

Ordering of As impurities in a Si dislocation core

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We demonstrate by *ab initio* calculations that segregation of As in a dislocation core in Si occurs in the form of an ordered chain of As atoms running along the dislocation pipe. All As atoms in the chain achieve threefold coordination and the segregation energy is close to 1 eV per As atom.

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Plastically deformed materials release excess strain by creating extended defects such as dislocations. In semiconductor devices, dislocations can severely affect the behavior of dopant impurities because: (1) the dislocation cores may provide a fast diffusion pathway to impurities, which severely influences the dopant profile in an uncontrolled way, and (2) impurities may get trapped in the core regions leading to preferential segregation and electrical deactivation of the impurity.

It has generally been believed that impurities get trapped at sites with imperfect bond order in dislocation cores. However, experimental¹⁻³ and theoretical⁴⁻¹² work has established that dislocations and grain boundaries in Si and Ge actually reconstruct in such a manner that all atoms are fourfold coordinated. Therefore, a single impurity atom occupying a substitutional site in the core does not experience any appreciable difference from its environment in the bulk material away from the core, resulting in small segregation energies. For example, in the case of As segregation in a symmetric tilt boundary in Ge, the segregation energy was found to be only of order 0.1 eV.¹² However, in a very recent *ab initio* study¹³ we found that As impurities form ordered chains of As dimers (a periodically repeated array of two substitutional As atoms at neighboring sites), or in some cases, perfectly ordered chains of As atoms along the grain boundary cores, with segregation energies as high as 0.5 eV per As atom. In such chain configurations, each As atom relaxes away from its partner atom in the dimer through repulsion, and attains its preferred threefold coordination, thereby lowering energy. It was also found that isolated As dimers lead to threefold coordination, but the excess binding energy over single substitutional As atoms is small, ~ 0.1 eV per atom, and sometimes there is no energy gain at all. It follows that the energy gain from attaining threefold coordination is largely cancelled by the elastic energy cost of distorting the Si backbonds. However, a significant additional energy gain occurs through chain formation.

In this letter, we show that As segregation at an isolated dislocation core in Si occurs in the same manner as in grain boundaries, namely in the form of ordered chains of threefold-coordinated As atoms. In fact, the strains associated with isolated dislocation cores are in general much larger than in grain boundaries. These strains lead to larger segregation energies in a dislocation core than in the grain

boundary, as high as ~ 0.9 eV per As atom. In earlier work using cluster calculations, Jones *et al.*⁷ found that As and P dimers in a dislocation core gain substantial energy by achieving threefold coordination. However, chains of threefold-coordinated impurities were not considered.

Before delving into computational details, a brief introduction to dislocation terminology is in order. The major operative slip system in diamond cubic structures involves the glide of $\{111\}$ planes along $\langle 110 \rangle$ directions. Well separated perfect glide dislocations lie primarily along $\langle 110 \rangle$ directions, and are either screw or 60° dislocations, the latter deriving its name from the fact that the angle between the dislocation line direction and the Burgers vector \mathbf{b} is 60° . In materials with low stacking fault energy, the 60° dislocation is often found to be dissociated into two Shockley partial dislocations separated by a stacking fault. These two Shockley partials have their Burgers vectors ($\mathbf{b} = \frac{a}{6}\langle 112 \rangle$) aligned, respectively, at 30° and 90° to their $\langle 110 \rangle$ line direction, and are commonly referred to as the 30° and 90° partials.¹⁴ In this work, we have chosen the 90° partial dislocation core in Si as a concrete system to perform our segregation study.

As in our previous work,¹³ the total energy calculations and structural relaxations were carried out using density functional theory with the exchange and correlation energy treated in the local density approximation. We used a non-cubic periodic supercell with two oppositely oriented 90° partial cores separated by a distance of 13 Å (Fig. 1). An energy cutoff of 150 eV was used, and the Brillouin zone integration was performed using two special k points, chosen according to the Monkhorst-Pack scheme.¹⁵ Atoms were re-

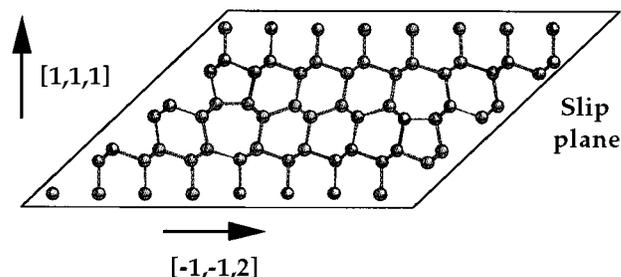


FIG. 1. View along the dislocation line of a periodic supercell containing two oppositely oriented 90° partials with the asymmetric reconstruction; the supercell for the symmetric reconstruction appears almost identical in the same view. The supercell contains 64 atoms and the cores are separated by 13 Å.

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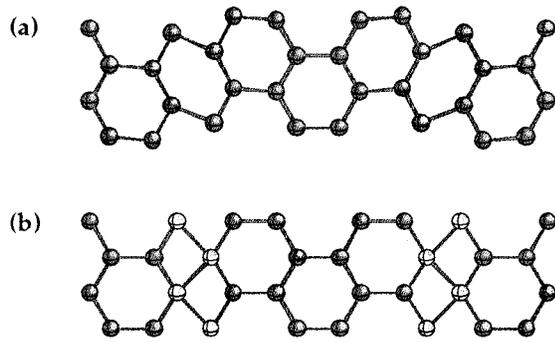


FIG. 2. Bonding structure of the 90° partial dislocation dipole in the slip plane, shown by doubling the supercell periodicity in Fig. 1 along the dislocation line for: (a) asymmetric reconstruction and (b) symmetric reconstruction. In the three-dimensional geometry, the asymmetric reconstruction [Fig. 2(a)] has all atoms fourfold coordinated, while the symmetric reconstruction [Fig. 2(b)] has some atoms, distinguished by lighter shading, quasi-fivefold-coordinated. See text.

laxed in small steps until the magnitude of the largest force component was less than 0.07 eV/\AA .

Previous studies found two models of reconstruction in the 90° partial dislocation core: (1) the asymmetric reconstruction, in which the mirror symmetry along the dislocation line is broken,^{16,17} and (2) the symmetric reconstruction, in which the mirror symmetry is kept intact.¹⁸ The asymmetric structure has all the atoms fourfold coordinated, while the symmetric structure has two quasi-fivefold-coordinated atoms per periodic segment of the core. Both these reconstructed cores look almost the same in the projection along the dislocation line (Fig. 1), but are clearly distinguishable in the bonding structures in the slip plane (Fig. 2). From *ab initio* relaxations we found that the asymmetric structure was stable, while the symmetric structure spontaneously transformed into the asymmetric structure, in agreement with an earlier *ab initio* study.¹⁹ All our segregation studies were thus performed exclusively on the asymmetric structure.

Single As atoms and As dimers were, respectively, placed at various sites and nearest neighbor site pairs of the dislocation core, as indicated in Fig. 3. In all cases, the energy of the relaxed structure was calculated relative to the geometry in which the As atoms in the core were exchanged with Si atoms in the bulk, i.e., away from the core. The negative of this energy, known as the segregation energy, is

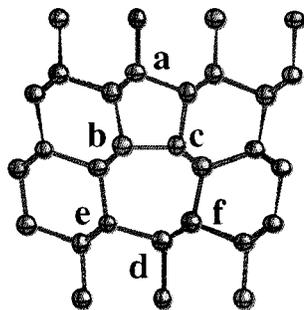


FIG. 3. Various sites of an isolated 90° partial core, viewed along the dislocation line, on which single As atoms and As dimers are placed. Segregation energies are listed in Table I.

TABLE I. Segregation energies of single As atoms and As dimers placed substitutionally at various sites of an asymmetrically reconstructed core. For the dimer geometries the relaxed distance between the two dimer companion atoms ($d_{\text{As-As}}$) and the corresponding distance between the first As atom and the periodic image of its dimer companion ($d_{\text{As-As}^*}$) are also indicated. See Fig. 3 for site denominations.

As site (s)	Segregation energy (eV/As atom)	$d_{\text{As-As}}$ (\AA) (Dimer geometries)	$d_{\text{As-As}^*}$ (\AA) (Dimer geometries)
Bulk	0.00		
[d]	-0.15		
[a]	0.14		
[b], [c]	0.33		
[d,f]	0.01	2.57	2.42
[d,e]	0.13	2.90	4.53
[b,c]	0.88	2.87	2.95

listed in Table I for all different As configurations considered.

Let us first consider the single As atoms in the dislocation core. Four different sites were chosen. The strain distribution is very different at different sites, as is apparent from comparing the site-associated bond lengths with the bulk Si-Si bond length of 2.35 \AA , making the segregation energy strongly site dependent. Thus the strain is: (i) compressive at site a, with bond lengths (2.29, 2.31, 2.31, and 2.34 \AA); (ii) tensile at site d, with bond lengths (2.37, 2.41, 2.43, and 2.44 \AA); (iii) mixed compressive/tensile at sites b and c with bond lengths (2.31, 2.34, 2.41, and 2.43 \AA). The resulting segregation energy for As is largest for sites b and c, moderate but positive at site a, and even negative for site d. The largest segregation energy of 0.33 eV (sites b,c) is much larger than the average binding at a grain boundary.^{12,13} Also, the wide variation of segregation energy from site to site is to be contrasted with a much smaller dispersion in a grain boundary,¹³ where the strain distribution is much more uniform. In all cases of single substitutional As, the relaxation from the initial Si site is very small, just as in a grain boundary.

Segregation studies of periodic chains of As dimers yield more dramatic results. To interpret these results, it should be reemphasized that two As atoms placed on nearest neighbor Si sites, which we call As dimers, seek to repel and relax away from each other. In this way, each As atom achieves its preferred threefold coordination, leaving all the Si atoms fourfold coordinated.¹³ The three largest bonds in the dislocation core, i.e., [d,f], [d,e], and [b,c] were chosen for investigation. Table I displays the segregation energies for these three dimers. It also lists, for each relaxed geometry, the distance of an As atom from: (a) its dimer companion (column 3), and (b) the nearest periodic image (As^*) of the dimer companion in the dislocation line direction (column 4). The distinct behaviors of the three dimers are clearly evident from Table I, as discussed below:

- (i) [d,f]: In this case the orientation of the dimer is such that site d is the nearest neighbor of both f and its nearest periodic image f^* in the dislocation line direction. Thus, in the periodic chain of dimers, all the As atoms are too close to each other. This allows only a small stretching of the As-As separation, to only

2.57 Å, while the As–As* distance (2.42 Å) changes very little from the equilibrium Si–Si bond distance of 2.35 Å. Consequently, the relaxed structure consists of a chain of essentially fourfold-coordinated As atoms, resulting in negligible binding.

- (ii) [d,e]: In this case the orientation of the dimer is nearly perpendicular to the dislocation line direction, and sites d and e* are only second neighbors. This allows the As dimer atoms to relax away from each other, stretching the As–As separation to 2.90 Å, thereby leading to threefold coordination of each As atom. However, the transverse orientation of the dimer keeps it well separated from its periodic images in the dislocation line direction, as is evident from the large As–As* distance. We therefore have an array of nearly isolated As dimers. This leads to a positive but low segregation energy (0.13 eV per As), just as in a grain boundary.¹³
- (iii) [b,c]: In this case the dimer is oriented such that although b and c* are second nearest neighbors, their distance before relaxation is much less than the separation of d and e* in case (ii). Consequently, the As–As stretch is accompanied by As and As* getting closer to each other. In the final relaxed geometry, the As–As* separation (2.95 Å) is only slightly larger than the As–As separation (2.87 Å) and we have a nearly perfect chain of As atoms leading to a large segregation energy (0.88 eV per As).

In order to elucidate further the source of energy gain through the formation of dimer chains, we have examined the electronic energy levels in the As dimers in the dislocation core and compared them with those of isolated As atoms in the bulk. As one would expect, the isolated As atom has a shallow donor level at less than 0.1 eV below the conduction band edge. In the [b,c] dimer chains, on the other hand, each As atom has an electron at a level in the midgap region.²⁰ Further analysis indicates that the level in the gap is a member of the lone-pair states that As atoms have when they are threefold coordinated. Because of the close proximity of the threefold coordinated As atoms, these lone-pair states split, with half of them in the band gap and half of them in the valence band. Thus, the gain in energy could be viewed as a result of the shallow donor level being driven deep into the band gap by the lattice relaxation accompanying dimer formation, or, equivalently, as arising from the fact that dimer formation leads to lone-pair states that are lower in energy than the states that are available when an As atom is fourfold coordinated.

In summary, using the 90° partial dislocation as a concrete example, we find that As likes to decorate a core in Si in an ordered chain fashion. All As atoms in the chain achieve threefold coordination through repulsion between alternating As atoms. Overall behavior of single impurities, isolated dimers, and chains in the dislocation core is similar to the behavior we found in a Si grain boundary.¹³ However, the segregation energy of both single As atoms and those in a chain are much larger in the dislocation core, with the result for the chain being as high as 0.9 eV per As atom.

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