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<th>著者</th>
<th>Tsukahara D., Baba M., Honda S., Imai Y., Hara K. O., Usami N., Toko K., Werner J. H., Suemasu T.</th>
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Potential variations around grain boundaries in impurity-doped BaSi2 epitaxial films evaluated by Kelvin probe force microscopy


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Potential variations around grain boundaries in impurity-doped BaSi2 epitaxial films evaluated by Kelvin probe force microscopy


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Potential variations around the grain boundaries (GBs) in antimony (Sb)-doped n-type and boron (B)-doped p-type BaSi2 epitaxial films on Si(111) were evaluated by Kelvin probe force microscopy. Sb-doped n-BaSi2 films exhibited positively charged GBs with a downward band bending at the GBs. The average barrier height for holes was approximately 10 meV for an electron concentration \( n \approx 10^{17} \text{ cm}^{-3} \). This downward band bending changed to upward band bending when \( n \) was increased to \( n = 1.8 \times 10^{18} \text{ cm}^{-3} \). In the B-doped p-BaSi2 films, the upward band bending was observed for a hole concentration \( p \approx 10^{18} \text{ cm}^{-3} \). The average barrier height for electrons decreased from approximately 25 to 15 meV when \( p \) was increased from \( p = 2.7 \times 10^{18} \) to \( p = 4.0 \times 10^{18} \text{ cm}^{-3} \). These results are explained under the assumption that the position of the Fermi level \( E_F \) at GBs depends on the degree of occupancy of defect states at the GBs, while \( E_F \) approached the bottom of the conduction band or the top of the valence band in the BaSi2 grain interiors with increasing impurity concentrations. In both cases, such small barrier heights may not deteriorate the carrier transport properties. The electronic structures of impurity-doped BaSi2 are also discussed using first-principles pseudopotential method to discuss the insertion sites of impurity atoms and clarify the reason for the observed n-type conduction in the Sb-doped BaSi2 and p-type conduction in the B-doped BaSi2.

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I. INTRODUCTION

Photovoltaic solar cell materials, such as Si, Cu(In,Ga)Se2 (CIGS), CdTe, and III-V compound semiconductors have been extensively studied. At the same time, intensive efforts have been made to explore different materials other than the above conventional materials. Among such materials, we have specifically targeted realizing pn junction solar cells using semiconducting barium disilicide (BaSi2). Composed of earth-abundant elements, BaSi2 is an indirect band gap semiconductor with a band gap of approximately 1.3 eV, and has large absorption coefficients exceeding \( 3 \times 10^4 \text{ cm}^{-1} \) for photon energies higher than 1.5 eV.\(^1\)\(^-\)\(^4\) Large absorption coefficients come from the band structure of BaSi2, where the localized Ba d-like states form flat energy bands in the conduction band.\(^5\)\(^-\)\(^7\) Minority-carrier properties, such as a long minority-carrier diffusion length (\( ca.10 \mu \text{m} \))\(^8\)\(^,\)\(^9\) and a long minority-carrier lifetime (\( ca.10 \mu \text{s} \))\(^10\)-\(^12\) in a-axis-oriented undoped n-type BaSi2 epitaxial films spurred interest in this material. One of the striking features of this material is the fact that both large minority-carrier diffusion length and large absorption coefficient are available. This facilitates the collection of photogenerated carriers in BaSi2, and thereby leads to a large photocurrent.

Grain boundaries (GBs) in semiconductor films often deteriorate electrical and optical properties of the films. Therefore, a lot of studies have been conducted on GBs in solar cell materials, such as polycrystalline Si and chalcopyrite semiconductors to improve efficiency.\(^13\)\(^-\)\(^26\) One of the powerful tools for studying GBs properties is Kelvin probe force microscopy (KFM) method. Measurements with KFM yield the electrostatic properties of GBs and are used to determine the band diagrams across GBs. KFM revealed that random GBs have negative influences on solar cell performance compared to those with low \( \Sigma \) values in polycrystalline Si,\(^27\)\(^,\)\(^28\) and that the electron-hole pairs are well separated at GBs in high-efficiency CIGS solar cells.\(^29\)\(^-\)\(^31\) According to our previous work on the potential variations around the GBs using KFM,\(^32\) the potentials were higher at GBs by approximately 30 meV than those in the BaSi2 grain interiors in the undoped n-type BaSi2 films, suppressing the charge carrier recombination at the GBs. This explains the reason why the minority-carrier diffusion length (\( ca.10 \mu \text{m} \)) is much longer than the average grain size of undoped n-BaSi2 (\( ca.0.2 \mu \text{m} \)), which is to be an active layer in a BaSi2 pn junction solar cell. Therefore, the potential variations around the GBs are a measure of the minority carrier properties.

A classic solar cell uses a pn junction. Therefore, it is of essential importance to investigate the properties of GBs in impurity-doped n- and p-type semiconductor films.\(^33\)\(^,\)\(^34\) Impurity doping of group-III and group-V elements enables us to control the carrier type and conductivity of BaSi2 experimentally.\(^35\)\(^-\)\(^39\) Among them, boron (B) and antimony
(Sb) atoms are considered suitable for p- and n-type dopants, respectively, because the carrier concentration can be controlled in a wide range between $10^{17}$ and $10^{20}$ cm$^{-3}$ at room temperature (RT).$^{35,38}$

This article reports on the surface potential variations around the GBs in Sb-doped n-BaSi$_2$ and B-doped p-BaSi$_2$ films, and discusses their dependence on carrier concentrations. We also discussed their densities of states (DOSs) and total energies using first-principles pseudopotential method to clarify the possible insertion sites of impurity atoms, and the reason for the observed n-type conduction in Sb-doped BaSi$_2$ and p-type conduction in B-doped BaSi$_2$. There have been no theoretical reports on what happens when Sb or B atoms are doped into BaSi$_2$. Regarding indium (In) or gallium (Ga) doping into BaSi$_2$, Imai and Watanabe calculated their electronic structures,$^{40}$ and found that the In (Ga)-doped BaSi$_2$ was expected to be p-type, and that substitution of Si in the BaSi$_2$ lattice by In (Ga) is more favorable than that of Ba from the energetic point of view.

BaSi$_2$ belongs to the space group of $Pnma$. There are two crystallographically inequivalent sites for Ba (Ba(1) and Ba(2)), and three inequivalent sites for Si (Si(3), Si(4), and Si(5)) in the unit cell of BaSi$_2$. The unit cell contains eight formula units. Therefore, the stoichiometric description of the unit cell is Ba$_8$Si$_{16}$, and the atoms are distributed over 4Ba(1), 4Ba(2), 4Si(3), 4Si(4), and 8Si(5). Hereafter, we describe the compound, for example, as Ba$_8$Sb$_3$Si$_{15}$, where one of the Si(3) sites of Ba$_8$Si$_{16}$ is substituted with Sb. The formation energies of the Ba$_8$Si$_{16}$ substituted with In or Ga were calculated by using the first-principles method.$^{40}$ In the case of Ga doping, the formation energies of Ba$_7$Ga$_1$Si$_{16}$ and Ba$_8$Ga$_2$Si$_{15}$ are higher than those of Ba$_8$Ga$_3$Si$_{15}$, Ba$_8$Ga$_4$Si$_{15}$, and Ba$_8$Ga$_5$Si$_{15}$. On the other hand, the energy differences between Ba$_7$Ga$_1$Si$_{16}$ and Ba$_7$Ga$_2$Si$_{16}$ and between Ba$_7$Ga$_3$Si$_{15}$, Ba$_8$Ga$_4$Si$_{15}$, and Ba$_8$Ga$_5$Si$_{15}$ are small. The same was true for In doping.$^{40}$ Hence, we chose one Ba$^{3+}$ site for Ba substitution, and one Si$^{3+}$ site for Si substitution in this article although there are another Ba site, Ba$^{2+}$, and the other two Si sites, Si$^{4+}$ and Si$^{5+}$, in Ba$_8$Si$_{16}$.

II. METHODS

A. Formation of Sb- or B-doped BaSi$_2$ films and characterizations

$a$-axis-oriented Sb-doped n-type and B-doped p-type BaSi$_2$ epitaxial films were formed on Si(111) by molecular beam epitaxy (MBE). The details of the growth procedure were already reported.$^{35,38}$ An ion-pumped MBE system equipped with standard Knudsen cells for Ba, Sb, and B, and an electron-beam evaporation source for Si was used. We adopted the growth condition so that the hole concentration, $p$, in the B-doped BaSi$_2$ becomes much higher than the electron concentration, $n$, in the Sb-doped BaSi$_2$. This is because we plan to use n-BaSi$_2$ as an active layer in a solar cell owing to its long minority-carrier diffusion length.$^{8,9}$ and the sharp $p^+/n$ interface due to small diffusion coefficients of B in BaSi$_2$. The value of $n$ in the Sb-doped BaSi$_2$ films, samples S1–S3, was controlled by changing the substrate temperature, $T_S$, as 580, 550, and 520°C, respectively, while the temperature of Sb crucible, $T_{Sb}$, was fixed at 250°C. Undoped n-BaSi$_2$ ($n = 5 \times 10^{15}$ cm$^{-3}$) in Ref. 32, was used as sample S0 for comparison. The value of $p$ in the B-doped BaSi$_2$ films, samples B1–B3, was controlled by varying the temperature of B crucible, $T_B$, as 1300, 1400, and 1450°C, respectively, while $T_S$ was fixed at 650°C. The sample preparation is summarized in Table I. The carrier concentration was measured at RT by Hall measurement using the van der Pauw method. The crystalline quality of the grown films was characterized by reflection high-energy electron diffraction (RHEED) and x-ray diffraction (XRD) measurements with a Cu Kz source to confirm epitaxial growth of the layers. Surface topographies and potential variations were characterized by Shimazu SPM-9600 atomic force microscopy (AFM) and KFM, respectively. In order to investigate the GBs of BaSi$_2$ and B precipitates, samples for transmission electron microscopy (TEM) observations were prepared by mechanical polishing and ion milling, and their cross sections were observed using TOPCON EM-002B operated at 120 kV.

B. Computational details

We calculated the DOSs and the binding energies of Sb-doped Ba$_8$Si$_{16}$ and B-doped Ba$_8$Si$_{16}$ using the VASP code$^{43}$ based on the density-functional theory (DFT) with the projector-augmented wave pseudopotential$^{44}$ and Perdew-Wang Generalized Gradient Approximations method.$^{45}$ The optimized structure of Ba$_8$Si$_{16}$ is shown in Fig. 1. The total energy minimization was obtained via an optimization of the lattice parameters and a relaxation of the atomic positions in a conjugate gradient routine. The convergence in the total energy was better than 1 meV/atom using the energy cutoff of 600 eV and the $6 \times 8 \times 4$ grid of Monkhorst–Pack points.$^{46}$ We also explored the possibility of interstitial compound with Ba$_2$Si$_2$. There are 16 candidate interstitial sites in the Ba$_2$Si$_2$ lattice. According to Imai and Watanabe,$^{47}$ the most probable insertion sites are the 4c sites, where an impurity atom is surrounded by three Si atoms, one of which is at a peak of one Si-tetrahedron and the other two of which are composing an edge of the other Si-tetrahedron. Thus, we chose one of the 4c sites, the fractional coordinate of which is (0.5841, 0.25, 0.2251). This compound is described as Ba$_8$Si$_{16}$Sb. We also calculated the DOSs and the formation energies of aluminum (Al)-doped BaSi$_2$ and In-doped BaSi$_2$. The optimization of the Ba$_8$Si$_{16}$Sb was obtained by a conjugate gradient routine. The convergence in the total energy was better than 1 meV/atom using the energy cutoff of 600 eV and the $6 \times 8 \times 4$ grid of Monkhorst–Pack points.$^{46}$

TABLE I. Sample preparation: substrate temperature ($T_S$), Sb crucible ($T_{Sb}$) or B crucible temperature ($T_B$), BaSi$_2$ layer thickness ($t$), and carrier concentration are specified.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_S$ ($^\circ$C)</th>
<th>$T_{Sb}$ ($^\circ$C)</th>
<th>$T_B$ ($^\circ$C)</th>
<th>$t$ (nm)</th>
<th>Carrier concentration ($cm^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S0</td>
<td>580</td>
<td>...</td>
<td>...</td>
<td>100</td>
<td>$n = 5 \times 10^{15}$ (undoped)</td>
</tr>
<tr>
<td>S1</td>
<td>580</td>
<td>280</td>
<td>...</td>
<td>100</td>
<td>$n = 1.2 \times 10^{17}$</td>
</tr>
<tr>
<td>S2</td>
<td>550</td>
<td>280</td>
<td>...</td>
<td>100</td>
<td>$n = 3.2 \times 10^{17}$</td>
</tr>
<tr>
<td>S3</td>
<td>520</td>
<td>280</td>
<td>280</td>
<td>200</td>
<td>$n = 1.8 \times 10^{18}$</td>
</tr>
<tr>
<td>B1</td>
<td>650</td>
<td>...</td>
<td>1300</td>
<td>100</td>
<td>$p = 2.7 \times 10^{18}$</td>
</tr>
<tr>
<td>B2</td>
<td>650</td>
<td>...</td>
<td>1400</td>
<td>100</td>
<td>$p = 4.0 \times 10^{18}$</td>
</tr>
<tr>
<td>B3</td>
<td>650</td>
<td>...</td>
<td>1450</td>
<td>100</td>
<td>$p = 2.0 \times 10^{19}$</td>
</tr>
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</table>
for comparison. In our framework of first-principles calculations, we cannot take into account thermal effects at the finite temperature to the DFT calculation.

III. RESULTS AND DISCUSSION

A. Calculation results

Table II shows the summary of calculated electronic energies for Ba₈Si₁₆ doped with an impurity atom (Sb, B, Al, or In). The binding energy of Ba₈Si₁₆ was calculated to be −133.696 eV. The total energy after impurity doping is calculated using the binding energies of the optimized structures as follows. In the case that an Sb atom replaces a Ba atom in the Ba¹ site, the total energy of Ba₈Sb¹Si₁₅ + Ba is given by

\[ (-129.389) + (-1.912) = -131.301 \text{ eV}. \]

In another case that an Sb atom replaces a Si atom in the Si⁽³⁾ site, the total energy of Ba₈Sb¹⁺Si₁₁⁺Si is

\[ (-132.273) + (-5.417) = -137.690 \text{ eV}. \]

![Figure 1](image1.png)

FIG. 1. Optimized structure of Ba₈Si₁₆. An open dotted circle shows the location of an interstitial 4c site. The fractional coordinate of the 4c site is (0.5841, 0.25, 0.2251).

In the same way, the total energy of Ba₈Si₁₆Sb is calculated to be −135.861 eV. These results imply that replacement of Si with Sb is most likely to occur in Sb-doped BaSi₂ from the energetic point of view. The same assumption can be applied to B-, Al-, or In-doped BaSi₂. This result agrees well with Ref. 40. However, in the case of B-doped BaSi₂, we note that not only the Si substitution with B but also the interstitial insertion of B into the 4c site is energetically favorable. We speculate this difference results from a smaller atomic radius of B than those of Sb, Al, and In.

Figure 2 shows the total DOSs of (a) undoped Ba₈Si₁₆, (b) Ba₈Sb⁽³⁾Si₁₅, (c) Ba₈B⁽³⁾Si₁₅, (d) Ba₈Si₁₂B, (e) Ba₈Al⁽³⁾Si₁₁, and (f) Ba₈In⁽³⁾Si₁₁ near the Fermi level, \( E_f \). The energy zero of the DOS curve is taken at their \( E_f \). As shown in Fig. 2(b), \( E_f \) crosses the bottom of the conduction band, \( E_C \), in Ba₈Sb⁽³⁾Si₁₅, and hence the doped BaSi₂ will perform as the n-type. Needless to state, this does not necessarily mean that Sb-doped BaSi₂ becomes degenerated. Concentration of the doped element would be much lower in the actual fabrication than that assumed in the present calculations. In contrast, when Si was replaced with B, Al, or In, \( E_f \) crosses the top of the valence band, \( E_V \), and the doped BaSi₂ will work as the p-type as shown in Figs. 2(c), 2(e), and 2(f), respectively. These results agree well with those experimentally obtained. 35–39 BaSi₂ is a Zintl phase compound consisting of an electropositive Ba and an electronegative Si, where the electropositive Ba donates its electrons to

![Figure 2](image2.png)

FIG. 2. Total DOSs of (a) undoped Ba₈Si₁₆, (b) Ba₈Sb⁽³⁾Si₁₅, (c) Ba₈B⁽³⁾Si₁₅, (d) Ba₈Si₁₂B, (e) Ba₈Al⁽³⁾Si₁₁, and (f) Ba₈In⁽³⁾Si₁₁ near \( E_f \). The energy zero of the DOS curve is taken at their \( E_f \).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Total energy (eV)</th>
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<tr>
<td>8Ba + 16Si → Ba₈Si₁₆</td>
<td>-133.696</td>
</tr>
<tr>
<td>Ba₈Si₁₆ + Sb → Ba₈Sb⁽¹⁾Si₁₅ + Ba</td>
<td>-131.301 (−129.389−1.912)</td>
</tr>
<tr>
<td>Ba₈Si₁₆ + Sb → Ba₈Sb⁽³⁾Si₁₅ + Si</td>
<td>-137.690 (−123.273−5.417)</td>
</tr>
<tr>
<td>Ba₈Si₁₆ + Sb → Ba₈Sb₁⁺Si₁₆</td>
<td>-135.861</td>
</tr>
<tr>
<td>Ba₈Si₁₆ + B → Ba₈B⁽¹⁾Si₁₆ + Ba</td>
<td>-132.758 (−130.846−1.912)</td>
</tr>
<tr>
<td>Ba₈Si₁₆ + B → Ba₈B⁽³⁾Si₁₅ + Si</td>
<td>-138.209 (−132.792−5.417)</td>
</tr>
<tr>
<td>Ba₈Si₁₆ + B → Ba₈Si₁₂B</td>
<td>-138.999</td>
</tr>
<tr>
<td>Ba₈Si₁₆ + Al → Ba₈Al⁽¹⁾Si₁₆ + Ba</td>
<td>-130.609 (−128.697−1.912)</td>
</tr>
<tr>
<td>Ba₈Si₁₆ + Al → Ba₈Al⁽³⁾Si₁₅ + Si</td>
<td>-136.494 (−131.077−5.417)</td>
</tr>
<tr>
<td>Ba₈Si₁₆ + Al → Ba₈Si₁₂Al</td>
<td>-135.698</td>
</tr>
<tr>
<td>Ba₈Si₁₆ + In → Ba₈In⁽¹⁾Si₁₆ + Ba</td>
<td>-130.420 (−128.508−1.912)</td>
</tr>
<tr>
<td>Ba₈Si₁₆ + In → Ba₈In⁽³⁾Si₁₅ + Si</td>
<td>-135.586 (−130.169−5.417)</td>
</tr>
<tr>
<td>Ba₈Si₁₆ + In → Ba₈Si₁₂In</td>
<td>-133.857</td>
</tr>
</tbody>
</table>
the Si, which uses the electrons in the formation of covalent bonds in Si₄ tetrahedra to satisfy valence. It was confirmed from both theory and experiment that the Si 3p state is dominant around Eᵥ in BaSi₂. Thus, replacement of Si with Sb increases valence electron concentration and causes the change of BaSi₂ to the n-type, whereas replacement of Si with B, Al, or In decreases it, and forms the p-type. However, localized states appear in the band gap of Ba₈Si₁₆B as shown in Fig. 2(d). Thus, it is difficult to clarify the conductivity type of this compound.

### B. GBs in Sb-doped n-BaSi₂

We observed streaky RHEED patterns, and a-axis-oriented diffraction peaks in the θ-2θ XRD patterns for all the samples. These results show that a-axis oriented BaSi₂ films doped with Sb and those with B atoms were formed on Si(111). As summarized in Table I, we fabricated Sb-doped BaSi₂ films with n ranging from \( n = 1.2 \times 10^{17} \) to \( n = 1.8 \times 10^{18} \) cm\(^{-3}\) and B-doped BaSi₂ films with \( p \) ranging from \( p = 2.7 \times 10^{18} \) cm\(^{-3}\) to \( p = 2.2 \times 10^{20} \) cm\(^{-3}\). The carrier concentrations increased significantly in the impurity doped-BaSi₂ compared with undoped one, sample S0.

FIG. 3. (a)–(d) AFM topographic and (a')–(d') KFM potential images, measured for samples S0–S3, respectively, with their cross sectional profiles along white broken lines in the same areas. The positions of GBs are indicated by colored lines in the cross sectional profiles. We see that the potentials at the GBs are higher than those of grain interiors for sample S0 in Figs. 3(a) and 3(a'). This means that the GBs are positively charged. This result shows that band bending occurs downwards at GBs as shown in Fig. 4(a'). This tendency was also observed in other Sb-doped n-BaSi₂ films, samples S1 and S2 in Figs. 4(b') and 4(c'), except sample S3. The downward band bending in n-type BaSi₂ is beneficial for the suppression of recombination of minority carriers (holes). These holes experience a repelling force near the GBs. In contrast, the potentials are smaller at the GBs than those of the grain interiors in sample S3, meaning that the GBs are negatively charged.

Next, we evaluated the potential barrier height, \( \Delta E_{\text{GB}} \), at GBs by

\[
\Delta E_{\text{GB}} = -q(V_{\text{GB}} - V_{\text{G,ave}}),
\]

where \( V_{\text{GB}} \) and \( V_{\text{G,ave}} \) are the potential at GBs and the average potential in the inner parts of two adjoining grains, respectively. The symbol \( q \) denotes the elementary charge. The same procedure was repeated for approximately 30 GBs in each sample. The histograms of barrier height are shown in Figs. 4(a)–4(d). The barrier height for holes (minority-carriers) was positive for samples S0–S2 in Figs. 4(a')–4(c'), and negative for sample S3 in Fig. 4(d'). The average barrier height for holes was approximately 30 meV for sample S0, and 10 meV or smaller for samples S1 and S2. On the other hand, the average barrier height for electrons was approximately 15 meV for sample S3. Minority-carriers (holes) are attracted by the electric fields towards the GBs and thereby may recombine at the GBs in this case. However, these barrier heights are almost the same as the thermal energy of 26 meV at RT (25 °C). Thus, we may expect that such small barrier heights observed in samples S0–S3 do not deteriorate carrier transport properties. Note that more heavily doping of Sb may increase attractive electric fields for holes towards the GBs, leading to recombination. Therefore, \( n \) should be designed as small as possible for use as an active layer.

The band diagram across the GBs facilitates an estimate of the area density of charges at GBs, \( \sigma_{\text{GB}} \). We take here sample S0, for example, and derive \( \sigma_{\text{GB}} \) in one dimensional approximation. The positive charge \( \sigma_{\text{GB}} \) at the GBs is shielded by the negative charge consisting of majority carriers (electrons) in the band bending region with a width 2\( W \). The electron concentration \( n(x) \) at a position \( x \ (0 \leq x \leq W) \) from the GB is given by the following Poisson’s equation:

\[ \nabla^2 \psi = n(x) - \rho \]

where \( \psi \) is the electric potential, \( n(x) \) is the electron concentration, and \( \rho \) is the electric charge density.
The Boltzmann constant, $e$, and the temperature. Equation (2) can be solved numerically using the two boundary conditions, that is, $\phi(0) = 30 \text{ mV}$ and $\phi(W) = 0 \text{ mV}$. Numerical simulations show that the barrier height at $x = 0$ reaches $30 \text{ mV}$ when $W = 120 \text{ nm}$. The value $W \approx 100 \text{ nm}$ matches well to the cross section in Fig. 3(a’). The area density of charges $\sigma_{\text{GB}}$ present at the GBs is thus obtained by using charge neutrality\(^{20}\)

$$
\sigma_{\text{GB}} = 2 \int_0^W n(x) dx \approx 2 \times 10^{11} \text{ cm}^{-2}.
$$

$\sigma_{\text{GB}}$ was also calculated to be of the order of $10^{11} \text{ cm}^{-2}$ in samples S1 and S2. In the case of sample S3, the negative sheet charge at the GBs is compensated by the positively charged space-charge region with a width $2W$. Assuming complete ionization of Sb atoms and their uniform distribution in the grain interiors, $\sigma_{\text{GB}}$ is given by\(^{20}\)

$$
\sigma_{\text{GB}} = 2WN_{\text{D}}^+ = 2Wn \approx 10^{13} \text{ cm}^{-2}
$$

for $W \approx 100 \text{ nm}$. Here, $N_{\text{D}}^+$ is the ionized Sb concentration. One explanation for the negative charge at the GBs is that the electrons supplied from the heavily Sb-doped $n$-BaSi$_2$ grain interiors to the GBs outnumbered the positive charges in samples S0–S2, giving rise to the band diagram as shown in Fig. 4(d’).

The change of barrier height is explained at least qualitatively, assuming that $E_f$ is pinned at GBs, whereas $E_c$ approaches the bottom of the conduction band, $E_c$, in the BaSi$_2$ grain interiors with increasing $n$. The cause for the downward band bending in the undoped $n$-BaSi$_2$, sample S0, is explained as follows. The GBs in the $\alpha$-axis-oriented BaSi$_2$ films are mostly composed of BaSi$_2$(011)/(0–11) planes, and on these planes Ba atoms are dominant. Detailed discussions were given in Ref. 8. In the $\alpha$-axis-oriented BaSi$_2$ films on Si(111), there are three epitaxial variants of $n$BaSi$_2$ grains oriented around the surface normal.

In the course of the epitaxial growth of $\alpha$-axis-oriented BaSi$_2$, the (011) plane of one BaSi$_2$ grain coalesces with the (0–11) plane of another BaSi$_2$ grain by lateral growth, forming the GBs. Thus, it is reasonable to think that the GBs are in excess of Ba atoms compared with the BaSi$_2$ grain interiors. Due to the difference in electronegativity between Ba and Si, the Ba atoms are positively charged, and the Si$_4$ tetrahedra are negatively charged in BaSi$_2$. We speculate that this is why the potentials are higher at the GBs than those in the grain interiors of the undoped BaSi$_2$. Regarding Sb-doped $n$-BaSi$_2$, Si atoms are favorably replaced with Sb atoms as discussed in Table 1, and thus $E_f$ approaches $E_c$ with increasing $n$. However, this is not likely to occur at the GBs because Ba atoms are dominant. This might be the cause of the observed change in barrier height.

We next discuss the barrier height at GBs. The effective density of states in the conduction band, $N_c$, is approximately $2.6 \times 10^{19} \text{ cm}^{-3}$ from the principle-axis components of the effective mass tensor for electrons and four equivalent valleys at $E_c$. The $E_c-E_f$ are calculated to be approximately 0.22, 0.14, 0.11, and 0.07 eV for samples S0–S3, respectively, from the equation

$$
E_c - E_f = k_B T \ln \left( \frac{N_c}{n} \right)
$$

using their $n$ values. Considering that the average barrier height for holes is approximately 30, 10, and 10 meV in samples S0–S2, and that for electrons is approximately 15 meV in sample S3, the values of $E_c-E_f$ are estimated to be approximately 0.19, 0.13, 0.1, and 0.09 eV, respectively, at the GBs. This discussion clearly shows that the slight change of $E_f$ is necessary to occur at the GBs to account for the observed change in barrier height. We think that defect states...
exist at GBs, and the position of $E_f$ at the GBs is changed according to the degree of occupancy of those states by electrons.$^{53}$

**C. GBs in B-doped p-BaSi$_2$**

Next, we discuss B-doped p-BaSi$_2$. Figures 5(a)–5(c) show the AFM topographic and KFM potential images, measured for samples B1–B3, respectively. Their cross sectional profiles along white broken lines in the same areas are also shown. The positions of colored lines correspond to those of GBs. We see that the potentials at the GBs are smaller than those in the BaSi$_2$ grains, indicating that the GBs are negatively charged compared with the grain interiors, and thereby band bending occurs upwards at the GBs as shown in Figs. 6(a) and 6(b). The upward band bending in p-type BaSi$_2$ is favorable for the suppression of recombination of minority carriers (electrons). These electrons are not attracted towards the GBs in samples B1 and B2. Regarding sample B3, it was difficult to distinguish the position of GBs from AFM. However, it is safe to state that the potential variations became smaller with increasing $p$ as shown in Figs. 5(a)–5(c). The negative charge at the GBs is shielded by the majority carriers (holes) in the band bending region with a width $2W$. Using similar equations like Eqs. (2)–(4), $\sigma_{GB}$ was calculated to be of the order of $10^{15}$ cm$^{-2}$ for samples B1 and B2.

Next, we evaluated the potential barrier height $\Delta E_{GB}$ for electrons at GBs using Eq. (1) for samples B1 and B2. The histograms of barrier height at GBs are shown in Fig. 6. The average barrier height was decreased from approximately 25 meV in sample B1 to 15 meV in sample B2. Such small barrier heights also may not disturb the carrier transport properties across the GBs in B-doped BaSi$_2$. The change of barrier height is explained qualitatively under the assumption that $E_f$ is pinned at the GBs while $E_f$ in the grain interiors approached $E_V$ with increasing $p$ by replacement of Si atoms in the BaSi$_2$ with B atoms. The effective density of states in the valence band, $N_V$, is approximately $2.0 \times 10^{19}$ cm$^{-3}$ from the principal-axis components of the effective mass tensor for holes and two equivalent valleys at $E_V$. The $E_f$–$E_V$ are calculated to be approximately 0.05 and 0.04 eV for samples B1 and B2, respectively, from

$$E_f - E_V = k_BT \ln \left( \frac{N_V}{\rho} \right).$$

(7)

Considering that the upward band bending occurs even for sample B2 ($p = 4.0 \times 10^{18}$ cm$^{-3}$), $E_f$ seems to be located very close to $E_V$ at the GBs as shown in Figs. 6(a) and 6(b). Regarding the different positions of $E_f$ in p-BaSi$_2$ from that in n-BaSi$_2$, we interpret that this result comes from emptying the defect states at the GBs by heavily B doping. Figure 7 shows the bright-field TEM cross section of a 0.53-μm-thick B-doped p-BaSi$_2$ layer on undoped BaSi$_2$/Si(111) grown by MBE using the same growth condition as sample B3. We see lots of B precipitates gathering along the GBs indicated by white arrows. This result suggests that BaSi$_2$ around the GBs

![FIG. 5. (a)–(c) AFM topographic and (a')–(c') KFM potential images with their cross sections along white broken lines for samples B1–B3, respectively.](image1)

![FIG. 6. Histograms of barrier height at GBs for samples (a) B1 and (b) B2. Schematic band diagrams across the GB are also shown in (a') and (b').](image2)
We have evaluated the potential variations at the GBs in $\alpha$-axis-oriented Sb-doped n-BaSi$_2$ and B-doped p-BaSi$_2$ epitaxial films by KFM, and compared them with those in undoped BaSi$_2$. In the Sb-doped n-BaSi$_2$ films, the band bending occurred downwards at the GBs and the average barrier height for holes was approximately 10 meV when $n$ was $1.2 \times 10^{17}$ and $3.2 \times 10^{17}$ cm$^{-3}$. This downward band bending changed to the upward band bending with a barrier height of approximately 15 meV when $n$ was increased to $1.8 \times 10^{18}$ cm$^{-3}$. Much higher Sb doping may induce stronger attractive electric fields for holes (minority carriers) towards the GBs. Thus, n-type doping should be designed as small as possible for use as an active layer. In the B-doped p-BaSi$_2$ films, the potential variations became smaller with increasing $p$. Upward band bending was observed when $p$ was of the order of $10^{18}$ cm$^{-3}$. The average barrier height for electrons decreased from approximately 25 to 15 meV when $p$ was increased from $2.7 \times 10^{18}$ to $4.0 \times 10^{18}$ cm$^{-3}$. In both Sb-doped n-BaSi$_2$ and B-doped p-BaSi$_2$ films, the change of barrier height was explained under the assumption that $E_f$ was varied depending on the degree of occupancy of the defect states at the GBs, while $E_f$ approached $E_C$ or $E_V$ in the BaSi$_2$ grain interiors with increasing carrier concentrations. First-principles calculations revealed that Si substitution with Sb is energetically favorable and forms n-type BaSi$_2$. In the case of B-doped BaSi$_2$, Si substitution with B forms p-type BaSi$_2$; however, the interstitial insertion of B atoms at the 4c site is also energetically favorable. The interstitial insertion induces localized states in the band gap.

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