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Structural transformation in the 90° partial dislocation in Si due to Ga impurities

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Ga impurities in the 90° Shockley partial dislocation in silicon have been investigated using first-principles total-energy pseudopotential calculations. The results indicate that Ga segregates to the core of the dislocation and destabilizes the asymmetric fourfold coordinated structure, which is known to be the low-energy configuration in pure Si. The segregation energy for Ga in the symmetric core configuration is 0.53 eV/atom. The atomic mechanism for this spontaneous transformation to the symmetric structure is the passivation of quasifive-fold sites in the symmetric core by Ga. [S0163-1829(98)01744-5]

In semiconductors, dopants and dislocations can have strong interactions that can alter dopant distributions and electronic structures. The 90° Shockley partial $[\mathbf{b}=(a/6)\langle 112\rangle]$ is one of the most common dislocations in plastically deformed silicon.[1] These dislocations lie in $\{1,1,1\}$ planes along $\langle 110\rangle$ directions separated from 30° Shockley partials by intrinsic stacking faults.[2] Their occurrence in semiconductor devices and at interfaces has motivated a number of investigations of their atomic and electronic structures. The 90° partial has been studied in pure silicon and in the presence of impurities both experimentally[3,4] and theoretically. [5–15]

First-principles calculations by Bigger *et al.*[12] have resolved the question of the structure of the core of the 90° partial in Si. Olsen and Spence used electron microscopy to image the core along the $\langle 110\rangle$ dislocation line direction, where 5- and 7-member rings were observed in projection.[16] However, the bonding in the $\{111\}$ plane that contains the two partials and the stacking fault could not be observed. As shown in Figs. 1 and 2, there are two models for the core structure that give the same apparent 5- and 7-member rings in the [110] projection: (1) an asymmetric structure [Fig. 1(a)] in which all the atoms are fourfold coordinated;[3,6] and (2) a symmetric configuration [Fig. 1(b)] in which some of the core atoms are ‘‘quasifivefold’’ coordinated.[9,12] Classical simulations using semiempirical potential models did not clarify the situation. With the Tersoff potential,[17] the asymmetric structure is preferred, but with the Stillinger-Weber model,[18] only the symmetric structure is stable. Bigger *et al.* found that the asymmetric structure was lower in energy by 0.23 eV/Å and that the symmetric configuration was unstable, transforming spontaneously into the asymmetric structure when the mirror plane normal to the dislocation line was broken by a small distortion.

Recently, there have been a number of theoretical studies of impurity segregation in grain boundaries and dislocations in semiconductors.[13,15,19–21] Two of these studies have examined the 90° partial in Si. Jones *et al.*[13] used *ab initio* cluster methods to investigate B, P, N, As, O, and C impurities. They considered the asymmetric core structure and predicted that both G_V=P and As would form pairs in the core with bonds to their nearest Si neighbors and G_V-G_V separations appreciably larger than the G_V-Si and Si-Si bonds. Similarly, Maiti *et al.*[15] later found that As impurities could achieve an even larger segregation energy by forming a chain of As dimers along the core of the 90° partial with bonding to three Si nearest neighbors accompanied by repulsion of the As-As pairs. In these *ab initio* studies, the asymmetric core configuration was found to be the lowest energy structure.

Here, we present results of first-principles calculations for the 90° partial dislocation with substitutional Ga impurities. Ga, having only three electrons in its outer shell, has the potential to favor threefold coordination. The quasifivefold sites in the symmetric configuration offers the Ga atoms the opportunity to bind to three silicon nearest neighbors in this atomic arrangement, but not to their two Ga neighbors after relaxation occurs. In fact, we will show that when Ga atoms are placed in a string of core sites of the asymmetric configuration, they spontaneously induce a transformation to the symmetric core structure.

In order to avoid spurious strains, periodically repeated computational unit cells were constructed in the manner de-

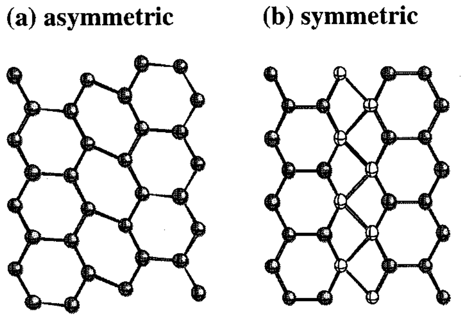


FIG. 1. The (a) asymmetric and (b) symmetric reconstructions in the core of the 90° Shockley partial dislocation in Si on the (111) slip plane. The lighter shaded atoms in the symmetric core are quasifivefold coordinated. Crystallographic directions in the slip plane are $[1,-1,0]$ (vertical) and $[1,1,-2]$ (horizontal). The thickness along the $[1,-1,0]$ direction is four times that of the unit cell used in the calculations.

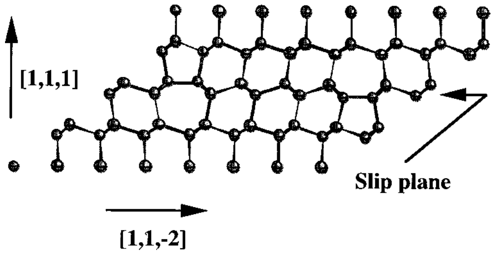
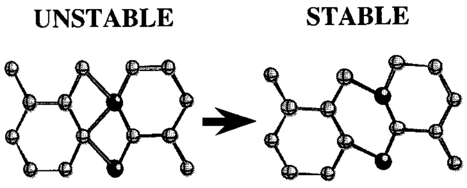


FIG. 2. [110] projection of the 64-atom periodic unit cell for the 90° dislocation dipole. In this projection, the symmetric and asymmetric structures appear to be sensibly identical.

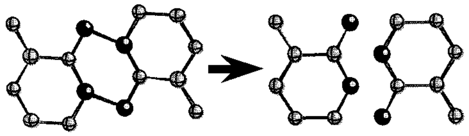
scribed by Bigger *et al.*[12] The unit cell, shown in Fig. 2 along [110], is in the form of a parallelopiped containing a dislocation dipole, and includes 64 atoms. The dislocations in the dipole have their Burgers vectors $\mathbf{b}=(a/6)\langle 112\rangle$ aligned at 90° to their $\langle 110\rangle$ line directions and are separated by a stacking fault approximately 13 Å wide. The structures were first relaxed classically at constant pressure using the Tersoff potential[17] for the asymmetric structure and the Stillinger-Weber potential[18] for the symmetric configuration. As previously noted, the asymmetric structure is stable for the Tersoff potential while only the symmetric is found with Stillinger-Weber. These structures were then doped substitutionally with Ga and relaxed at constant volume using *ab initio* methods.

The total energy pseudopotential calculations and structural relaxations were done using density-functional theory with the exchange and correlation energy treated in the local-density approximation with the computer code CETEP (Ref. 22) on the parallel Intel computers at ORNL. A plane-wave energy cutoff of 200 eV was used, and the Brillouin zone integration was carried out using three special k points $[k=(0,0,0),(0,0,0.2),(0,0,0.4)]$ chosen according to the Monkhorst-Pack scheme.[23] The convergence criteria imposed were that the forces on any atom be less than 0.1 eV/Å, and that the energy change in the final cycle be less than 0.0001 eV/atom. The Si and Ga atoms are represented by nonlocal, normconserving pseudopotentials that give bulk-lattice constants within a few percent of the experimental values.

We first considered a single Ga impurity substituted in the glide plane of both dislocations in the unit cell. Since the cell is periodically repeated, the result is to create a line of alternating Si atoms and Ga impurities running along the core of the dislocations. When the Ga atom was placed in the asymmetric structure [Fig. 3(b)], the system remained stable. In contrast, when the Ga impurity was placed in the corresponding site in the symmetric configuration as shown in Fig. 3(a) and allowed to relax, the system spontaneously transformed into the asymmetric structure. In the relaxed asymmetric core, the Ga atoms are fourfold coordinated with Ga-Si bonds that vary from 2.33 to 2.47 Å (the Ga-Si bond length in bulklike sites in the unit cell is about 2.36 Å), and the segregation energy is 0.28 eV/atom. Segregation energies were determined from the total energies of the relaxed structures referenced to a similarly relaxed structure with Ga exchanged with Si atoms in the bulklike sites furthest from the core.



(a) symmetric (b) asymmetric



(c) asymmetric (d) symmetric

FIG. 3. Core structures of the 90° partial, with Ga atoms darker: (a) symmetric configuration, with alternating Ga and Si sites along the core; (b) symmetric final structure obtained starting from (a); (c) asymmetric structure fully doped with Ga; (d) symmetric configuration into which (c) transforms spontaneously. Here, the thickness along the $\langle 110\rangle$ dislocation line direction is twice that of the unit cell used in the calculations.

The results change dramatically when additional Ga is substituted to form a string of Ga atoms running down the core axis of the dislocation. When Ga is substituted in this fashion into the asymmetric core [Fig. 3(c)], the system spontaneously transforms from the asymmetric to the symmetric configuration with all quasifivefold sites occupied by Ga impurities, shown in Fig. 3(d) after relaxation. When Ga atoms are substituted directly into the corresponding sites in the symmetric starting structure, the system remains in this structure after relaxation. In the final structure, each Ga atom bonds to three nearest-neighbor Si atoms with a bond length of 2.34 Å. From the calculated charge densities, nearest Ga pairs do not form bonds and are separated by 2.7 Å. The segregation energy for Ga in the symmetric structure saturated with Ga is 0.53 eV/atom, which is nearly twice the segregation energy for the fourfold coordinated, alternating Ga-Si strings in the asymmetric configuration.

The equilibrium structure is determined by the free energy. The difference in the Hemholtz free energys ΔA between the doped-symmetric and doped-asymmetric structures is estimated by including the contributions from the configurational entropy along with the internal energy,

$$\Delta A=\Delta E-kT\ln\left[2\left(\frac{1-c}{c}\right)^{2}\right],$$

where c is the concentration of Ga impurities and $\Delta E=0.406$ eV/Å is the difference in internal energy for the two dislocation structures. (For $\Delta A>0$ the doped symmetric structure is stable.) The crossover from symmetric to asymmetric structure occurs when the concentration drops below

$$c=\left[1+\frac{\exp(\Delta E/2kT)}{\sqrt{2}}\right]^{-1}.$$

For $T=300$ K, $c=1.14\times 10^{-13}$, which correspondes to a Ga doping of $5.7\times 10^{9}/\mathrm{cm}^{3}$. This is the doping level roughly equal to the intrinsic carrier concentration at room temperature, and many decades below levels useful in devices (except in those demanding exceptionally pure Si).

From the results, we see for the impurity concentrations of interest that all of the lowest energy structures contain only fourfold coordinated Si. There is a greater cost in energy when Si is forced to be over-coordinated than the energy reduction obtained by allowing Ga to attain its preferred coordination. The symmetric core structure with a fully Ga-doped core allows both Si and Ga to achieve their preferred bonding. As a result, Ga segregation to the 90° partial dislocations in Si can cause a structural transformation. This should have an impact on other properties. Ga segregation to the dislocations may increase markedly, and the (nearly) fully doped partials may form conducting paths (quantum wires) through the silicon. The asymmetric structure with a fully doped core is unstable and spontaneously transforms to the symmetric configuration. This is a striking example of a structural transformation in an extended defect in silicon due to impurities. Indeed, one may speculate that this phenomenon is quite common in diamond-cubic and zinc-blende semiconductors. It is possible that the electrical and mechanical properties associated with extended defects are often not the result of the intrinsic structure, but rather are significantly affected by segregated impurities in unexpected ways. Certainly, similar reactions would be expected for the other smaller dopants B and Al, and for group-III impurities in some other dislocation and grain-boundary structures.

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