Dopant Segregation at Semiconductor Grain Boundaries through Cooperative Chemical Rebonding

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Recent theoretical work found that isolated As impurities in Ge grain boundaries exhibit minimal binding, leading to the suggestion that the observed segregation is likely to occur at defects and steps. We report *ab initio* calculations for As in Si and show that segregation is possible at defect-free boundaries through the cooperative incorporation of As in *threefold-coordinated* configurations: As dimers, or *ordered chains* of either As atoms or As dimers along the grain boundary dislocation cores. Finally, we find that As segregation may drive structural transformations of certain grain boundaries. [S0031-9007(96)00811-3]

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Polycrystalline semiconductors are used in microelectronics. Dopants, which control the electrical properties of these materials, are known to segregate in grain boundaries in electrically inactive configurations [1–4]. The fraction of dopants in the grain boundaries is governed by the *segregation energy,* i.e., the energy difference between a dopant atom in the grain boundary and a dopant atom in the bulk crystal. For the specific case of As segregation in Si and Ge grain boundaries, experimental values of the segregation energies range from 0.41 to 0.65 eV [1–4].

Clearly it would be very important for technologists to know if the large segregation energy is an intrinsic property of a defect-free grain boundary or is caused by defects that could, in principle, be avoided. The origin of the segregation energy has not, however, been accounted for so far. Experiment [5] and theory [6,7] have established that tilt grain boundaries in undoped Si and Ge rebond so that all host atoms are fourfold coordinated. The only first-principles theoretical study of segregation was reported recently by Arias and Joannopoulos [8]. These authors examined the segregation energies of isolated As atoms placed at different substitutional sites in a Ge grain boundary and found values only of order 0.1 eV. They proposed that the observed segregation energies are likely to arise from As atoms bound to steps or other defects. No calculations were pursued to explore such possibilities.

The motivation for the present work was the recognition that the observed large segregation energies may occur in defect-free grain boundaries because As atoms achieve their preferred threefold coordination, as they are known to do in amorphous Si and Ge [9]. Simple bond counting suggests that if a single As atom were to achieve threefold coordination in a Si or Ge grain boundary, at least one Si (Ge) atom would have to have odd coordination (3 or 5), which is energetically costly. Clearly threefold-coordinated As atoms would be far more likely if they were incorporated in a grain boundary in a *cooperative* manner, at least two at a time. The simplest possibility would be two As atoms at nearest-neighbor sites. We have performed systematic first-principles calculations for such possibilities in Si, which is technologically more important, and found that As dimers do form in grain boundaries with segregation energies up to 0.2 eV per As atom. Dimer binding occurs through *repulsion:* The two As atoms repel each other seeking to achieve threefold coordination (Fig. 1); the energy gain from this *chemical rebonding* is larger than the elastic energy cost from backbond distortions. Furthermore, we find that larger segregation energies (0.3–0.5 eV per As atom) are achieved through the formation of chains of As dimers or fully ordered chains of threefold-coordinated As atoms. Finally, we find that the formation of such chains may induce a structural transformation of certain grain boundaries.

Calculations were performed for a $\Sigma = 5\{310\}\langle 001\rangle$ symmetric tilt boundary in Si. This grain boundary is parallel to the $\{310\}$ plane of the original crystalline lattice. It has a minimum periodicity of one conventional lattice parameter ($a = 5.431$ Å) in the $\langle 001\rangle$ direction and a periodicity of $a\sqrt{5/2} = 8.587$ Å in the direction perpendicular to the $\langle 001\rangle$ axis. In the discussion below, we follow the convention that the x axis is perpendicular to the grain boundary plane, the z axis is parallel to the $\langle 001\rangle$ axis of the original crystalline lattice, and the y axis runs parallel to the grain boundary plane in a direction perpendicular to the z axis. We used periodic supercells that contain two oppositely oriented $\Sigma = 5$ grain boundaries. In a supercell with N planes of atoms along

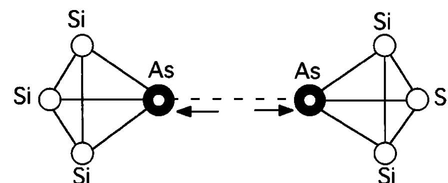

FIG. 1. Schematic showing how the member atoms of an As dimer placed substitutionally in neighboring Si sites would move away from each other into threefold coordination, and thus lower energy.

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the x direction, the grain boundaries are separated by $N/2$ planes. The actual supercells used in the calculations will be discussed later.

The calculations were based on density functional theory [10] with local exchange-correlation energy as parametrized by Perdew and Zunger [11]. The atomic cores are represented by nonlocal, norm-conserving pseudopotentials of the Kerker type [12] in a separable Kleinmann-Bylander form [13], and defined on a real-space grid [14]. The calculations were performed using the code CETEP [15], which was run on 128 processors of the Intel Paragon XP/S 35 at Oak Ridge National Laboratory. The integration over the Brillouin zone was performed using two special k points chosen according to the Monkhorst-Pack scheme [16]. The electronic wave functions were expanded in a plane wave basis set with an energy cutoff of 150 eV, verified to yield accurate lattice constant and bulk modulus for the pure crystal. For each geometry the electronic wave functions were first relaxed by the conjugate gradient scheme of Payne *et al.* [17] until they reached a local minimum (the Born-Oppenheimer surface). The ions were then moved according to the Hellman-Feynman forces until the largest force on any ion in any direction was less than 0.08 eV/Å. Energy changes due to changes in supercell dimensions, known to be small [8], were neglected.

Calculations were performed with $N = 30$ and 40 planes of atoms, with the corresponding supercells containing, respectively, 60 and 80 atoms for the minimum periodicity in the grain boundary plane. Computed segregation energies changed by less than 0.02 eV, indicating that the two grain boundaries in the supercell are adequately isolated from each other. In order to isolate the As dimers from each other in the grain boundary plane, calculations were performed with double the primitive cell and $N = 30$. Most calculations were performed using only the primitive cell in the grain boundary plane and $N = 40$, resulting in chains of interacting dimers.

The calculations for the undoped $\Sigma = 5$ grain boundary yielded a fully relaxed structure, which we label GB1, that is the same as described in Ref. [8] for Ge. We found, however, a second low-energy structure, which we label GB2, with a total energy that is higher by only 0.15 eV per periodic segment of the grain boundary plane. Figures 2 and 3 display xy projections of the structures. The two structures differ in the relative z shift of the two grains forming the boundary, by $a/8 = 0.68$ Å, and also in the nature of the dislocation cores comprising the boundaries. The cores of GB1, formed by terminating planes coming from the same grain, are of the pure edge type ($\mathbf{b} = \frac{a}{2}\langle 100\rangle$). The cores of GB2 are formed by terminating planes coming from different grains, have the Burger's vector at 45° to the z direction ($\mathbf{b} = \frac{a}{2}\langle 101\rangle$), and therefore have mixed screw and edge character.

We studied segregation of As atoms in both GB1 and GB2 because the two structures contain different dislocation cores that are components of many different grain boundaries. Figures 1 and 2 show labels for the sites where As atoms were placed: [a] through [e] are sites in the GB1 grain boundary, whereas [f] and [g] are sites in the bulk; [a′] through [f′] denote corresponding sites for GB2. Symmetry has been used to reduce the number of possible distinct As sites and site pairs. Thus using the symbol "∼" to indicate symmetry equivalence, we have for GB1: a ∼ c and d ∼ e. It follows that for GB1 the possible distinct sites for atom segregation are [a] ([c]), [b], and [d] ([e]). The distinct site pairs for dimer segregation are [a, c], [a, d], [b, c], and [d, e]. In addition, we have also studied the dimer [f, g] where two atoms are placed at nearest-neighbor sites in the bulk crystal. For GB2 we have the equivalence $b' \sim c' \sim e'$. The resulting distinct site pairs are [a′, d′], [d′, e′], [b′, c′], and [a′, c′].

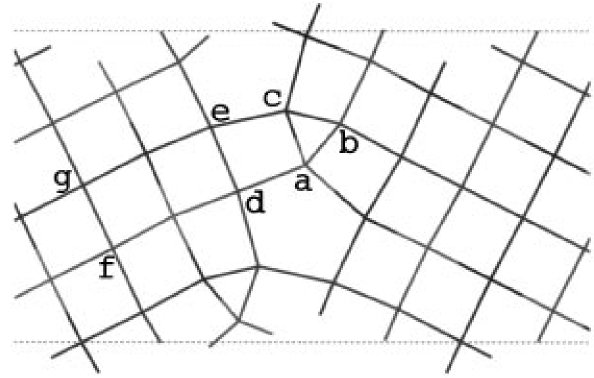

FIG. 2. 2D projection (normal to the tilt axis) of an atomically relaxed structure of the $\Sigma = 5\{310\}\langle 001\rangle$ symmetric grain boundary of Si in its ground state (GB1). In the actual 3D structure, the atoms in the bulk lie on four different planes. The letters a–g denote various sites at which segregation of isolated As atoms and As dimers are investigated. The dislocation cores comprising this grain boundary are of the pure edge type.

The results for isolated As substitutionals are shown in the top halves of Tables I and II. We find that all sites except [a] ([c]) on GB1 and [a′] on GB2 have a binding energy of ∼0.1 eV, the same value obtained for isolated

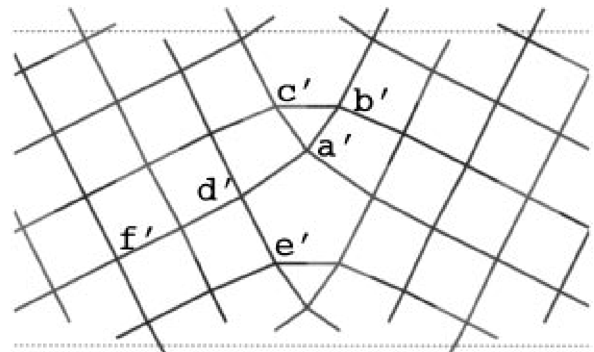

FIG. 3. Grain boundary of Fig. 2 in a metastable state (GB2) in the same projection view. The letters a′–f′ denote various sites at which segregation of isolated As atoms and As dimers are investigated. The dislocation cores comprising this grain boundary have mixed screw and edge characters.

TABLE I. Segregation energies (normalized per As atom) for isolated As atoms and As dimers placed at various sites on GB1. The equilibrium As-As distance for the dimers is also indicated. The sites are described in Fig. 2.

As site(s)	Segregation energy eV/As atom	As-As distance (Å) (dimer geometries)	As-As* distance (Å) (dimer geometries)
[f]	0.00		
[a], [c]	0.03		
[b]	0.11		
[d], [e]	0.11		
[f, g]	−0.01	2.71	4.59
[a, d]	0.10	2.71	5.20
[d, e]	0.19	2.79	4.70
[a, c]	0.20	2.89	3.76
[b, c]	0.32	3.43	3.43

As atoms in a similar boundary in Ge [8]. The smaller binding of [a] can be explained from the *similarity* of its environment, characterized by the surrounding bond-length and bond-angle distribution, to that of a bulk site [f] or [g], while an opposite effect occurs for [a′]. In all cases of isolated As substitutionals, the lattice is found to undergo only a very small relaxation, in agreement with the results of Ref. [8].

We now turn to the dimer configurations. As we noted earlier, we performed calculations with both minimal and double periodicity in the grain-boundary plane, corresponding to dimer chains and isolated dimers, respectively. The latter calculations are extremely time consuming even on the Paragon supercomputer and were therefore performed only for selected pairs of sites. We found that dimer formation in the grain boundary is energetically favored. If two As atoms are placed at neighboring substitutional sites in the bulk crystal, they repel each other seeking to achieve threefold coordination (pair [f, g] in Table I). The equilibrium As-As distance is 2.71 Å compared to a Si-Si bond length of 2.35 Å. The overall energy goes up by a tiny amount (0.01 eV per As atom) as compared with isolated substitutional atoms because of the elastic energy cost. In contrast, As dimers in the grain boundary lead to an overall lowering of the energy. The selected calculations we performed for the isolated dimers yielded net binding of order 0.05–0.2 eV/atom, indicating that the elastic energy cost in the grain boundary can be smaller than in the bulk. Dimer formation in the grain boundary is the result of *repulsion* between neighboring As atoms and occurs because this repulsion can be accommodated easier in the grain boundary than in the bulk crystal.

The results for chains of As dimers are even more dramatic and are displayed in detail in Tables I and II for the two grain-boundary structures, respectively. We see that segregation energies range from 0.1 to 0.5 eV/atom, the latter being in agreement with the measured values [1–3]. In Tables I and II, the third column contains the As-As distance in the dimer, which is to be compared with the normal Si-Si distance of 2.35 Å. The fourth column contains the As-As* distance between As atoms of neighboring dimers (dimers in neighboring supercells).

We note three classes of results: (i) Cases where the As-As* distance is significantly larger than the As-As distance, suggesting that the dimers in the chain are fairly well separated. The segregation energy is small, less than 0.2 eV/atom, comparable to that of truly isolated dimers that we discussed earlier. (ii) Cases where the As-As and As-As* distances are comparable but different (e.g., [a, c] in GB1 and [a′, c′] in GB2) where the segregation energy ranges from 0.2 to 0.5 eV/atom. (iii) A case where the As-As and As-As* distances are identical ([b, c] in GB1), corresponding to a fully ordered chain of As atoms, with an intermediate segregation energy of 0.32 eV/atom. Figure 4 displays the electronic charge density in a slice passing through the plane containing the As atoms in the [b, c] geometry of GB1. There is no significant charge

TABLE II. Segregation energies and As-As distance at various sites on GB2 (Fig. 3).

As site(s)	Segregation energy eV/As atom	As-As distance (Å) (dimer geometries)	As-As* distance (Å) (dimer geometries)
[f′]	0.00		
[b′], [c′], [e′]	0.12		
[d′]	0.13		
[a′]	0.22		
[a′, d′]	0.08	2.43	5.25
[d′, e′]	0.09	2.72	4.84
[b′, c′]	0.11	2.42	4.29
[a′, c′]	0.52	2.76	3.54

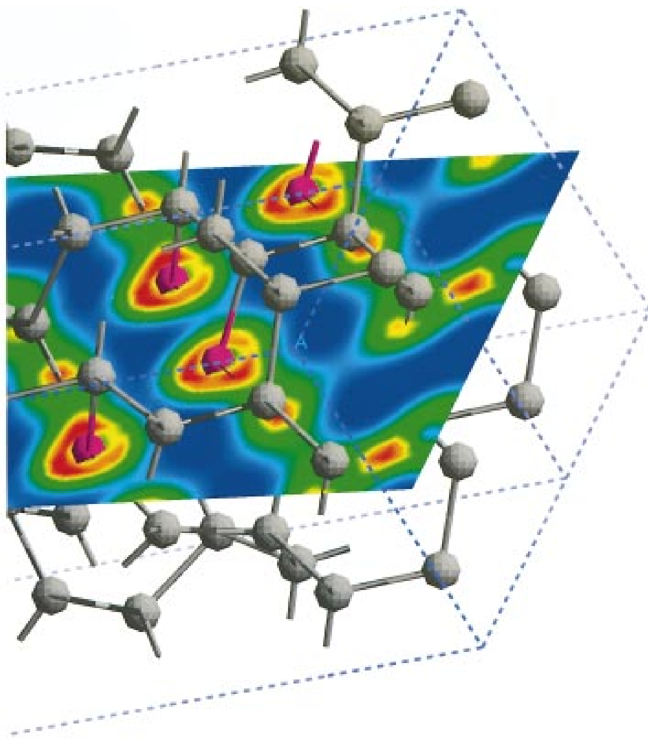

FIG. 4(color). A 2D plot of the electronic charge density on a slice passing through the perfect As chain [b, c] in GB1. The As atoms are magenta and Si atoms gray. The color scheme is red → yellow → green → light blue → deep blue for maximum to minimum charge density.

in the region between two neighboring As atoms in the chain, proving conclusively the threefold coordination of each As atom. The charge density for all other dimer configurations is qualitatively similar.

An examination of the local three-dimensional topologies corresponding to Fig. 2 and 3 suggests that the most stable dimer geometries in a chain are the ones in which one or both of the component As atoms can relax *into* the dislocation cores, where the average atomic density is lower than the crystalline bulk. Such relaxation reduces the strain in the Si backbonds, thereby yielding a larger segregation energy. It is interesting to note that the most stable chain of dimers [a′, c′] in GB2 has its component atoms on two different dislocation cores, a configuration possible only in relatively large-angle grain boundaries, while the chain of dimers [b, c] on GB1 has only one of its atoms (c) lying on a dislocation core, and could occur in any dislocation core of the perfect edge type.

Finally, it is particularly interesting to note that the highest segregation energy in GB2 is significantly larger than in GB1 and might actually drive a structural transformation. In other words, the injection of a high concentration of As into polycrystalline Si may convert a grain boundary with perfect edge dislocations into one with mixed dislocations. Similar solute-induced grain boundary transformations have long been known to occur in metals [18], but we are not aware of any prior reports in semiconductors. From the relative total energies of the two grain boundaries we estimate that the transformation from GB1 to GB2 would require a critical As concentration of ~19% in the column of the favored dimer sites. However, such a transformation involves a relative shift (sliding) of the two grains at the boundary, and the above estimate does not take into account any elastic energy cost that may be required to maintain integrity at triple junctions during the sliding process.

In summary, cooperative phenomena involving chains of threefold-coordinated As atoms or dimers result in much larger segregation energies than isolated As substitutionals. Segregation energies thus obtained are in agreement with experimental values. This provides a mechanism for As segregation that does not require the presence of steps or other defects. Chains of As dimers in mixed dislocation cores have lower energies, raising the intriguing possibility that As segregation may drive a structural transformation in grain boundaries containing pure edge dislocations.

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