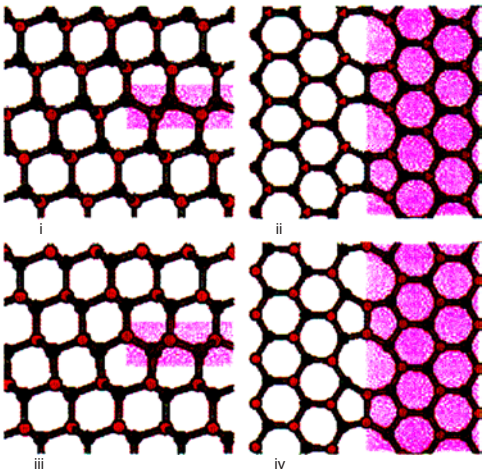

Figure 1. The reconstruction of the 30° partial dislocation. The first row corresponds to the α-cores and the second row the β-cores. The core of the dislocation is shown in the left column ((i) and (iii)) and the glide plane in the right column ((ii) and (iv)). The light atoms represent arsenic and the dark atoms represent gallium. The highlighted region is the stacking fault.

be present along the dislocation core (figure 1). The repeat distance along the core direction is double that of the equivalent direction in the perfect crystal.

The structure of the 90° partial dislocation in diamond cubic semiconductors is a bit more controversial. The earliest theory of the core structure of these dislocations in Si was proposed independently by Hirsch [7] and Jones [8], and is similar to the structure shown in figure 2(a). Here, the dangling bonds along the dislocation core are saturated by means of a Γ-point reconstruction leading to a shift along the core direction. The repeat distance along the core direction is identical to that of the bulk in the equivalent direction, and is consequently referred to as a single-period reconstruction. It was later argued by Bennetto *et al* [9] that, for Si, a competing double-period (figure 2(b)) structure is lower in energy than the single-period structure. Lehto and Öberg [10] countered that the relative energies of the two core reconstructions depend on the choice of boundary conditions.

The implication of Lehto and Öberg's work is that one must consider in detail the role that boundary conditions play in computations of dislocation core structures and energies. The primary difficulty stems from the long-ranged nature of the stress and strain fields associated with a dislocation core, and the fact that one can model accurately the energies of only a small number of atoms. Currently published calculations fall into three classes (figure 3):

(i) periodic calculations employing supercells containing dislocation dipoles,
(ii) cluster calculations (see [11] for example), and
(iii) periodic calculations employing a supercell containing one dislocation and either a substantial vacuum region or an unrelaxed, disordered but dense boundary region [12].

Lehto and Öberg [10] demonstrated the flexibility and utility of the periodic supercell method. Specifically, they proved that in contrast to earlier claims [13], one can use a variety of periodic configurations based on supercells containing dislocation dipoles to compute dislocation core structures. This idea was explored further in [14–16] where it was demonstrated that these cells can be used to study the stress dependence of the relative energies of the dislocation cores. This demonstration relied upon a summation technique developed in the late 1980s to compute the stress field from a periodic array of edge dislocations within

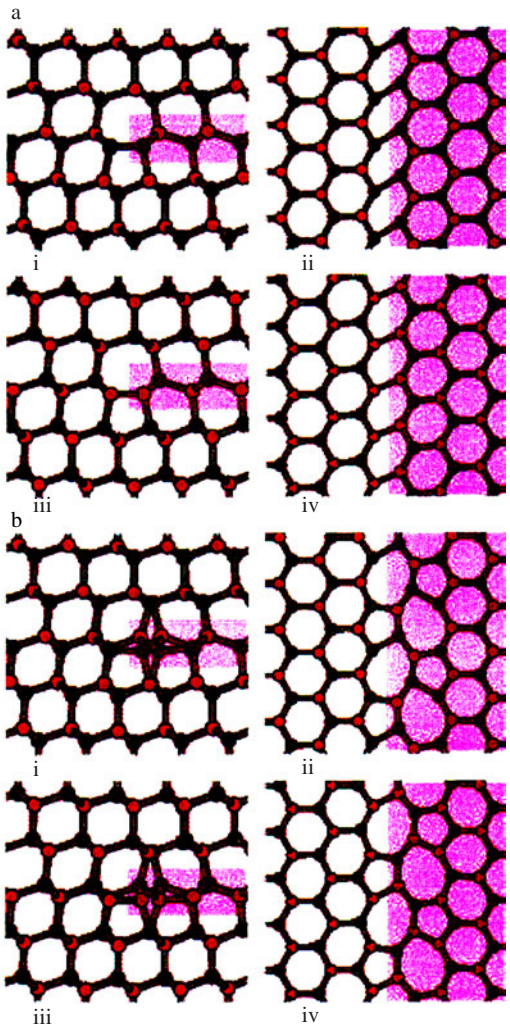

Figure 2. The reconstruction of the 90° partial dislocation. Parts (a) and (b) show the proposed single-period and double-period structures. The core of the dislocation is shown in the left column and the glide plane in the right column. Rows one and three show the α-cores ((i), (ii)) and rows two and four show the β-cores ((iii), (iv)). The light atoms represent arsenic and the dark atoms represent gallium. The highlighted region is the stacking fault.

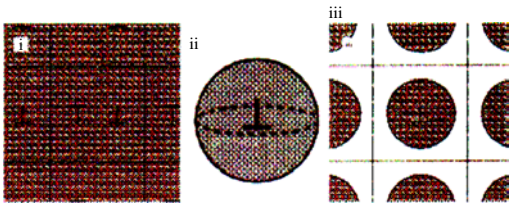

Figure 3. The boundary conditions frequently used to compute dislocation core structures: the periodic, dipolar supercell (i); the cluster method (ii); the 'cylindrical' supercell (iii).

isotropic elasticity theory [17]. More recently, Cai *et al* [18] have extended the analysis to the anisotropic case and used the technique to compute Peierls stresses for some metals. It appears that periodic calculations employing dipolar supercells are a viable means of studying dislocation cores in diamond cubic semiconductors.

The study of dislocations within heteropolar, zinc-blende, semiconductors poses more of a challenge. Each partial dislocation appears in one of four configurations, the so-called α- and β-cores of the glide and shuffle sets. The present discussion is limited to the glide set dislocations. In GaAs, glide set dislocations terminating in As atoms are referred to as α-cores, and glide set dislocations terminating in Ga atoms are β-cores. Within a single dipolar unit cell, i.e. the case (i) of figure 3, one dislocation of each type must appear. Hence it is not possible to compute directly the energy differences between the α- and β-cores. One can calculate

$$\begin{aligned} \Delta E^{\beta} &= E^{\beta}_{DP} - E^{\beta}_{SP} \\ \Delta E^{\alpha} &= E^{\alpha}_{DP} - E^{\alpha}_{SP} \end{aligned} \tag{1}$$

where E^{β}_{DP} (E^{α}_{DP}) is the energy per unit length of the double-period β-core (α-core) and E^{β}_{SP} (E^{α}_{SP}) is the energy per unit length of the single-period β-core (α-core). (One can compute the energy difference $(E^{\beta}_{DP} + E^{\alpha}_{DP}) - (E^{\beta}_{SP} + E^{\alpha}_{SP})$ directly [19].) It is possible to mix double- and single-period cores within the same unit cell, but the nature of the single-period reconstruction, and in particular the offset along the core direction, implies that unusual strains will be imposed on each of the cores in the mixed cell configuration.

To avoid these stresses and strains it is reasonable to explore the use of 'cylindrical' supercells, i.e. case (iii) above, for the prediction of dislocation core structures in GaAs. The coupling of *ab initio* electronic structure total energy calculations to the periodic cylindrical cell geometry poses difficulties of its own. Typically, one tries to embed the dislocation core within a medium that mimics, to the greatest extent possible, a large, perfect crystal. Recently, Woodward and Rao [12] have demonstrated how one can employ a lattice Green function to achieve this goal, though to the knowledge of the present authors, this technique has not yet been applied to semiconductors. A simpler method is to use anisotropic elasticity theory to fix the positions of an outer ring of atoms, and then relax the atoms within this ring by *ab initio* electronic structure total energy techniques. The method, while not as elegant as the lattice Green function method, allows for a preliminary and relatively inexpensive investigation of the structure of the dislocation cores within GaAs, and is the method employed for the current study.

In this paper, the core structures of the 30° and 90° partial dislocations in GaAs are computed using the ultrasoft pseudopotential formalism embodied in the Vienna *ab initio* simulation package (VASP) [20, 21]. The structure of the 30° partial is compared with that obtained experimentally using high-resolution electron microscopy (HREM). It is also concluded that, within the accuracy of the present approach, the double- and single-period reconstructions of the 90° partial are nearly degenerate in energy.

2. Approach

The structures of the partial dislocations in GaAs are determined using a 'cylindrical' supercell, as shown in figure 4. The partial dislocation is taken to lie in an infinite column of GaAs. The column axis is in the $[10\bar{1}]$ direction, and the (111) plane is chosen as the glide plane. The stacking fault extends in the $[\bar{1}2\bar{1}]$ direction. The supercell is taken to be periodic along the dislocation line, so the unreconstructed structure has a periodicity of $a/\sqrt{2}$. The structure is a periodic in all other directions. The initial positions of the Ga and As atoms are chosen in accord

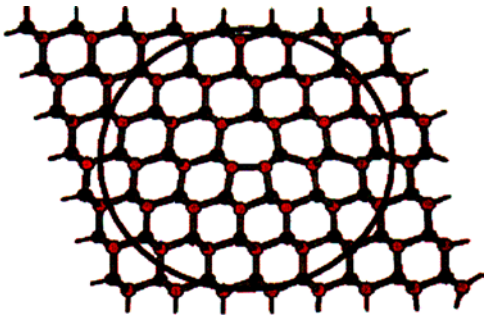

Figure 4. The 'cylindrical' supercell used in the calculations presented here. The Ga and As atoms outside the black circle are fixed in the positions predicted by anisotropic elasticity theory. The passivating 'hydrogen' atoms cap the surface bonds. The passivating 'hydrogen' atoms and the atoms interior to the black circle are relaxed.

with anisotropic elasticity theory and the elastic constants predicted by theory (employing a 'reasonable' choice for the position of the singularity[5]). The bonds on the surfaces of the cylinder are capped by hydrogen-like atoms with $H_{z=3/4}$ capping As bonds and $H_{z=5/4}$ capping Ga bonds [23, 24]. A region of vacuum, at least 12 Å thick, insulates one column from those in the neighbouring cells.

From this initial configuration, the structure is relaxed. The 'hydrogen' atoms and the Ga and As atoms within 9.25 Å of the dislocation core, as denoted by the ring in figure 4, are allowed to move. The Ga and As atoms on the perimeter of the cylinder are held fixed at their initial positions. The relaxing atoms (interior GaAs and 'hydrogen') are allowed to relax until the forces on the relaxing atoms are <0.1 eV Å^{-1}.

The total energy and force calculations are performed with VASP [20, 21] employing ultrasoft pseudopotentials [25, 26]. To ensure that the solutions provided by VASP are accurate within the operating regime, the lattice constant and elastic constants of GaAs are calculated. The effects of the spin–orbit interaction were neglected. The cubic lattice parameter of GaAs is calculated to be $a = 5.591$ Å, a value that compares well with the experimental value $a = 5.653$ Å [27]. The predicted elastic constants, in Pa, are $c_{11} = 1.2524(10^{11})$, $c_{12} = 0.5473(10^{11})$, and $c_{44} = 0.6287(10^{11})$, which are within 6% of the experimental values, $c_{11} = 1.1877(10^{11})$, $c_{12} = 0.5372(10^{11})$, and $c_{44} = 0.5944(10^{11})$ [28]. These results suggest that the ultrasoft pseudopotential formalism of VASP describes well the structure of GaAs near its equilibrium structure.

For the dislocation core structure calculations, the plane-wave energy cut-off was chosen to be 18.4 Ryd (necessary for the 'hydrogen' atoms). Six $\boldsymbol{k}$-points along the dislocation line were used (three for the double-period cells) to ensure convergence[6].

3. Results

The resulting structures for the 90°α- and β-partial cores are shown in figure 2. It is clear that there is substantial difference between the single- and double-period reconstructions, in terms of both the bonding lengths and the bond angles. The reconstructed bond lengths along the

[5] The choice of origin for the singularity is expected to introduce only small errors into the estimates of relative core reconstruction energies. A similar approach when applied to Si modelled via Tersoff potentials suggests that the error in energy difference induced by a poor choice is of the order of 10 meV Å^{-1} [22].

[6] Equivalent $\boldsymbol{k}$-points were chosen for the single- and double-period cells.

Table 1. A comparison of bond lengths along the dislocation core.

Bond	Figure	Length (Å)	Literature
Equilibrium Ga–As bond		2.421	2.43 [29]
90° partial, double period, As–As bond	2(b), (i), (ii)	2.59	
90° partial, single period, As–As bond	2(a), (i), (ii)	2.66	2.58 [29]
90° partial, double period, Ga–Ga bond	2(b), (iii), (iv)	2.46	
90° partial, single period, Ga–Ga bond	2(a), (iii), (iv)	2.50	2.41 [29]
30° partial, As–As bond	1, (i), (ii)	2.56	2.63 [3] [a]
30° partial, Ga–Ga bond	1, (iii), (iv)	2.47	2.45 [3] [a]

[a] Assuming the Ga–As bond length 2.421 Å.

core are listed in table 1 below and are compared literature values. Quantitatively this agrees with Bennetto's assessment of the single- and double-period reconstructions in silicon [9]. A through quantitative analysis of these structures will be conducted elsewhere.

One can compute the energy difference between the two core reconstructions using directly the results of the calculations. The predicted energy differences, scaled by the repeat length of the unit cell in the dislocation direction, are found to be $1.4(10^{-2})$ eV Å^{-1} for the α-cores and $-1.0(10^{-2})$ eV Å^{-1} for the β-cores. So for a length of dislocation equal to the double-period repeat length, 7.90 Å, one finds that the corresponding energy difference is 0.110 eV for the α-cores and -0.082 eV for the β-cores, which can be compared to the absolute energy from a double-period cell calculation which is approximately -1265 eV.

Given the numerous approximations in the computation, including the use of the local density approximation, the unknown effects of the surface passivation, possible charge accumulation [30], the uncertainty in the choice of origin for the anisotropic elastic singularity, and the electric fields arising from the polar nature of the unit cell, one must conclude that to within the resolution of our computations, the two core structures are degenerate. If this is so, one expects to find both core structures present along the core at any given time and one expects this to have an impact on experimental observation of the core structures, the optoelectronic properties of the core, and the mechanical properties of GaAs. The details of these effects are left to future research. Using the approach presented here, it is not possible to assess accurately the relative stability of the α- and β-cores.

Using methods identical to those above, 30°α- and β-partial dislocations were generated and relaxed. The resulting structure can be seen in figure 1. The reconstruction bond lengths are displayed in table 1.

Due to recent advances in microscope performance, electron microscopy can be used to investigate the quality of theoretical predictions to a sub-ångström resolution [31, 32]. Figure 5(a) displays a HREM experimental image of a 30° partial dislocation in a heavily Be doped sample of GaAs obtained using an exit phase reconstruction technique [33, 34]. To compare the predicted structure to the HREM image, the predicted structure of the 30° dislocation in figure 1(b) was scaled by the ratio of the experimental to the theoretical lattice parameter. These scaled positions were used to generate a 'predicted' HREM exit phase reconstruction image, shown in figure 5(b). Quantitative analysis of the images indicates that the scaled theory result agrees with the experimentally measured column positions to better than 0.27 Å, a satisfying level of agreement between experiment and theory. It is noted that the experimental image displays systematic distortions not captured in the predicted image. A detailed discussion of image reconstruction procedures as well as quantitative analysis will be published elsewhere.

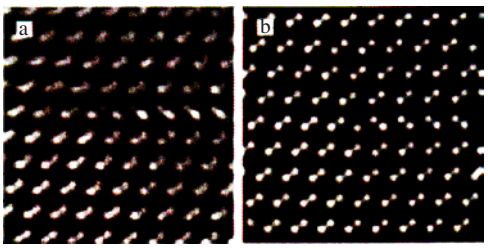

Figure 5. HREM exit phase reconstruction images. Panel (a) shows the experimentally obtained image and panel (b) shows the image from the predicted structure.

4. Conclusions

In conclusion, an *ab initio* electronic structure total energy technique has been applied to the computation of the structure of glide set dislocations in GaAs. The single-period and double-period reconstructions for the 90° partials are found to be nearly degenerate (for the α- and β-dislocations separately—no conclusions can be drawn concerning the relative energies of the α- and β-cores). This degeneracy is certain to have an impact on the characterization of the dislocations, as well as their optoelectronic and mechanical properties. The predictions for the 30° partials agree well with prior calculations. Further, the predicted structure of the β-partial, when scaled to the experimental lattice constant, agrees favourably with the structure determined using HREM.

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