Atomic Configurations and Energetics of Arsenic Impurities in a Silicon Grain Boundary

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We report direct atomic-resolution Z-contrast imaging of arsenic impurities segregated in specific atomic columns in a silicon grain boundary. Through a combination of image intensity analysis, first-principles calculations, and statistical mechanics, we establish that segregation occurs in the form of *isolated dimers.* The formation of As dimers in the boundary is shown to be favored over ordered chains by entropic considerations and kinetic constraints. The observed segregation is consistent with known solubilities. [S0031-9007(98)06523-5]

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Interfaces and grain boundaries play a critical role in determining the physical and electrical properties of complex materials and structures. Impurity segregation in interfaces and grain boundaries often alters these properties in dramatic ways. Thus, the ability to create novel materials and structures ultimately depends on a fundamental understanding of the physics of segregation, especially the bonding arrangements between impurities and host atoms. In Si, dopants such as As tend to segregate in grain boundaries in electrically inactive configurations [1–5]. The causes and nature of this segregation remain active areas of research, both for fundamental understanding and technological control.

Electron microscopy has developed into a powerful tool for atomic-resolution imaging of buried interfaces [6–10], but determination of low concentrations of impurities and their bonding has been beyond reach. Although As segregation in Si grain boundaries has been detected [11], no information could be extracted on segregation sites and bonding configurations. Atom-probe studies are sensitive to single impurity atoms [12,13], but have not yet been able to locate the specific atomic sites of the segregated species. First-principles calculations have proven to be a reliable way to determine the energies of atomic configurations in solids; but in complex materials such as grain boundaries, the theoretical determination of the true equilibrium configuration, without reliable starting configurations, remains a difficult task. Several papers recently addressed the question of impurity segregation in grain boundaries [14–16] and determined the relative energies of several configurations.

In this Letter, we combine atomic-resolution images and theoretical calculations to establish that As impurities segregate in a Si grain boundary in the form of isolated dimers [17]. The atomic-resolution Z-contrast images clearly show increased brightness in selected columns. Undoped control samples show no such extra brightness. Intensity analysis indicates that the extra brightness corresponds to approximately 2 As atoms out of the roughly 40 Si atoms in each column of the sample. Combining this result with first-principles calculations, we conclude that the extra brightness is due to the formation of isolated As dimers. This analysis is consistent with the experimentally determined As concentration, the solubility limit of As in bulk Si, and the temperature used to equilibrate the structure. Further theoretical analysis using statistical mechanics leads to the conclusion that, even though As chains [18] have been found to be a low energy configuration in Si tilt boundaries, their formation is inhibited by entropic limitations and kinetic constraints. The results suggest that the precise atomic configuration around the segregation site and the edge or screw character of the dislocation core are equally important in determining segregation energies.

The experimental studies were performed on a Si bicrystal wafer containing a 23° $\Sigma = 13$ $\{510\}$ $\langle 001 \rangle$ tilt boundary (i.e., the bicrystal contains a boundary on the $\{510\}$ plane common to the two crystals; this boundary results from a 23° rotation, about the common $\langle 001 \rangle$ direction, of one grain relative to the other). In this investigation, the boundary is viewed edge on along this $\langle 001 \rangle$ tilt axis. For the present study, samples were implanted at 450 °C with As ions (450 keV, 3×10^{16} ions/cm^2) and subsequently annealed for one week at 1000 °C followed by one week at 700 °C. An unimplanted control sample was given the same thermal treatment. Using the reported diffusivity of As in bulk Si of $\sim 2 \times 10^{-15}$ cm^2/sec at 1000 °C [1,3–5], we estimate that a ~ 0.35 μm width of the implanted layer can diffuse into the boundary. The diffusivity of As in a Si grain boundary at 1000 °C is $\sim 2 \times 10^{-10}$ cm^2/sec [19,20], thus, exposing 110 μm of boundary to the diffusing As.

Plan view samples with a $\langle 001 \rangle$ surface normal were prepared by mechanical polishing and ion milling with 1–3 keV Ar ions, then characterized by high resolution Z-contrast imaging using a VG Microscopes HB603U scanning transmission electron microscope operating at 300 kV. In this microscope, the objective lens is used to form a tightly focused electron probe (0.13 nm diameter), which is scanned across the sample. A Z-contrast image is obtained serially by detecting scattered electrons synchronously with an annular detector. The detector averages over interference effects in the scattering and leads to an image with incoherent characteristics in which each atomic column can be directly located [21]. Increasing the inner detector angle increases the fraction of thermal diffuse scattering and decreases the coherence length within a given atomic column. For our inner detector angle of 45 mrad, and a 5.43 Å atomic spacing along each column, each atom scatters incoherently [22], with a relative cross section that approaches the Rutherford Z^2 value, making composition quantification straightforward [23].

Figure 1(a) is a Z-contrast image of the unimplanted control sample as viewed along the tilt axis. The structure of this intrinsic boundary is seen to be periodic with a 0.54 nm repeat length along the tilt axis and a 1.38 nm repeat length perpendicular to the tilt axis. The grain boundary core can be described as a contiguous array of six dislocations [see Fig. 1(c)], consisting of a perfect edge dislocation (1) and two perfect mixed dislocations $(2, 3)$ arranged as a dipole followed by the same sequence $(1', 2', 3')$ mirrored across the common $\{510\}$ boundary plane. In the $\langle 001 \rangle$ projection, the grain boundary core appears to be a connected array of pentagonal and triangular arrangements of atomic columns. However, neither of these arrangements are planar; they are composed of spirals of five and three atoms, respectively, along the tilt axis.

Figure 1(b) is a Z-contrast image of this same symmetric tilt boundary doped with As, revealing periodic bright features. Within each boundary period, two of the six triangular features show a statistically significantly enhanced intensity compared with the undoped boundary. All atomic columns within the grain boundary core region show somewhat reduced intensity compared to the perfect crystal due to the effects of surface relaxation in the strain field of the dislocation cores. However, along the boundary structure there are many triangular features of similar spacing, and only in the doped boundary do one-third of them appear brighter than the others. Analyzing a total of 90 triangular features, we found the average intensity of the bright features to be $(18.4 \pm 8.2)\%$ above the average intensity of the remaining triangular features. The same analysis on the undoped boundary, given the same two-stage annealing treatment, showed no extra intensity $(0.4 \pm 6.6)\%$. We concluded that the extra intensity in the doped boundary is due to As segregation. Quantitative analysis shows that the extra intensity corresponds, on the average, to an extra 5 at. % As in each bright triangular feature. It is noteworthy that the bright features correspond to just one of the two mixed dislocation cores in the structure [see Fig. 1(c)]. We will return to this point later.

We estimate a thickness of the order of 20 nm in the area of the sample that was imaged, corresponding to approximately 40 atoms per column. Therefore, an As concentration of 5% corresponds, on the average, to six As atoms in the three columns of a bright triangle. This small number of impurity atoms explains the variability in the intensities from individual columns and the need to average over many columns to obtain a statistically significant result.

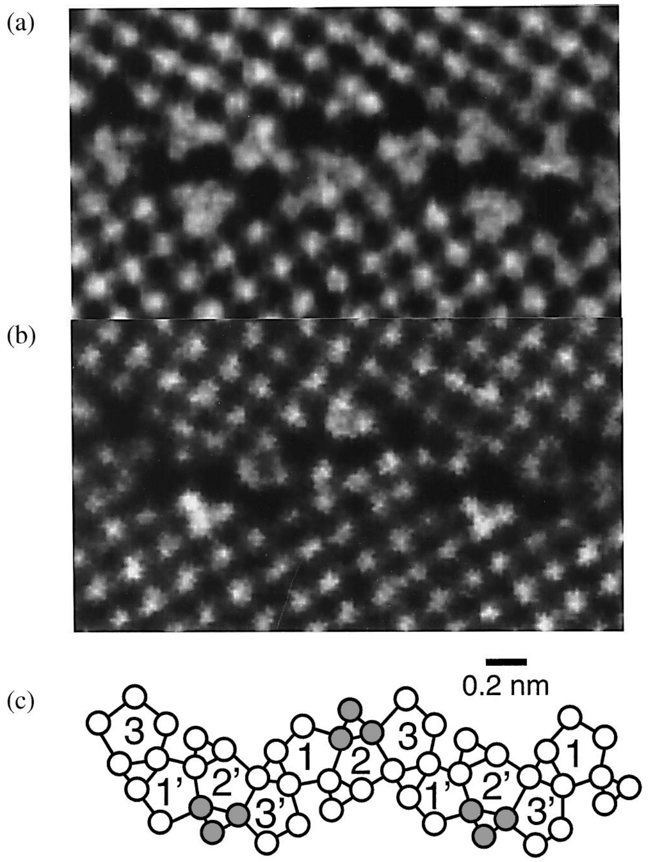

FIG. 1. (a) Z-contrast image of a symmetric 23° $\langle 001 \rangle$ tilt boundary in silicon. The dark features correspond to open channels formed in the center of the boundary dislocations in this $\langle 001 \rangle$ projection. (b) Z-contrast image of the same grain boundary after it has been doped with arsenic. The extra intensity seen at particular sites in the boundary indicates arsenic segregates to special sites in the boundary without otherwise changing the boundary structure. (c) A schematic of the projected atomic column positions obtained directly from the image. The columns associated with arsenic segregation, shown solid in the schematic, are significantly brighter than the other triangular features in the doped boundary. These bright features, which are periodically repeated every 0.69 nm, are not observed in the undoped bicrystal (a) in which all of the triangular features are seen to exhibit similar average intensities.

First-principles calculations of As segregation to the $\Sigma = 13$ $\{150\}$ $\langle 001 \rangle$ tilt grain boundary were performed using periodic supercells containing two oppositely oriented boundaries. These calculations were carried out using density functional theory with the exchange and correlation energy treated in the local density approximation and the atomic cores represented by norm-conserving pseudopotentials. The wave functions were expanded in a plane wave basis set with an energy cutoff of 150 eV, and the Brillouin zone integration was performed using two special k points. A force tolerance of 0.08 eV/Å was used for the atomic relaxations. Additional details can be found in Ref. [16].

We found that for isolated substitutional As impurities the segregation energy is ~0.1 eV at all boundary sites, in agreement with earlier work on the $\Sigma = 5$ tilt boundary [14,16]. This result clearly implies that the experimentally observed extra intensity in very specific boundary columns is not due to isolated As segregants.

In Ref. [16] it was found that As dimers have lower energy than isolated As atoms, and As chains have even lower energy. We have performed calculations for As chains in various columns of the $\Sigma = 13$ boundary, but corresponding calculations for isolated dimers were not practical because the geometry of this boundary requires a prohibitively large supercell. Nevertheless, the As chain results for the $\Sigma = 13$ boundary are very instructive. We find that As chains have larger segregation energies (0.25–0.3 eV/As atom) only in the triangular features of the projected boundary structure. In all other chain configurations, the segregation energies are ~0.1 eV/As atom, i.e., the same as isolated As atoms.

Inspection of the geometrical arrangements of the atoms in the chains reveals a very significant difference among the three inequivalent triangular features of this boundary. In triangles 1 and 3, the dimers rotate *toward* the tilt axis, reducing the dimer-dimer separation and forming chains. Rotation of the dimers *toward* the tilt axis reflects interdimer *attraction*. In the case of the $\Sigma = 5$ boundary [16], it was found that As chains in certain column pairs have much larger segregation energy per As atom than do isolated dimers in the same columns. Examination of the geometry in that case reveals that the extra binding in the chains is indeed accompanied by a rotation of the dimers toward the tilt axis. In contrast, the dimers in triangle 2 rotate *away from* the tilt axis, increasing the dimer-dimer separation and indicating interdimer *repulsion*. Even though there is no parallel behavior in any columns of the $\Sigma = 5$ boundary, we can safely conclude that in triangle 2 the calculated segregation energy for chains is entirely due to dimer formation. In fact, isolated dimers in triangle 2 are likely to have even larger segregation energies than those obtained for full As chains. We conclude that the observed preference for dimer formation in only triangle 2 is a result of the local geometry of the dislocation cores that constitute the grain boundary. In these sites, As atoms can pair without the need to form complete As dimer chains.

Finally, we present a thermodynamic analysis that shows that entropic considerations favor the formation of dimers as opposed to longer chains. By maximizing the partition function for an equilibrium system consisting of As atoms, dimers, trimers, tetramers, etc., the average concentration of As i-mers (where $i = 1$ means isolated As atoms) is given in the dilute limit by

$$n_i = \left\{ \frac{n_B}{1 - n_B} \exp(\Delta_i / k_B T) \right\}^i . \tag{1}$$

Here n_B is the equilibrium As concentration in the bulk crystal adjacent to the grain boundary, Δ_i is the segregation energy of an "i"-mer per As atom, k_B is the Boltzmann constant, and T is the final annealing temperature. The total As concentration in any triangular feature is obtained by summing the values of n_i. Figure 2 shows this concentration in triangle 2 or 2′ (denoted as bright triangles) and in triangles 1, 1′, 3, or 3′ (denoted as normal triangles) as a function of the bulk As concentration (n_B) at 700 °C. Following our foregoing analysis of the segregation energies for single As atoms, isolated dimers, and dimer chains, we used $\Delta_1 = 0.1$ eV for all sites, $\Delta_2 = 0.3$ eV for bright triangles, and $\Delta_2 = 0.1$ eV for normal triangles; Δ_3 and Δ_4 were taken as weighted averages of the corresponding values of Δ_1, Δ_2, and that for the chain [24]. The contribution from chains of more than four As atoms is insignificant in the dilute limit. It follows from Fig. 2 that the experimental estimate of 5% excess As atoms in the bright triangles corresponds to less than 1.5% of As in the normal triangles and 0.5% of As in the bulk. This estimate of the bulk concentration necessary to produce the observed bright and normal triangles is in close agreement with the maximum electrically active concentration of As in bulk crystalline Si, which is ~0.6% [12–16]. It is important to note that, in this case, the As contribution in Fig. 2 comes from isolated atoms and dimers only, with contribution from larger clusters being insignificant. We note that this analysis suggests that the As concentration in the samples is below the threshold for detection by either electron energy loss spectroscopy or energy dispersive spectroscopy with a beam spot that encompasses several columns. The best available microscope for such measurements (the VG Microscopes HB501UX) cannot resolve individual columns, and cannot, therefore, provide additional verification of the As distribution in the grain boundary.

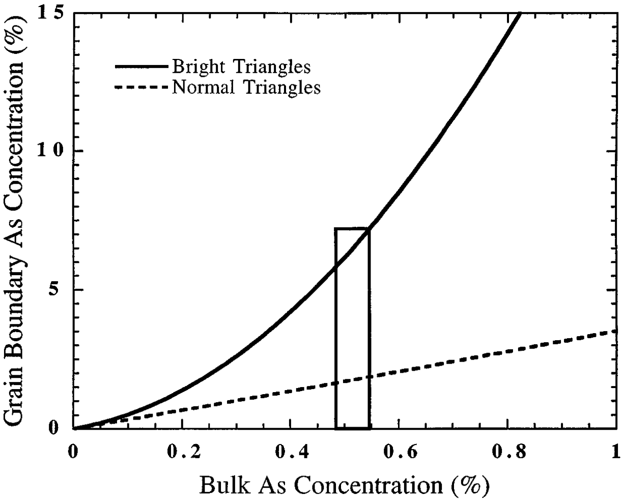

FIG. 2. Plot of the As concentration expected in particular sites in the grain boundary as a function of the bulk arsenic concentration at 700 °C. The vertical rectangle in the middle of the graph highlights the region corresponding to our experimentally measured 5% excess As concentration in the bright triangular features (2, 2′) relative to that in the normal triangular features (1, 1′, 3, 3′).

In addition to the entropic considerations, we note that formation of chains is inhibited by kinetic constraints: A chain must be built up by the successive addition of *dimers*. For example, a third atom does not bind to an existing dimer because it cannot, by itself, acquire threefold coordination, which is the origin of the binding energy. Dimers are unlikely to diffuse easily, and isolated As atoms are unlikely to arrive simultaneously. Thus, chain formation is unlikely.

In summary, we have presented Z-contrast images of a Si bicrystal in which As impurities were incorporated and annealed. In contrast with undoped samples, these micrographs show statistically significant excess brightness in selected columns of the grain boundary. Theoretical calculations and analyses find that these are the columns where As atoms segregate preferentially in the form of dimers. Our synergistic application of experiment and theory provides a complex, but remarkably consistent, atomic-scale picture of segregation, highlighting how the precise atomic configurations of host atoms and impurities determine important segregation phenomena.

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