Molecular beam epitaxy of BaSi₂ thin films on Si(001) substrates

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An attempt was made to grow BaSi₂ epitaxial films on Si(001) substrates using molecular beam epitaxy. The structure and morphology of the films were investigated using reflection high-energy electron diffraction, X-ray diffraction, electron backscatter diffraction, atomic force microscopy, and transmission electron microscopy. The BaSi₂ film grown was *a*-axis oriented, despite a large lattice mismatch. The measurements indicated that there are two

20 possible epitaxial relationships of $\text{BaSi}_2(100)//\text{Si}(001)$ with $\text{BaSi}_2[010]//\text{Si}[110]$ and
21 $\text{BaSi}_2[001]//\text{Si}[110]$, due to the fourfold symmetry of $\text{Si}(001)$. X-ray reciprocal space
22 mapping revealed that the BaSi_2 film was almost strain-free. Plan-view transmission electron
23 microscopy clarified the grain size and the existence of grain boundaries in the BaSi_2 film.

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1. Introduction

Until quite recently, the solar cell market has been growing rapidly with the increasing demand for renewable energy. A decrease in material consumption by decreasing the absorption layer thickness is required, while at the same time improving the energy conversion efficiency to encourage the application of solar cells throughout the world. Most solar cells currently produced are based on crystalline Si, because Si is an abundant and well-known material in the semiconductor industry. However, Si solar cells have two fundamental problems: a low absorption coefficient and an inappropriate band gap (1.1 eV). For these reasons, a sub-millimeter thick Si absorption layer is required, although the maximum conversion efficiency is theoretically limited to ca. 27% in a single pn junction structure [1]. To solve these two problems, we have focused on semiconducting silicides that are composed of abundant elements, and have a large absorption coefficient and an ideal band gap that matches the solar spectrum. Some of these silicides, such as BaSi₂ and β -FeSi₂, have a large absorption coefficient [2-4]. Among them, orthorhombic BaSi₂ has particularly favorable characteristics for a solar cell; the absorption coefficient reaches $3 \times 10^4 \text{ cm}^{-1}$ at 1.5 eV and the band gap of 1.3 eV is more favorable than crystalline Si [5]. We have achieved large photoresponsivity for photon energies greater than the band gap [6,7]. Orthorhombic BaSi₂ is stable at ambient conditions and room temperature (RT), and has lattice constants of $a=0.891$, $b=0.672$, and $c=1.153 \text{ nm}$ [8-10]. This material can be grown epitaxially on a

44 Si(111) substrate with the orientation alignment of BaSi₂(100)//Si(111), with a small lattice
45 mismatch of 1.0% for BaSi₂[010]//Si[112] and 0.1% for BaSi₂[001]//Si[110] [11,12]. With
46 respect to the lattice mismatch, we have considered that the (111) facet of a Si substrate is best
47 for BaSi₂ growth, although the grain size of BaSi₂ is as small as approximately 0.1 μm (as
48 shown later), due to three epitaxial variants rotating around each other by 120° in the surface
49 normal. Many grain boundaries and other defects in a film would deteriorate the optical and
50 electrical properties.

51 We have attempted to grow BaSi₂ on Si(001) substrates rather than Si(111) substrates
52 with an aim to enlarge the grain size by decreasing the number of possible epitaxial variants.
53 A few reports have already demonstrated monolayer-thick BaSi₂ epitaxial growth on Si(001)
54 using reactive deposition epitaxy (RDE), which involves Ba deposition on a hot Si substrate
55 [13,14]. Mckee and Walker reported the epitaxial growth of BaSi₂ thin films on both Si(111)
56 and Si(001) substrates using RDE [15]. *a*-Axis oriented BaSi₂ was surprisingly grown on the
57 Si(001) substrate, despite the large lattice mismatch of 0.1% for BaSi₂[001]//Si[110] and
58 12.5% for BaSi₂[010]//Si[110]. They presented a reflection high-energy electron diffraction
59 (RHEED) pattern and cross-sectional transmission electron microscopy (TEM) image as
60 evidence for the epitaxial growth. However, the detailed growth conditions were not described.
61 In addition, the grown thickness was limited to less than 20 nm. On the basis of the epitaxial
62 relationship they reported, we can expect the epitaxial growth of BaSi₂ films with two

possible epitaxial variants, and enlargement of the grain size by decreasing the number of epitaxial variants from three for BaSi₂ on Si(111) to two for BaSi₂ on Si(001).

2. Experimental procedures

A two stage growth method was adopted, which included RDE and molecular beam epitaxy (MBE; codeposition of Ba and Si) to form thick BaSi₂ films [12]. The RDE process was conducted for deposition of a template layer as a BaSi₂ precursor prior to the subsequent MBE process. The same growth method was successfully utilized for the epitaxial growth of semiconducting β -FeSi₂ films on both Si(001) and Si(111) substrates [16,17]. An ultrahigh vacuum (UHV) chamber equipped with a Knudsen cell for Ba and an electron beam gun for Si was employed. Exact Si(001) substrates were used. Prior to the growth, the Si substrates were prepared by the following treatment. Firstly, the substrates were washed using RCA clean steps, which involved the removal of organic and metallic contaminants. The substrates were then annealed at 830 °C for 30 min in the UHV chamber to evaporate the protective SiO₂ layers. After annealing, a $2\times 1/1\times 2$ streaky RHEED pattern was observed, which indicates that a clean Si surface was obtained.

In the first experiment, the growth temperature was varied over the range from 440 to 530 °C to investigate the crystallinity and morphology of the BaSi₂ films formed after 5 min RDE process. The Ba deposition rate was fixed at 0.9 nm/min. In the second experiment, the

growth temperature of RDE was set at 530 °C and the growth time was increased up to 120 min with a Ba rate of 0.5 nm/min to cover the entire Si(001) surface. MBE growth was conducted after this process at 580 °C. The total thickness of the film was approximately 120 nm. For reference, 240 nm thick BaSi₂ layers were epitaxially grown on Si(111) using the growth conditions presented in Ref. 12. The crystalline quality of the film was evaluated using RHEED and θ -2 θ X-ray diffraction (XRD) measurements. Both pole figure measurement with an azimuthal (ϕ) scan for out of BaSi₂ plane and electron backscatter diffraction pattern (EBSP) measurement were also conducted to determine the crystal orientation of the BaSi₂ variants. The EBSP measurement was carried out at intervals of 0.1 μ m. The surface morphology of the film was investigated using atomic force microscopy (AFM) and the strain in the film was evaluated using X-ray reciprocal space mapping (RSM). Plan-view TEM samples were prepared by mechanical polishing and ion milling, and observed using TOPCON EM-002B operated at 120 kV to investigate grain size, grain boundaries, and dislocations in the film.

3. Results and discussion

Figure 1 shows RHEED patterns obtained along the Si<110> azimuth after 5 min Ba deposition on the Si(001) substrate at various temperatures. Figure 2 presents AFM images of these films, where Si[110] is fixed in an upward direction. We were able to observe a faint

streaky pattern for the sample grown at 440 °C in Fig. 1(a) and two clear sets of streaky patterns with different spacings for the samples grown above 490 °C in Figs. 1(b) and 1(c). The ratio of wide streaky spacing to narrow spacing is approximately 1.7, which is explained by the ratio of $1/b$ to $1/c$. Taking into account that the electron beam was incident along the Si<110> azimuth, these two streaky patterns with different spacings indicate the existence of epitaxial variants rotating 90° to each other in the surface normal, as discussed later; BaSi₂(100)//Si(001) with BaSi₂[010]//Si[110] and BaSi₂[001]//Si[110]. BaSi₂ microcrystals were grown on the surface at 440 °C, and a relatively flat surface was obtained at 490 °C, as shown in Figs. 2(a) and (b), respectively. At 530 °C, three-dimensional islands were grown with a very smooth rectangular-shaped facet. Single-height steps corresponding to the lattice constant a of BaSi₂ were observed on these islands in the cross-sectional line-scan profile shown in Fig. 2(d). The rectangular shape is attributed to the a -axis oriented orthorhombic BaSi₂ unit cell. The crystalline quality of the film grown at 530 °C was excellent, and it was thus decided to conduct the RDE growth at 530 °C.

Figure 3 presents RHEED and θ -2 θ XRD patterns of the BaSi₂ film grown on the Si(001) substrate after MBE. The RHEED pattern observed along the Si<110> azimuth maintained the same two sets of streaky patterns with different spacings during the MBE growth as those observed for the RDE-grown BaSi₂ shown in Figs. 1(b) and 1(c). In Fig. 3, diffraction peaks of only (100)-oriented planes, such as (200), (400), and (600) of BaSi₂, were

observed. It was therefore concluded that the entire film was an a -axis oriented BaSi₂ epitaxial film on the Si(001) substrate. The AFM image shown in Fig. 4 revealed a cross-hatched pattern for the surface of the BaSi₂ film, which is caused by two epitaxial variants having different crystallographic orientation. The white arrow in Fig. 4 indicates the Si<110> direction. Steps were observed on every rectangular island after the MBE growth.

EBSP mapping observed along the normal direction (ND), reference direction (RD), and transverse direction (TD) are shown in Fig. 5. The color in the maps corresponds to the indices of BaSi₂ in the inverse pole figure shown in Fig. 5(d). For the ND map, the green area is dominant in the film, which indicates that BaSi₂ is a -axis oriented, and is consistent with the θ - 2θ XRD results. For the RD and TD maps, there are two colored areas, blue and red, which represent the (010) and (001) planes of BaSi₂, respectively. The RD is perpendicular to the TD; therefore, the red area in the RD map changes to blue in the TD map, and vice versa. Figures 6(a) and 6(b) show an X-ray pole figure and ϕ scan pattern for the BaSi₂(301) plane. Four inner peaks of the BaSi₂(301) plane were detected near the center of the circle and each peak has 90° spacing in the ϕ angle. Four other outer peaks caused by the BaSi₂(203) plane were also detected due to the small difference in the lattice spacing between the (301) and (203) planes. This is because the BaSi₂ film has two variants and fourfold symmetry with respect to the Si(001) substrate, as illustrated in Fig. 7. On the basis of these results, the epitaxial relationship of BaSi₂(100)//Si(001) with BaSi₂[001]//Si[110] and

BaSi₂[010]//Si[110] was confirmed. This epitaxial relationship explains the RHEED and EBSD results presented. However, considering the crystal orientation of the epitaxial variants, a large lattice mismatch of 12.5% was presumed along BaSi₂[010]//Si[110]. RSM measurement was conducted to evaluate the distortion in the film and revealed that the BaSi₂ film was almost strain-free. For the RSM of BaSi₂ (502) and (620), the lattice constants of *a*, *b*, and *c* in BaSi₂ were determined to be 0.8898, 0.6777, and 1.1588 nm, respectively, as deduced from the peak positions presented in Figs. 8(a) and 8(b). These values were almost the same as those of bulk BaSi₂, which indicates no significant distortion in the in-plane and normal directions of the film. It was considered that the epitaxial BaSi₂ film was grown using the point-on-line configuration, which is well known as the organic crystal growth mode [18,19]. Orthorhombic BaSi₂ has low symmetry and an extremely large lattice mismatch with respect to Si(001), so that it is impossible to induce distortion in the BaSi₂ film.

Figure 9(a) shows a plan view bright-field TEM image of the film. We can see the grains of more than 1 μm in diameters, and maximum grain size determined in this observation was about 6 μm. Moreover, some small dislocations and grain boundaries were observed, but there were not any remarkable defects in this area. Several dark lines are bend contour which indicate crystal lattice bending, and not dislocations. It is assumed that these lattice bending were occurred in TEM sample preparation. Figs. 9(b) and (c) are selected-area electron diffraction (SAED) patterns observed along the [100] zone axis of BaSi₂ for areas I

and II, respectively. The SAED patterns in the neighboring areas I and II, separated by a grain boundary were hexagonal shaped with rotational symmetries through 90° , as shown in Figs. 9(b) and 9(c). Similar SAED patterns showing the coexistence of 90° rotational domains were observed for a -axis oriented orthorhombic β -FeSi₂ on Si(001) [20]. These results also support our discussion regarding the BaSi₂ variants and confirm that a decrease in the number of the epitaxial variants is quite effective to increase the volume per one grain. Figure 9(d) shows a typical example of a plan view bright-field TEM image for the BaSi₂ epitaxial film on Si(111); approximately 120° sharp grain boundaries due to epitaxial variants of BaSi₂ rotating each other by 120° in the surface normal are evident [12]. Comparing the plan view TEM images shown in Figs. 9(a) and 9(d), it was concluded that the grain size of BaSi₂ on Si(001) is much larger than that on Si(111). We speculate that the large grain of BaSi₂ on Si(001) is partly due to the reduced number of epitaxial variants. However, the difference in grain size is significantly larger than expected. Thus, further studies are required to clarify the mechanism that explains this difference.

4. Conclusions

Epitaxial BaSi₂ films were successfully grown on a Si(001) substrate using a two step growth method including RDE and MBE. The RDE growth temperature was quite effective for the growth mode of BaSi₂ on Si(001) substrate. RHEED, θ - 2θ and pole figure

177 XRD measurements, and EBSP provided evidence that the BaSi₂ film is *a*-axis oriented with
178 90° rotational epitaxial variants: BaSi₂(100)//Si(001) with BaSi₂[010]//Si[110] or
179 BaSi₂[001]//Si[110]. The BaSi₂ film was almost strain-free, despite a large lattice mismatch.
180 Plan-view TEM revealed that the grain size of BaSi₂ on Si(001) was much larger than that on
181 Si(111).

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Fig. 1. RHEED patterns of BaSi₂ films grown on Si(001) substrates at (a) 440, (b) 490, and (c) 530 °C along the Si<110> azimuth after 5 min RDE process.

Fig. 2. AFM images of BaSi₂ films grown on Si(001) substrates at (a) 440, (b) 490, and (c) 530 °C after 5 min RDE process.

Fig. 3. RHEED and θ -2 θ XRD patterns of BaSi₂ film on Si(001) substrates using two step growth including RDE (at 530 °C) and MBE (at 580 °C) processes.

Fig. 4. AFM images showing a cross-hatched pattern taken from the 120 nm thick BaSi₂ film on a Si(001) substrate.

Fig. 5. (a) ND, (b) RD, and (c) TD maps of EBSD for the 120 nm thick BaSi₂ film on Si(001) substrate. (d) Inverse pole figure of BaSi₂ corresponding to the colors indicated in the maps.

Fig. 6. (a) X-ray pole figure and (b) ϕ scan for BaSi₂ (301) exhibiting fourfold symmetry.

Fig. 7. Schematic model of BaSi₂ film having two epitaxial variants on Si(001).

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237 **Fig. 8.** RSM for BaSi₂ (502) and (620) of the 120 nm thick BaSi₂ film on a Si(001) substrate.

238 Red and blue colors indicate the highest and lowest intensities, respectively.

239

240 **Fig. 9.** (a) Plan view bright-field TEM image of the 120 nm thick BaSi₂ film on a Si(001)

241 substrate. The incident electron beam direction was parallel to BaSi₂ [100] zone axis. SAED

242 patterns for (b) area I and (c) area II. The 90° rotational symmetry of the SAED patterns for

243 areas I and II indicates the coexistence of 90° rotational domains of *a*-axis oriented BaSi₂. (d)

244 Plan view bright-field TEM image of the 240 nm thick BaSi₂ film on a Si(111) substrate.

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