Diffusion Coefficients of Impurity Atoms in BaSi$_2$ Epitaxial Films Grown by Molecular Beam Epitaxy

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Abstract
Sb layers deposited on BaSi$_2$ epitaxial films on Si(111) substrates were annealed at different temperatures, and the diffusion coefficients of Sb were evaluated using secondary ion mass spectrometry with Cs$^+$ ions. The activation energies of lattice and grain boundary diffusions in BaSi$_2$ are 0.64 eV and 1.20 eV, respectively.

1. Introduction
BaSi$_2$ has the bandgap of about 1.3 eV and a large optical absorption coefficient, reaching 3×10$^4$ cm$^{-1}$ at 1.5 eV experimentally [1-3]. In addition, the minority-carrier diffusion length in undoped BaSi$_2$ films reaches a value as large as 10 µm [4]. Also a-axis-oriented BaSi$_2$ can be grown epitaxially on Si(111) and Si(001) surfaces [5-7]. Therefore, BaSi$_2$ is considered one of the new materials for high-efficiency thin-film solar cells. There is a requirement to control the conductivity of BaSi$_2$ by impurity doping to make a p-n junction which is the basic structure of a solar cell. Impurities with small diffusion coefficients and large carrier concentrations are needed. Up to the present, we have already done a lot of studies on Al and B which are p-type dopants for BaSi$_2$ [8,9]. However there have been no reports about diffusion coefficients of n-type dopants for BaSi$_2$. In this study, we aimed to evaluate the lattice and grain boundary (GB) diffusion coefficients of Sb, the n-type dopant for BaSi$_2$.

2. Experimental procedure
A two-stage growth method was applied, that is, reactive deposition epitaxy (RDE; Ba deposition on hot Si) for BaSi$_2$ template layers, and the subsequent molecular beam epitaxy (MBE; codeposition of Ba and Si on Si) at 580 °C to form a 600-nm-thick a-axis-oriented BaSi$_2$ epitaxial film on Si(111). Then, an approximately 100-nm-thick Sb film was evaporated onto the undoped BaSi$_2$ layers at room temperature (RT) by vacuum evaporation. Then the sample was cut into several pieces and annealed in an Ar atmosphere at different temperatures and durations, that is, 200 °C for 4 h, 250 °C for 4 h, and 300 °C for 1 h. Finally we investigated the depth profiles of Sb in BaSi$_2$ using secondary ion mass spectrometry (SIMS) measurement with Cs$^+$ ions, and evaluated its lattice and GB diffusion coefficients. Crystalline quality of grown films was characterized by reflection high-energy electron diffraction (RHEED), θ-2θ X-ray diffraction (XRD), and plan-view transmission electron microscopy (TEM) along the BaSi$_2$[100] azimuth.

3. Results and Discussion
A streaky RHEED pattern and (100)-oriented diffractions in the XRD pattern in Fig. 1 show that a-axis-oriented epitaxial layers were formed.

![Fig. 1 RHEED pattern observed along Si [11-2] and θ-2θ XRD pattern of undoped BaSi$_2$.](image1.png)

Figure 2 shows the bright-field plan-view TEM image of the undoped BaSi$_2$ film observed along BaSi$_2$[100]. Because of the three epitaxial variants rotated by 120° around the surface normal of Si(111), grain boundaries exist in the epitaxial layers. Thus, not only the lattice diffusions, but also GB diffusions must be considered.

![Fig. 2 Bright-field plan-view TEM image observed along BaSi$_2$[100].](image2.png)
atoms in other silicides are also shown for comparison. Here, we set the GB width $\delta$ to be 0.5 nm [11]. We see that the diffusion coefficients of Sb are found to be much larger than those of B, and almost the same as those of Al in BaSi$_2$ [8, 12]. The activation energies of lattice diffusion and GB diffusion for Sb in BaSi$_2$ are 0.64 eV and 1.20 eV, respectively. On the basis of these results, we conclude that Sb atoms easily diffuse in BaSi$_2$. As a next step, we plan to go into As, another $n$-type dopant candidate.

Figure 3 shows the depth profiles of Sb atoms in BaSi$_2$ layers after annealing at 200 °C for 4 h, 250 °C for 4 h, and 300 °C for 1 h. To fit these experimentally obtained SIMS profiles, Eqs. (1) and (2) were adopted for lattice diffusion and GB diffusion, respectively. The concentration distribution $C(x, t)$ of impurity atoms due to the lattice diffusion is given by Eq. (1) [10], where $x=0$ is set at the Sb/BaSi$_2$ interface, and $C_0$ the Sb concentration at $x=0$, $D_l$ the lattice diffusion coefficient, and $t$ the annealing duration.

$$C(x, t) = C_0 \exp \left(-\frac{x^2}{4D_l t}\right) \quad (1)$$

Meanwhile, the concentration distribution due to GB diffusion follows Eq. (2) [11], where $s$ is the segregation factor, $\delta$ the grain boundary width, and $D_{GB}$ the GB diffusion coefficient.

$$sD_{GB}x^2 = 1.332[D_l/t]^{1/3} [\delta \ln C(x, t)/\delta x]^{1/3} \quad (2)$$

We see that the lattice diffusion coefficient $D_l$ and the product of segregation factor and GB diffusion coefficient $sD_{GB}$ of Sb and other atoms.

4. Conclusions

The lattice and GB diffusion coefficients of Sb were evaluated using the BaSi$_2$ epitaxial films capped with Sb layers. The activation energies of diffusion of Sb in the undoped BaSi$_2$ are 0.64 eV and 1.20 eV for lattice diffusion and GB diffusion, respectively.