First-principles study of impurity segregation in edge dislocations in Si

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Using *ab initio* calculations, the segregation of As, Ga, and Ge atoms in the core regions of perfect edge dislocations in Si is examined. When all nearest neighbors of an impurity are Si atoms, As favors the core site at maximum compression and has a segregation energy of 0.25 eV/atom. Ga and Ge impurities favor sites under maximum tension and have segregation energies of 0.44 and 0.19 eV per atom, respectively. For As impurities, however, a pairing mechanism yields an even larger segregation energy of 0.64 eV/atom.

I. INTRODUCTION

Strain in semiconductors such as that which occurs at heterojunctions can be relieved by the creation of dislocations. Dopant distributions and the effect of dopants on device performance can be directly impacted by these dislocations through trapping and by providing fast diffusion pathways.

The advent of the new parallel supercomputers has enabled researchers to apply first principles methods to sufficiently large systems that now extended defects such as dislocations and grain boundaries can be adequately treated. These methods have been applied to a few studies of intrinsic dislocations in Si. These include the work of Bigger *et al.* on the 90° partial,[1] Arias and Joannopoulos[2] on a $\langle 110 \rangle$ screw dislocation, and Liu *et al.* on the perfect edge dislocation.[3] There have also been a few first principles studies of impurities in dislocations and grain boundaries. Arias and Joannopoulos[4] looked at As in a $\Sigma 5$ grain boundary in Ge. For Si, Jones[5] employed a cluster approximation to study a number of different impurities in a 90° partial, and Maiti *et al.* have investigated As in both the 90° partial[6] and the $\Sigma 5$ grain boundary.[7]

We present here results of *ab initio* calculations of $(a/2)\langle 110 \rangle$ edge dislocation dipoles doped with As, Ga, and Ge impurities. The Ge and Ga segregate to the core regions that are in tension and have segregation energies of 0.19 and 0.44 eV, respectively. The As when surrounded entirely by Si atoms segregates to the regions of maximum compression with a segregation energy of 0.25 eV. When As impurities are allowed to pair, even larger binding energies are found. In the pair, each As atom can relax away from its partner and can attain the preferred threefold coordination. Pairs segregate to the region of maximum tension in the core and have a segregation energy of 0.64 eV/atom.

II. CALCULATIONS AND RESULTS

In the calculations, a dipole with two $\pm(a/2)\langle 110 \rangle$ edge dislocations separated by 15 Å along the [110] direction is considered. The computational cell contained 128 atoms and is a parallelepiped. Figure 1 shows a [110] projection of the computational cell. For a more detailed discussion of the construction of the cell see our previous work.[3] In this previous work,[3] we studied an intrinsic dislocation dipole in Si. We found it was necessary to employ large computational cells in order to properly describe the electronic structure of an edge dislocation. We considered computational cells containing 32, 72, 128, 200, and 288 atoms. The largest cell showed the upper most valence band shifted into the crystalline Si gap by almost 0.2 eV while for the smallest cell there was virtually no shift at all. The increase in the valence-band shift correlated with the increase in strain in the dislocation cores as the separation between the two dislocations in the dipole increased. For the 128-atom computational cell, the strain energies and valence-band shift were sufficiently converged and we chose to use this size system to study the effects of impurities.

The *ab initio* total energy calculations and structural relaxations were done using density functional theory in the local-density approximation with the computer code CETEP (Ref. 8) as in our previous work.[3] A plane-wave energy cutoff of 200 eV was used, and the Brilliouin zone integration was carried out using four special k points $[\mathbf{k} = (0,0,1/16),(0,0,3/16),(0,0,5/16),(0,0,7/16)]$. The conver-

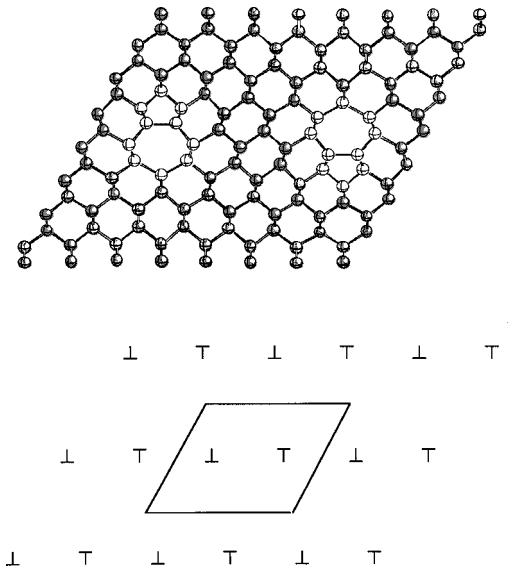

FIG. 1. [110] projection of the 128 atom unit cell for the edge dislocation dipole, with the atoms in the core shaded more lightly (top), and the periodic lattice in which the calculations are done (bottom).

gence criteria imposed were that the forces on any atom are less than 0.1 eV/A, and that the energy change in the final cycle is less than 0.0001 eV/atom. The Si, As, Ga, and Ge atoms are represented by nonlocal, normconserving pseudopotentials that give bulk lattice constants within a few percent of the experimental values.

Single impurities were considered first. As, Ga, or Ge atoms were placed at substitutional sites in the core region. The segregation energies were determined from the total energies of the relaxed structures referenced to a similarly relaxed structure with the dopants exchanged with Si atoms in bulklike sites furthest from the core. The segregation energy as a function of position is plotted in Fig. 2 for each of the three impurities. We find segregation energies for As, Ga, and Ge of 0.25, 0.44, and 0.19 eV per atom, respectively. Note that the periodic repeat along the dislocation in the computational cell is 3.83 Å. As a result, the impurities are not truly isolated. Rather we have created a chain of alternating Si atoms and dopants running along the core of the dislocation.

In order to see the effect of strain on segregation, the sum of the diagonal elements of the stress tensor in the intrinsic Si dislocation dipoles is plotted as a function of position in Fig. 2. The stress tensor was calculated[9] using the relaxed structure determined from first principles methods and the Tersoff potential.[10] This method is expected to provide a reasonably accurate approximation for the stress tensor in the system since the structure obtained by direct relaxation with the Tersoff potential is very close to that produced by first principles methods. The Ge and Ga impurities segregate to the regions of maximum tension (largest bond lengths) while the As impurity segregates to the position of maximum compression (smallest bond length). Since Ge is electronically similar to Si, it forms a diamond structure lattice and the covalent bond lengths (2.34 Å for Si and 2.44 Å for Ge) when compared show that Ge favors regions under tension. Since Ga and As have different electronic configurations

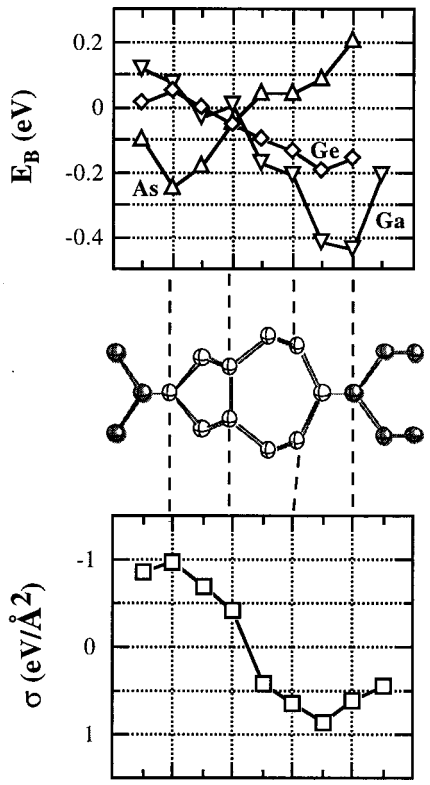

FIG. 2. Binding energies E_B for single Ga, Ge, and As impurities in the dislocation core (top), and stress $\sigma=(\sigma_{xx}+\sigma_{yy}+\sigma_{zz})/3$ in the core for dislocations in pure Si (bottom).

than Si and Ge, a comparison of equivalent structures is not possible.

Since As has 5 electrons in its outer shell it prefers to be threefold coordinated. This configuration can be achieved while leaving the Si atoms fourfold coordinated by placing As atoms in adjacent substitutional sites. In this way, the paired As atoms can move away from one another leaving themselves with bonds only to the adjacent Si atoms. The resulting segregation energy of the pair is determined by a competition between the electronic and elastic mechanisms. There are two general types of pairing sites available in the dislocation core. One set will produce pairs that are separated from their periodic pair image by an intervening Si atom. These are site pairs (a,b), (d,c), (c,e) and (f,g) which are indicated in Fig. 3 along with their respective bond lengths in the undoped dislocation core. The other set of paired sites will produce connected chains of atoms running along the core where each site in the pair is a nearest neighbor of a site in its periodic image. The segregation energies and the bond lengths between the As atoms in the pair and in their periodic image are listed in Table I. For the nonchain forming pairs, (f,g), the pair with the largest bond length in the intrinsic dislocation, has the largest binding energy, 0.64 eV/atom (see Fig. 3). For the connected chains, the largest binding energy of 0.44 eV/atom is still significantly larger than that for the single As impurity.

Since the As atoms need to relax away from one another to attain threefold coordination, it is quite reasonable that the (f,g) pair, which has the largest bond length in the intrinsic dislocation yields the largest segregation energy. This result shows that the pairing mechanism studied by Jones[5] by clus-

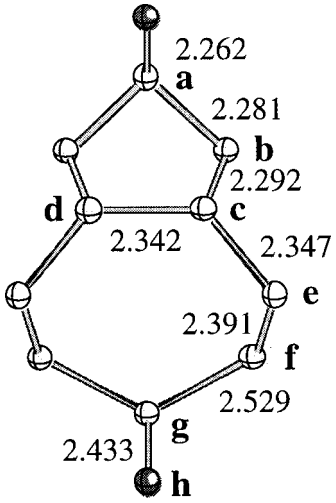

FIG. 3. Site labels and bond lengths in angstroms for pure Si in the dislocation core.

ter calculations for the 90° partial is the most important one for segregation of As in edge dislocations in Si. However, the connected pairs show that the competition between achieving threefold coordination and elastic effects is more complex. In the (e,f) pair, a relatively large binding energy of 0.44 eV/atom is attained by achieving a connected chain with intermediate bond lengths between impurities. The (g,h) pair, despite having longer As bond lengths, results in larger elastic strains which yield a much lower binding energy, 0.04 eV/atom. These results are consistent with the work of Maiti *et al.* on the 90° partial[6] and the $\Sigma 5$ boundary.[7]

TABLE I. Segregation energies E_B, As separations, and types of periodic chains (U=unconnected, C=connected) of As pairs substituted at various nearest neighbor sites in the reconstructed core. See Fig. 3 for the description of As site positions. As* is the position of the periodic image.

As positions	E_B (eV/atom)	d(As-As) (Å)	d(As-As*) (Å)	Chain type
(a,b)	0.24	2.35	3.83	U
(c,d)	0.17	2.61	3.83	U
(f,g)	0.64	3.12	3.83	U
(b,c)	0.17	2.369	2.365	C
(e,f)	0.44	2.514	2.534	C
(g,h)	0.038	2.536	2.536	C

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