Segregation mechanism of arsenic dopants at grain boundaries in silicon

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**ABSTRACT**

Three-dimensional distribution of arsenic (As) dopants at \(\Sigma 3\{111\}, \Sigma 9\{221\}, \Sigma 9\{114\}, \) and \(\Sigma 9\{111\}/\{115\}\) grain boundaries (GBs) in silicon (Si) is examined by correlative analytical methods using atom probe tomography (APT) combined with low-temperature focused ion beam (LT-FIB), scanning transmission electron microscopy, and ab initio calculations. \(\Sigma 3\{111\}\) GBs, consisting of only 6-membered rings with small bond distortions, do not exhibit an apparent As segregation. Meanwhile, it is hypothesized that As atoms would segregate in 5-membered rings in the other GBs via anisotropic bond distortions spontaneously introduced so as to lower the donor level, as Jahn-Teller distortions. In addition, APT combined with LT-FIB suggests preferential As segregation around stretched \(\langle 1\bar{1}0\rangle\) GBs reconstructed in \(\Sigma 9\{114\}\) and \(\Sigma 9\{111\}/\{115\}\) GBs, that are inevitably introduced in the \(\langle 1\bar{1}0\rangle\) tilt GBs with the tilt angle larger than \(70.5^\circ\). It is hypothesized that As atoms would form As dimers at stretched \(\langle 1\bar{1}0\rangle\) GBs and the adjacent \(\langle 1\bar{1}1\rangle\) bonds, due to the tendency of As with five valence electrons to form a three-coordinated configuration, which is efficiently attained by an As dimer of a long length. This work provides important insights into As segregation at GBs; it is mainly determined by electronic interactions depending on the characteristics of valence electrons of As atoms, as well as on local bond distortions at GBs, via anisotropic bond distortions and dimerization.

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1. Introduction

Silicon (Si) crystals in most electronic devices, including field effect transistors (FETs) and sensors, are doped with III or V group elemental impurities in order to achieve specific electrical properties. The characteristic size of the devices is scaling down over the past decades, and it is now below a few tens of nanometres, by using Si nanostructures, such as nanowires [1–3] and nano-fins [4–6].

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At this nanometre scale, three-dimensional (3D) distribution of dopant atoms has an important impact on the reliability and performance of individual devices, since a localized dopant fluctuation is increasingly affecting the electrical characteristics [7]. For example, inhomogeneous distribution of dopant atoms can be introduced in Si gates of nanometre-scale FETs via the segregation at structural defects such as grain boundaries (GBs) and interfaces, affecting device performance primarily through fluctuations in threshold voltage and channel current density of the FETs [8–11]. Similar structural defects can be introduced into Si nanowires during the crystal growth and device fabrication processes [12–14]. Therefore, in order to develop advanced Si nano-devices with a high reliability, we need a fundamental understanding of the segregation behaviour of dopant atoms [15].

Arsenic (As) atoms, as important n-type dopants in Si, are frequently used for Si nano-devices due to their excellent physical properties, such as high solubility ($1.8 \times 10^{21} \text{ cm}^{-3}$) needed for low resistivity [16], low diffusivity (about 1/10 in comparison with the other important n-type dopants of phosphorus atoms) used for diffused junctions and buried layers that can resist annealing processes [17], and the atomic radius similar to Si that do not induce large strains by doping [18]. Meanwhile, they can diffuse in GBs with a diffusivity four orders of magnitude higher than the single-crystal value [19], and therefore they preferentially segregate at GBs, rather than distribute homogeneously in grains, as visualized in polycrystalline Si by scanning transmission electron microscopy (STEM) [20] and atom probe tomography (APT) [8–11,21–23]. Using the visual data, the number of segregated As atoms per unit GB area is estimated [9,22,23], and the interaction energy between As and GBs (in a range of 0.28–0.65 eV) is discussed [9,20]. Those results are obtained from the GBs of which the GB character is unknown, in nanometer-scale FETs that are irradiated with As ions and then annealed at high temperatures. The segregation mechanism is, therefore, still uncertain because the diffusion and interaction of As atoms would depend on the GB structure and defects in the irradiated materials [24,25]. Recently, the interaction energy of As atoms is examined theoretically for four kinds of coincidence site lattice (CSL) GBs with the $\langle 110 \rangle$ tilt axis, which can usually account for over 50% of the total GB population in the standard polycrystalline Si grown by the cast-growth techniques [26,27], and the preferential segregation sites at those GBs are discussed in terms of GB characteristics (i.e., the intrinsic lattice distortion and dangling/extra bonds introducing deep levels) and the impurity properties [15]. The ab initio calculation predicts that As segregation is mainly caused by the deep levels due to dangling bonds at GBs, whereas it is irrespective of lattice distortions at GBs [15].

In the present work, however, we have experimentally shown that As atoms can segregate even at the GBs free from deep levels. We have systematically examined, by correlative analytical methods using APT combined with STEM and ab initio calculations, the segregation ability of four kinds of CSL GBs with the $\langle 110 \rangle$ tilt axis, i.e., $\Sigma 3[111]$ and $\Sigma 9[221]$ GBs as the typical GBs free from dangling bonds, and $\Sigma 9[114]$ and $\Sigma 9[111]/[115]$ GBs with the stretched $\langle 110 \rangle$ bonds that would contain some amount of dangling bonds. Preferential segregation sites, as well as the segregation mechanism, for the CSL GBs are discussed with an assistance of ab initio calculations.

2. Experimental procedure

A Si ingot doped with As atoms (about 0.15 at. %), free from cellular structures [28], was grown by the Czochralski (CZ) method, and coherent $\Sigma 3[111]$ GBs were intentionally introduced by applying thermal shocks in the growth process [29]. Those GBs were free from structural defects on the GB planes [29], unlike the non-coherent $\Sigma 3[111]$ GBs in cast-Si, on which extrinsic defects, such as facet junctions [30,31] and extrinsic GB dislocations [32–34], were frequently introduced [35]. Second-order twins of $\Sigma 9[221]$, $\Sigma 9[114]$ and $\Sigma 9[111]/[115]$ GBs free from extrinsic defects were spontaneously formed during the CZ growth [36], via interactions of $\Sigma 3[111]$ GBs [37,38]. The structural analysis of the GBs is summarized in the Supplemental material and references in it [77–85].

Needles for APT with the GBs free from extrinsic defects were cut with a focused-ion-beam (FIB) system (Helios NanoLab600i, FEI, Japan). Unless otherwise noted, FIB milling was performed at RT (RT-FIB). 3D distribution of As atoms at the GBs was examined by APT with a local electrode atom probe (LEAP4000X HR, Ametek, Japan), and the 3D atomic maps were reconstructed with the Integrated Visualization and Analysis Software (IVAS) protocol [39]. The detection limit for impurity atoms was 0.01 at. % with the spatial resolution less than 0.5 nm [40]. The GB location in a reconstructed 3D As map was determined with pole patterns in two-dimensional Si density maps [29].

In order to examine the stable structure model of each GB, a supercell with the GB was constructed with the corresponding HAADF-STEM data, and it was relaxed by ab initio calculations with the projector augmented wave method implemented in the Vienna
Ab initio Simulation Package (VASP) code [41–43]. The electrons of the 3s and 3p orbitals for Si and 4s and 4p orbitals for As were treated as valence electrons. Plane waves with an energy cutoff of 500 eV were used to expand the wave functions. The exchange–correlation energy was calculated using a revised version of the generalized gradient approximation of Perdew–Burke–Ernzerhof (GGA-PBEsol) [44]. The atomic positions were optimized until the force on each atom was less than 0.01 eV/Å. The energy

![Figure 1. Projected 3D As maps viewed parallel to the GBs for (a) Σ3{111}, (b) Σ9{221}, (c) Σ9{114}, and (d) Σ9{111}/115] GBs. The pair of dotted lines in each figure indicates the exact GB location. The inset in each figure shows the As concentration profile across the GB plane. The pair of solid lines in each profile indicates the background As concentration of 0.15 at.%. (e) Number of As atoms segregated at GBs $\Gamma_{As}$ plotted as a function of the GB energy $\gamma_{GB}$.}
convergence criterion was set to $10^{-6}$ eV. For the diamond structure of Si, $6 \times 6 \times 6$ and $18 \times 18 \times 18$ k-point meshes were used for structural optimization and analysis of density of states, respectively.

3. Results and discussion

3.1. Segregation abilities depending on GB structures

$\Sigma 3$[111] GBs do not exhibit an apparent As segregation (Figure 1(a)), indicating a small segregation ability for As atoms, such as boron, phosphorus, carbon, and oxygen atoms [29,35]. Meanwhile, As atoms segregate at the GBs except for $\Sigma 3$[111] GBs (Figure 1(b–d)). One-dimensional (1D) profiles of proxigram concentration for As atoms across the GBs, obtained by calculating the As concentration in disks of $0.5 \times 80 \times 80$ nm$^2$ at different distances from each GB plane, certainly show the GB segregation. No As cluster is observed at the GBs, unlike at stacking faults in heavily As-doped Si [45]. As atoms segregate within a range of about 5 nm across the GB planes, and this segregation thickness is much larger than the thickness assumed for equilibrium segregation at GBs (typically less than a few nm [8]). One possible origin of this large thickness is local magnification effects that occur during APT analyses [46]. Since As has a higher evaporation field than Si [47], the evaporation of an As segregation layer may form a protrusion of As atoms during APT analysis, changing the local curvature at the specimen surface. This causes a locally higher magnification (i.e., a defocusing effect), and thus the corresponding increase in the apparent thickness of the GB segregation layer [46]. This apparent thickness also depends on the angle between the GB and the tip axis, due to the difference between the depth and lateral resolutions [48]. Another possible origin is the FIB used for the preparation of APT specimens [49]. Since the temperature near the location irradiated with a FIB would increase locally, the diffusivity of As atoms would be enhanced under the irradiation. Also, As diffusivity may be enhanced by transient enhanced effects [24,25] due to point defects introduced during FIB processes, as well as by recombination-enhanced effects [50] under the irradiation of a high-energy FIB. As a result, those two effects lead to a spread of segregated As atoms, as well as to an underestimate of the peak concentration. We, therefore, discuss the Gibbbs interfacial excess for As atoms $I_{\text{seg}}$, because it is not biased as it is defined as the excess number of As atoms per unit GB area [51]. The $I_{\text{seg}}$ estimated for each GB is summarized in Figure 1(e) as a function of the GB energy $\gamma_{\text{GB}}$. Considering the detection limit of 0.01 at % expected for GB segregation in our experiments [40], $I_{\text{As}}$ would increase superlinearly with increasing $\gamma_{\text{GB}}$. The segregation characteristic for As dopants is, therefore, different from that for neutral impurity atoms, such as oxygen [36,52] and carbon [53,54], in which the number of segregating atoms would exhibits a linear correlation with $\gamma_{\text{GB}}$ via elastic interactions [36].

3.2. Segregation sites at $\Sigma 9$[221] GBs

Isolated As dopants in Si crystals would locate at the lattice points, as substitutional atoms. The average As-Si bond length in bulk Si, estimated to be 0.241 nm [55] and 0.244 nm [56], is about 3% longer in comparison with the Si-Si bond length in bulk Si (= 0.235 nm), inducing bond distortions. In addition, the Si-Si bonds near a GB plane are distorted even before As segregation, depending on the GB structure. In order to discuss the impact of the distortions on As segregation, we estimate the segregation energy $\gamma_{\text{seg}}$ of $\Sigma 9$[221] GB models with different supercell size by ab initio calculations. We define the energy $\gamma_{\text{seg}}$ as the difference between the total energy of the supercell in which an As atom locates in a GB site (in one of the lattice sites of nos. 1 to 16 in Figure 2(a)) and that in the bulk region. In order to estimate the latter energy, we choose the supercell in which an As atom locates in the site 18 in Figure 2(a), since the site is the farthest from the GB plane (about 0.8 nm) and the bond distortions at the site are negligible before As substitution; i.e., the Si-Si bond stretch before As substitution $\Delta S$, defined as the difference between the Si-Si bond length before As substitution and the Si-Si bond length in bulk Si of 0.235 nm, is close to zero (within a narrow range of $-8\times 10^{-4}$ to $+7\times 10^{-5}$ nm) for all bonds at the site (Figure 2(b)). As shown in Figure 2(c), each $\gamma_{\text{seg}}$ decreases with increasing the supercell length along the tilt axis of [110], and they almost converge when the length is 1.14 nm. This result means that bond distortions due to a substitutional As atom extend to a distance as long as 0.6 nm. We also confirm that both the atomic arrangement and the electronic structure do not change so much for larger models. The converged $\gamma_{\text{seg}}$ at the lattice sites nearby the site 18 are close to zero, showing that the site would be far enough away from the GB planes, and therefore, the site is considered to locate in the bulk region. The converged $\gamma_{\text{seg}}$ at the sites 1, 2, 3, 5, and 6 are apparently negative (lower than about $-0.1$ eV), indicating a significant segregation ability of $\Sigma 9$[221] GBs. It is interesting to note that all the segregation sites exist on 5-membered rings in the GB model.

According to an ab initio local stress calculation [57], before As segregation, the site 6 with the lowest $\gamma_{\text{seg}}$ of $-0.15$ eV is under the highest compressive hydrostatic stress (about $-3.5$ GPa), due to short Si-Si bonds (see the
site 6 in Figure 2(b)), while the site 8 with the highest $\gamma_{seg}$ of +0.06 eV is under the highest tensile one (about +2.0 GPa) in $\Sigma_9[221]$ GBs, due to long Si-Si bonds (see the site 8 in Figure 2(b)). Therefore, the origin of the As segregation is not due to elastic interactions that can reduce local hydrostatic stresses, since As atoms at Si lattice sites would induce compressive hydrostatic stresses due to their long covalent bonds [55,56]. In order to discuss electronic interactions of As atoms with $\Sigma_9[221]$ GBs, we examine the energy levels due to As atoms at the sites 6 and 8 by ab initio calculations (Figure 2(d)). The donor level at the site 6 is lowered by about 0.15 eV in comparison with the bulk region (at the site 18) at which the donor level locates just below the Fermi level $E_F$. The energy lowering of 0.15 eV is identical to the segregation energy at the site. This is consistent with segregation models that the binding energy of As atoms at $\Sigma_5[310]$ [58] and $\Sigma_3[111]$ [59] GBs is increased via the interaction with local energy levels generated at the GBs. Meanwhile, the donor level at the site 8 would be raised by about 0.2 eV, and the partial density of state (PDOS) at $E_F$ is significantly lowered in comparison with at the
bulk region. These results indicate that the As segregation is determined by the localization of donor electrons via electronic interactions.

Here, we discuss the energy lowering for As segregation in terms of bond distortions. When a lattice site is substituted by an As atom, each As-Si bond is longer than the Si-Si bond before the substitution. The As-Si bond stretch after As substitution $\Delta_{\text{As}}$, defined as the difference between the As-Si bond length after As substitution and the As-Si bond length in bulk Si (~ 0.243 nm [55,56]), depends on As segregation sites (Figure 2(b)). For the lattice sites at which the converged $\gamma_{\text{seg}}$ are almost zero, i.e. at the sites 4 and 9–16, $\Delta_{\text{As}}$ and $\Delta_{\text{Si}}$ have almost the same evolution tendency versus As segregation sites. When the scale for $\Delta_{\text{As}}$ is reduced by 20% with respect to the scale for $\Delta_{\text{Si}}$, the $\Delta_{\text{As}}$ for an As-Si bond is almost equal to the $\Delta_{\text{Si}}$ for the corresponding Si-Si bond (see the sites 4 and 9–16 in Figure 2(b)). Therefore, $\Delta_{\text{As}} \approx 1.2\Delta_{\text{Si}}$ for all bonds at these sites, and the equilibrium As-Si bond length $\Delta_{\text{eq}}$ can be defined as $\Delta_{\text{eq}} \approx 0.243 \text{ nm} + 1.2\Delta_{\text{Si}}$. This indicates isotropic bond stretches by As substitution, inducing hydrostatic strains that would not influence donor levels. Meanwhile, for the As segregation sites at which the converged $\gamma_{\text{seg}}$ is lower than about ~0.1 eV, i.e. at the sites 1, 2, 3, 5 and 6, the As-Si bonds in a 5-membered ring at each site are much shorter than $\Delta_{\text{eq}}$ and the remaining As-Si bond is longer than $\Delta_{\text{eq}}$; two and three As-Si bonds in a 5-membered ring are, respectively, shorter at the site 3 and the sites 1, 2, 5, and 6 (as shown with green marks in Figure 2(b)). Due to those anisotropic bond shrinking, tensile strains nearly along (100) or $\langle111\rangle$ would be induced. Ab initio calculations predict the decrease in electron effective masses by such anisotropic strains [60,61], inducing the lowering of donor levels. On the contrary, for the sites 7 and 8 at which the converged $\gamma_{\text{seg}}$ is positive, the three As-Si bonds in a 7-membered ring at each site are longer than $\Delta_{\text{eq}}$ (as shown with orange marks in Figure 2(b)) and the remaining As-Si bond is shorter than $\Delta_{\text{eq}}$, inducing the heightening of donor levels due to compressive strains nearly along $\langle111\rangle$. We hypothesize that As atoms would prefer to segregate at 5-membered rings via anisotropic bond distortions spontaneously introduced so as to lower the donor level, as Jahn-Teller distortions, even when the sites are unfavourable to segregate from an elastic point of view. Similar segregation characteristics can be observed for other donors such as phosphorus [15,59,62], antimony [45] and sodium [63].

### 3.3 Segregation sites at $\Sigma 9(114)$ GBs and $\Sigma 9(111)/\langle115\rangle$ GBs

Considering the number of 5-membered rings per unit GB structure for $\Sigma 9(114)$ and $\Sigma 9(111)/\langle115\rangle$ GBs (=3 rings), their high segregation abilities cannot be explained by the anisotropic bond distortion model discussed in Section 3.2. In order to discuss the segregation sites for As atoms in $\Sigma 9(114)$ GBs, 1D profile of As

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**Figure 3.** (a) As concentration profiles across a $\Sigma 9(114)$ GB obtained with APT specimens fabricated by (a) LT-FIB and (b) RT-FIB, overlaid on the corresponding HAADF-STEM image of the GB. The pair of solid lines in each profile indicates the background As concentration of 0.15 at %. 
concentration across the GBs is examined with a higher spatial resolution by using an APT specimen fabricated by FIB milling operated at a low temperature of −150°C (LT-FIB) [49]. The segregation thickness for the LT-FIB specimen, estimated to be 3 nm, is much narrower than for RT-FIB specimens, while the Gibbsian interfacial excess for the LT-FIB specimen is almost the same as for RT-FIB specimens (Figure 3). This result shows that the compositional modification at the GBs due to FIB irradiation can be suppressed by using LT-FIB technique, as reported [49,64,65]. Therefore, the concentration profile obtained by LT-FIB would significantly reflect the distribution of segregation sites, even though the impact of local magnification effects, about 0.5 nm in the segregation thickness [65], still remains.

Figure 3(a) shows that the 1D profile of As concentration peaks slightly off the GB plane, similar to the 1D profile of oxygen concentration [65]. Comparing the 1D profile with the atomic arrangement in the GB revealed by HAADF-STEM (shown in Figure 3), as well as with the distribution of atomic strains at the GB estimated by *ab initio* local stress calculations [57], it is hypothesized that a number of As atoms would segregate nearby the single atomic columns composed of the longest (1T0) reconstructed bonds, like oxygen segregation.

One possible origin of their high ability is As dimers proposed in Σ13{510} (100) tilt GBs by Chisholm [66] that would be originated from the tendency of As with five valence electrons to form a three-coordinated configuration so as to accommodate an excess electron in the dangling bond, which is efficiently attained by an As dimer of a long enough length without formation of additional Si dangling bonds [67]. Potential pairs of atomic sites for the formation of As dimers are the long Si-Si bonds existing around the longest (1T0) reconstructed bonds that are not introduced in Σ3{111} and Σ9{221} GBs, as suggested by APT combined with LT-FIB (Figure 3). We, therefore, examine the formation energy of As dimers γdimer by *ab initio* calculations, to discuss the potential formation of As dimers.

We first examine the γdimer in bulk Si with a single crystalline supercell with the supercell size of 2.72 × 2.72 × 2.72 nm³ (with 1000 atoms) that would be large enough to produce well converged results. We define the γdimer, as the difference between the total energy of the supercell in which two As atoms are set at a nearest neighbour sites and at a farthest ones separated by 2.35 nm. The γdimer is estimated to be a positive value of +0.33 eV, indicating an instability of As dimers in bulk Si; i.e. As dimers would be hardly generated in bulk Si.

We next estimate the γdimer around the longest (1T0) bonds in Σ9{411} GBs with the supercell shown in Figure 4. When the GBs are free from As atoms, a longest (1T0) bond and the adjacent (111) bonds, indicated with the numbers in Figure 4, are 0.7 to 4.6% longer in comparison with the Si-Si bond in bulk Si of 0.235 nm. We estimate the γdimer at each long bond as the difference between the total energy of the supercell in which two As atoms locate at both ends of the long bond and at the sites in bulk region shown in the orange squares in Figure 4. In periodic arrays of the supercells, the distance between the nearest As dimers (about 1.3 nm) and the nearest neighbour distance between isolated As atoms in bulk region (1.5 nm) would be far enough to relax bond distortions due to substitutional As atoms, extending within a distance of about 0.6 nm as discussed in Section 3.2. All the γdimer estimated for a longest (1T0) bond and for the adjacent (111) bonds are negative (Table 1), and the lowest γdimer of −0.497 eV is quite lower in comparison with the lowest Yseg in the anisotropic bond distortion model in Figure 2(c). Similar results are obtained around other stretched (1T0) bonds indicated with ‘A’ and ‘B’ in Figure 4, even though the γdimer are not so low and some of them are even positive (+0.030 to −0.271 eV around the A site, and −0.121 to −0.173 eV around the B site). Stretched (1T0) bonds are also introduced in Σ9{111}/(115) GBs (see Figure S2A(d) in the Supplemental material). Therefore, low γdimer at the long bonds around stretched (1T0) bonds, which are not reconstructed in Σ3{111} and Σ9{221} GBs, can explain well high segregation abilities of Σ9{411} and Σ9 (111)/[115] GBs.

Here, we consider the formation process of As dimers. All the dimers in Table 1 locate either end of a longest (1T0) bond in Figure 4. We examine the

![Figure 4](image-url)
Table 1. Formation energy of As dimers $\gamma_{\text{dimer}}$ around the longest $\langle 1\overline{1}0 \rangle$ bonds in $\Sigma 9 \{114\}$ GBs shown in Figure 4.

| As-As bond | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|------------|---|---|---|---|---|---|---|
| $\gamma_{\text{dimer}}$ [eV] | −0.314 | −0.053 | −0.162 | −0.213 | −0.261 | −0.465 | −0.497 |

Segregation energy of isolated As atoms $\gamma_{\text{seg}}$ at each end of the $\langle 1\overline{1}0 \rangle$ bond by *ab initio* calculations, and it is estimated to be positive values of +0.05 eV and +0.02 eV. This is consistent with the anisotropic bond distortion model discussed in Section 3.2, since both sites are under tensile hydrostatic stresses [36]. A positive value of $\gamma_{\text{seg}}$ indicates a difficulty forming an As dimer at a long bond around the $\langle 1\overline{1}0 \rangle$ bond so that isolated As atoms occupy both ends of the long bond one by one. Therefore, it is hypothesized that As dimers would not be formed via the migration of isolated As atoms, but would be formed directly during the Cz growth. According to the model, once As dimers are dissociated in some way, they would remain as isolated As atoms without forming As dimers. In order to confirm the hypothesis, we examine the segregation ability for As atoms in the $\Sigma 9 \{114\}$ and $\Sigma 9 \{111\}/\{115\}$ GBs annealed at 1000°C for 90 min. Considering the diffusion constant for As at 1000°C (about $10^{-15}$ cm$^2$/s [68]), As atoms segregating at the GBs would diffuse out from the GBs. Those diffusing As atoms would be isolated, since our *ab initio* calculations indicate an instability of As dimers in bulk Si. The As excesses at the annealed GBs are drastically decreased (Figure 5(a,b)). This result is consistent with the hypothesis that As dimers are hardly formed via the migration of isolated As atoms, as well as with the As dimer model in the initial GBs with high As densities in Figure 1.

Unfortunately, As dimers are hardly detectable by APT because of its spatial resolution that is larger than the As-As separation in As dimers (about 0.3 nm). Also, even though an As atom in bulk Si is detectable by STEM with a (001) incidence [69], this technique is inapplicable to the $\langle 1\overline{1}0 \rangle$ tilt GBs. Nevertheless, *ab initio* calculations reveal that the longest $\langle 1\overline{1}0 \rangle$ bonds would have a high segregation ability for As dimers, which is consistent with the high-resolution 1D As profile obtained by LT-FIB (Figure 3(a)), and the impossible formation of As dimers via the migration of isolated As atoms, which is consistent with the APT data after annealing (Figure 5(a)). These results strongly suggest the existence of As dimers around the longest $\langle 1\overline{1}0 \rangle$ bonds. Since $\langle 1\overline{1}0 \rangle$ bonds are inevitably reconstructed in the $\langle 1\overline{1}0 \rangle$ tilt GBs with the tilt angle

Figure 5. Projected 3D As maps viewed parallel to the GBs for (a) $\Sigma 9 \{114\}$ and (b) $\Sigma 9 \{111\}/\{115\}$ GBs after 1000°C annealing for 90 min. The pair of dotted lines in each figure indicates the exact GB location. The inset in each figure shows the As concentration profile across the GB plane. The pair of solid lines in each profile indicates the background As concentration of 0.15 at.%. (c) Number of As atoms segregated at GBs $\Gamma_{\text{As}}$ as a function of the number of 5-membered rings per unit GB length.
The segregation ability of the GBs would be enhanced via the preferential formation of As dimers. Figure 1(e) infers that the segregation ability due to the electronic dimerization effect would increase with \(\gamma_{GB}\).

According to our hypothesis, As atoms at the annealed \(\Sigma 9\{114\}\) and \(\Sigma 9\{111\}/\{115\}\) GBs in Figure 5(a) and 5(b) would be isolated, like As atoms at \(\Sigma 9\{221\}\) GBs. It is interesting to note that, the As excesses for those GBs increase with the number of 5-membered rings per unit GB length (Figure 5(c)). Therefore, as discussed in Section 3.2, As atoms would prefer to segregate at 5-membered rings via anisotropic bond distortions when they are isolated.

Finally, we briefly discuss another possible As segregation at \(\Sigma 9\{411\}\) and \(\Sigma 9\{111\}/\{115\}\) GBs. One potential origin of As segregation is dangling bonds. It is theoretically expected that defect sites with dangling bond are remarkably attractive for As segregation, as a result of the nature of group-V elements to be three-coordinated rather than four-coordinated [15]. During the crystal growth, dangling bonds can be introduced in the single atomic columns composed of \(\langle 1T0\rangle\) reconstructed bonds when the periodicity of the reconstruction is accidentally disturbed, like the reconstructed defects along dislocation lines so-called antiphase defects, phase-switching defects or solitons [71, 72]. Thus, some amount of dangling bonds would be generated in \(\Sigma 9\{411\}\) and \(\Sigma 9\{111\}/\{115\}\) GBs. A dangling bond is eliminated if the lattice site with the dangling bond is substituted by an As atom. Therefore, the initial density of dangling bonds is hardly examined in As-doped Si crystals. In order to discuss the initial density at \(\Sigma 9\{411\}\) GBs, a pure \(\Sigma 9\{411\}\) GB free from As segregation, introduced intentionally in an undoped Si crystal [40], is examined by PL imaging. The GB free from extrinsic structural defects is not recognized in the PL images, suggesting a low density of deep levels due to dangling bonds in the GB, that would act as non-radiative recombination centres, as well as a high formation energy of the defect. We tentatively conclude that the dangling bonds in \(\Sigma 9\{411\}\) and \(\Sigma 9\{111\}/\{115\}\) GBs would have less of an impact on As segregation due to their low density. The other potential origin of As segregation is junctions of nano-facets formed intrinsically in \(\Sigma 9\{111\}/\{115\}\) GBs [73]. They can affect the segregation ability like macroscopic facet junctions [31, 32], although the impact would not be so large [32]. It is difficult to examine experimentally the As atoms segregating at each junction, since the separation between the neighbouring junctions (about 1 nm) is close to the spatial resolution of APT (about 0.5 nm [40]). Further study such as large-scale ab initio calculations would be needed to determine the impacts of the intrinsic GB defects.

### 3.4. Segregation sites at \(\Sigma 3\{111\}\) GBs

Here, we discuss a low segregation ability of \(\Sigma 3\{111\}\) GBs, consisting of only 6-membered rings with small bond distortions. It is reported that As atoms can segregate at stacking faults (SFs) bound by dislocations [74], including an atomistic structure similar to \(\Sigma 3\{111\}\) GBs [75]. The As segregation is attributed to the electronic structure changes near the band gaps rather than to the elastic interactions [59], similar to the segregation mechanism discussed in Section 3.2, and the segregation energy due to the electronic interaction is estimated to be 0.07 eV [59, 76]. Comparing the atomistic structure between SFs and \(\Sigma 3\{111\}\) GBs, we can estimate the segregation energy for \(\Sigma 3\{111\}\) GBs to be about a half of the segregation energy for SFs (about 0.03 eV). This low segregation energy, presumably due to small bond distortions, is comparable to the thermal energy at RT, suggesting an infrequent As segregation at the GBs during the crystal growth at higher temperatures. Therefore, the number of As atoms segregated at \(\Sigma 3\{111\}\) GBs would be low in as-grown crystals, as observed in Figure 1(a), even though the segregation ability is expected to be a small finite value.

### 4. Conclusion

Segregation behaviour of As dopants at \(\Sigma 3\{111\}\), \(\Sigma 9\{221\}\), \(\Sigma 9\{114\}\) and \(\Sigma 9\{111\}/\{115\}\) GBs is examined by correlative analytical methods using APT combined with LT-FIB, HAADF-STEM and ab initio calculations.

1. \(\Sigma 3\{111\}\) GBs, consisting of only 6-membered rings with small bond distortions, do not exhibit an apparent As segregation, even though the segregation ability would be a small finite value.
2. As atoms segregate at \(\Sigma 9\{221\}\) GBs in which no defect level exists, while bond distortions exist. It is hypothesized that As atoms would prefer to segregate at 5-membered rings in the GBs via anisotropic bond distortions spontaneously introduced so as to lower the donor level, as Jahn-Teller distortions.
3. The segregation abilities for \(\Sigma 9\{114\}\) and \(\Sigma 9\{111\}/\{115\}\) GBs are much higher than the ability expected from the anisotropic bond distortion model. APT combined with LT-FIB suggests preferential As segregation around stretched \(\langle 1T0\rangle\) bonds, in addition to at 5-membered rings in the GBs. It is hypothesized that As atoms would form As dimers around the \(\langle 1T0\rangle\) bonds, due to the tendency of As with five
valence electrons to form a three-coordinated configuration so as to accommodate an excess electron in the dangling bond, which is efficiently attained by an As dimer of a long length. (4) Since stretched 〈1T0〉 bonds are inevitably reconstructed in the 〈1T0〉 tilt GBs with θ_{110} > 70.5°, their segregation abilities would be high via the formation of As dimers.

As a result, As segregation at GBs would be determined by electronic interactions depending on the characteristics of valence electrons of As atoms as well as on local bond distortions at GBs, via anisotropic bond distortions and dimerization. The insights into As segregation at GBs would be helpful to analyse GB segregation of various non-neutral impurities, which would induce complicated electronic effects, unlike neutral impurities.

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