

Effect of Grain Areas on Minority-carrier Lifetime in Undoped N-type BaSi₂ on Si(111)

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We have grown undoped *n*-BaSi₂ epitaxial films with different grain sizes on Si(111) and characterized their minority-carrier lifetime, τ . We found that τ value in undoped *n*-BaSi₂ did not depend on average grain area, but on surface condition. The samples with mirror surfaces had large τ of about 0.4 μ s and those with cloudy surface small τ of about 8 μ s. We tried to cap the sample surface *in situ* with a 3 nm Ba or Si layer in order to control the surface of BaSi₂, and succeeded to intentionally form BaSi₂ with large τ .

1. Introduction

Because of outstanding properties of semiconducting BaSi₂, we have studied extensively its fundamental properties. BaSi₂ has a suitable band gap for solar cell of approximately 1.3 eV, matching the solar spectrum [1]. In addition, it has a large absorption coefficient (*ca.* $\alpha=3\times 10^4$ cm⁻¹ at 1.5 eV) and long minority-carrier diffusion length (*ca.* $L=10$ μ m) [1,2]. Undoped BaSi₂ shows *n*-type conductivity with the electron concentration of about 10¹⁶ cm⁻³ [3]. In our previous work, we achieved high hole concentrations exceeding 10²⁰ cm⁻³ in B-doped *p*-type BaSi₂ [4]. Therefore, we aim to fabricate a BaSi₂ *pn* diode using the undoped *n*- and B-doped *p*-type BaSi₂. *a*-axis-oriented BaSi₂ can be grown on a Si(111) surface. Since these films have three epitaxial variant rotated by 120° with each other, a large number of grain boundaries (GBs) exist in the BaSi₂ epitaxial films [5]. According to our previous research using Kelvin probe force microscopy (KFM), the potential at GBs became higher than those in grain interior in undoped *n*-BaSi₂ [6]. We thus expect that photogenerated minority carriers, holes, are repelled back from the GBs and the carrier recombination are not likely to occur at the GBs. In order to clarify this assumption, we fabricated approximately 0.5- μ m-thick BaSi₂ films with various grain sizes, namely, various densities of GBs and characterized their minority-carrier lifetime, τ .

2. Experiment

We used an ion-pumped molecular beam epitaxy (MBE) system equipped with an electron-beam evaporation source for Si and a standard Knudsen cell for Ba. We employed two-step growth techniques. After the thermal cleaning of the Si substrate, Ba was deposited on the hot floating-zone *n*-Si(111) substrate ($\rho>1000$ Ω -cm) in order to fabricate the template layer, which works as seed crystals for subsequent layers [7]. Then, Ba and Si were co-deposited on the template layer at optimum growth temperature, 580 °C, by MBE. The layer thickness was about 0.5 μ m. We prepared 8 samples with various grain sizes by changing the growth temperature and Ba deposition rate during reactive deposition epitaxy (RDE) [8]. This is because various RDE growth conditions change the migration of Ba atoms on the Si substrate. We also prepared the films capped *in situ*

with a 3 nm Ba or Si. The details of sample preparation are shown in Table I. The grain size was characterized by electron backscatter diffraction (EBSD). The minority-carrier lifetime was measured by microwave-detected photoconductivity decay (μ -PCD) method. Electron-hole pairs were generated by a 349 nm laser pulse, and then, the photoconductivity decay curves were measured by the reflectivity of microwave with the frequency of 26 GHz [9]. We measured the decay curves with various excitation laser intensity ranging between 1.1×10^2 and 1.3×10^5 W/cm². The crystalline quality was characterized by reflection high-energy electron diffraction (RHEED). In order to evaluate the composition of the surface, x-ray photoelectron spectroscopy (XPS) were performed. Al K α radiation (1486.6 eV) was used for x-ray radiation source. The probing depth was about 3 nm.

Table I. Sample preparation: BaSi₂ layer thickness, surface condition, and BaSi₂ average grain area by EBSD are specified

Sample	Thickness (nm)	Capping	Surface	Average grain area (μm^2)
A	570	-	Mirror	2.6
B	420	-	Cloudy	8.3
C	450	-	Mirror	5.8
D	490	-	Cloudy	21.1
E	510	-	Cloudy	20.0
F	500	-	Cloudy	23.3
G	450	Ba (3 nm)	Mirror	3.8
H	450	Si (3 nm)	Mirror	5.9

3. Results and discussions

The 12×12 - μm^2 EBSD crystal orientation maps and distribution histograms of grain area fraction in samples A-H are shown in Fig. 1. Average grain areas calculated from the histograms are also shown. Red, blue, green in the EBSD crystal orientation maps indicate three epitaxial variants of

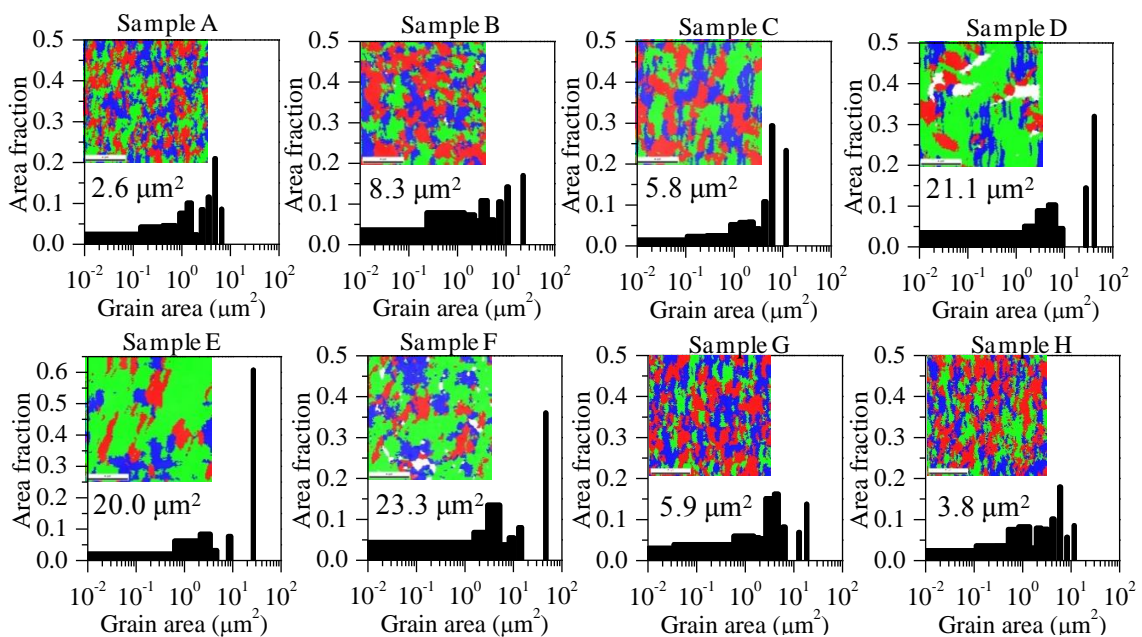


Fig. 1. 12×12 - μm^2 EBSD crystal orientation maps of the BaSi₂ epitaxial films and distribution histograms of BaSi₂ grain area fraction in sample A-H [10].

a-axis-oriented BaSi₂ on Si(111). As shown in Fig. 1, we fabricated BaSi₂ epitaxial films with various grain areas. Thus, it is safe to state that the density of BaSi₂ GBs decreases with increasing average grain area.

We next measured the minority-carrier lifetime in these samples by μ -PCD. Figure 2(a) shows the example of typical decay curve of BaSi₂, which was measured in sample H. We also presented the normalized μ -PCD decay curves of samples A and C in Fig. 2(b), and sample B and D-F in Fig. 2 (c). These curves were measured when excess carrier density, Δn , was $2.4 \times 10^{18} \text{ cm}^{-3}$, calculated from the absorption coefficient of BaSi₂ at a wavelength of 349 nm, and irradiated laser intensity. The decay rates of sample A and C became faster than the others. According to our previous studies, decay curve can be divided in two three modes from the viewpoint of decay rate, and was fitted well using the following equation.

$$I(t) = I_1 \exp\left(-\frac{t}{\tau_{\text{Auger}}}\right) + I_2 \exp\left(-\frac{t}{\tau_{\text{SRH}}}\right) + I_3 \exp\left(-\frac{t}{\tau_{\text{SRH-trapping}}}\right)$$

Here, I_1 , I_2 and I_3 are the coefficients and τ_{Auger} , τ_{SRH} and $\tau_{\text{SRH-trapping}}$ the time constants for each decay mode. In the initial mode, Auger recombination is dominant. This is because BaSi₂ has a large absorption coefficient, and high excitation occurs in the μ -PCD measurement. Thus, it is difficult to avoid the Auger recombination in this work. However, this high excitation is not likely to happen in the actual AM 1.5 irradiation. Therefore, we used the second decay curve due to Shockley-Read-Hall recombination to investigate the minority-carrier lifetime.

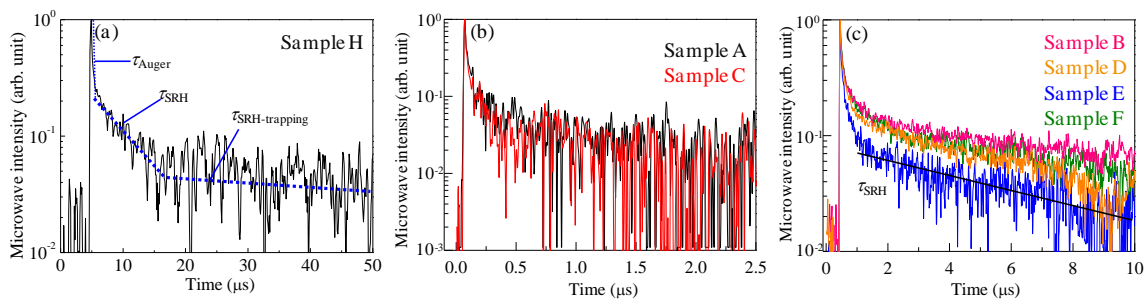


Fig. 2. Normalized μ -PCD decay curves of (a) sample H, (b) samples A and C, and (c) samples B and D-F when Δn is $2.4 \times 10^{18} \text{ cm}^{-3}$ [10].

Figure 3 shows the correlation between τ_{SRH} and average grain area. τ_{SRH} value can be separated into two groups, that is, about 0.4 and 8 μs . However, τ_{SRH} values did not depend on the average grain areas in each group. This result indicates that the GBs do not act as recombination centers for minority-carriers, holes. This is consistent with our KFM results [6]. On the contrary, the samples with large τ_{SRH} had cloudy surfaces and those with small τ_{SRH} mirror surfaces.

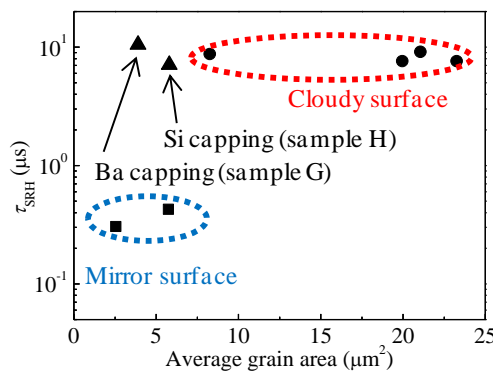


Fig. 3. Dependence of τ_{SRH} on BaSi₂ average grain area for all the samples [10].

The photographs of mirror- and cloudy surface of BaSi₂ are shown in Fig. 4(a) and (b), respectively. In order to clarify the reason why the surface became cloudy, we next investigated the crystalline quality of these samples. Figure 4(c) and (d) show the RHEED patterns of sample A and B taken just after the MBE growth. We see sharp streaky pattern in both samples and do not see any clear difference. Therefore, the surface condition did not become cloudy just after MBE growth in ultrahigh vacuum chamber, but after air exposure. We speculated that the sample surfaces were oxidized when the samples were exposed to air, and their oxidation layers may passivate the defects exist in the BaSi₂ surface. However, the problem was that we were not able to control the surface of BaSi₂. This means that the formation of the sample with large τ_{SRH} was out of control.

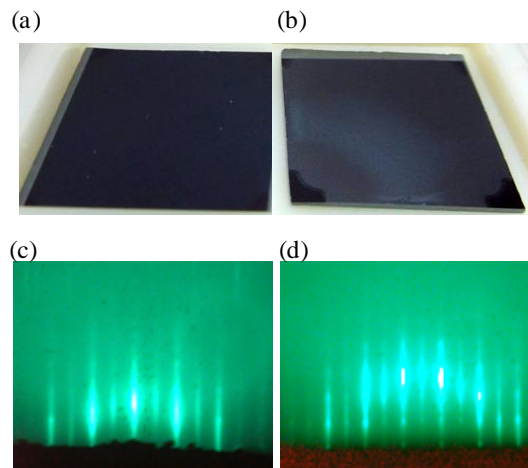


Fig. 4. Photographs of (a) mirror- and (b) cloudy surface of BaSi₂. RHEED patterns for (c) sample A and (d) sample B just after the MBE growth of BaSi₂ are also shown [10]

In order to solve this problem, we next grew two samples G and H. These samples were capped *in situ* with a 3 nm Ba or Si layer after MBE growth so that we could control the surfaces of the samples. The correlation between τ_{SRH} and average grain area of samples G and H are also presented in Fig. 3. The important point is τ_{SRH} value was approximately 10 and 7 μs , and almost the same as those with cloudy surfaces. This result indicates that we succeeded to intentionally form the BaSi₂ films with large τ_{SRH} by capping with a Ba or Si layer. In order to clarify the compositions of the surfaces, we performed XPS measurement. Figure 5 shows the normalized XPS spectra of (a) Ba 3d_{5/2}, (b) O 1s, (c) Si 2p, and (d) C 1s states for sample G and H. The clear peaks in Figs.5 (a), (b) and (d) imply that oxides such as BaCO₃ and BaO, and others like BaOH exist in the sample capped with a Ba layer. On the other hand, the formation of SiO₂ was promoted in sample H capped with a Si layer. However, we were not able to identify the origin of large τ_{SRH} only in these results. Table II shows the atomic percentages of O in the surface regions of BaSi₂ in sample A, B, G, and H, calculated from XPS spectrum. We can see here that the O ratio is smaller only in sample A than the others. Therefore, the samples with smaller τ_{SRH} had a small ratio of O. On the contrary, those with large τ_{SRH} had a large ratio of O. This result suggests that O atom may play an important role to achieve large τ_{SRH} . Therefore, we conclude that τ_{SRH} values were not determined by GBs, but surface conditions, and the capping with a Ba or Si layer leads us to fabricate BaSi₂ films with large τ_{SRH} . However, there are few data about passivation of BaSi₂. Thus, further studies are required.

Table II. Atomic percentages of O in the surface regions of BaSi₂ in sample A, B, G, H.

Sample	A	B	G	H
O ratio (at.%)	33.8	45.8	49.3	46.3

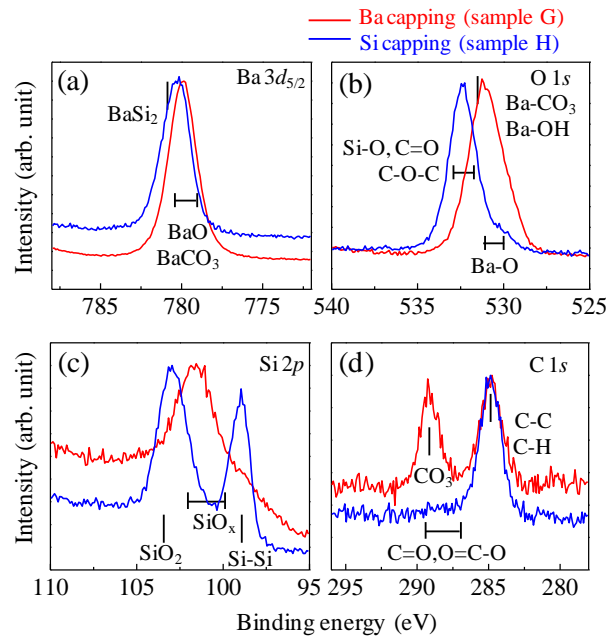


Fig. 5. Normalized XPS spectra of (a) Ba $3d_{5/2}$, (b) O $1s$, (c) Si $2p$, and (d) C $1s$ states for samples G and H [10].

4. Conclusions

We fabricated BaSi₂ epitaxial films with various average grain sizes ranging from 2.6 to 23.3 μm², and characterized their τ_{SRH} . We discovered that τ_{SRH} values were not influenced by the densities of GBs. Therefore, GBs do not work as recombination centers for minority-carrier. The important point is BaSi₂ films with cloudy surfaces had large τ_{SRH} of 8 μs, and those with mirror surfaces smaller τ_{SRH} of 0.4 μs. In order to control the surface of BaSi₂, we fabricated BaSi₂ films capped *in situ* with a Ba or Si layer, and these layer enabled us to form BaSi₂ with large τ_{SRH} .

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