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1 **Formation of large-grain-sized BaSi₂ epitaxial layers grown on Si(111)**
2 **by molecular beam epitaxy**

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4 M. Baba^a, K. Toh^a, K. Toko^a, K. O. Hara^b, N. Usami^{b,d}, N. Saito^c, N. Yoshizawa^c, and
5 T. Suemasu^{a,d}

6

7 ^a*Institute of Applied Physics, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan*

8 ^b*Institute for Materials Research, University of Tohoku, Sendai, Miyagi 980-8577, Japan*

9 ^c*Electron Microscope Facility, IBEC Innovation Platform, AIST, Tsukuba 305-8569*

10 ^d*Japan Science and Technology Agency, CREST, Chiyoda, Tokyo 102-0075, Japan*

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12 **Corresponding author:** T. Suemasu

13 Institute of Applied Physics, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan

14 TEL/FAX: +81-29-853-5111, Email: suemasu@bk.tsukuba.ac.jp

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18 BaSi₂ epitaxial films were grown on Si(111) substrates by a two-step growth method
19 including reactive deposition epitaxy (RDE) and molecular beam epitaxy (MBE). To enlarge
20 the grain size of BaSi₂, the Ba deposition rate and duration were varied from 0.25 to 1.0
21 nm/min and from 5 to 120 min during RDE, respectively. The effect of post-annealing was
22 also investigated at 760 °C for 10 min. Plan-view transmission electron micrographs indicated
23 that the grain size in the MBE-grown BaSi₂ was significantly increased up to approximately
24 4.0 μm, which is much larger than 0.2 μm, reported previously.

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29 grain

30

31 **1. Introduction**

32 The solar cell market has been growing rapidly with the increasing demand for
33 renewable energy, and new materials for high-efficiency thin-film solar cells are of significant
34 interest. However, little steadfast effort has been devoted to any materials other than Si, CIGS
35 (copper indium gallium selenide), CdTe and III-V compounds as far as inorganic
36 semiconductors are concerned. Among such materials, we have focused on barium disilicide
37 (BaSi_2) as a promising material for solar cell applications. Semiconducting BaSi_2 has a band
38 gap of approximately 1.3 eV and a very large absorption coefficient of $3 \times 10^4 \text{ cm}^{-1}$ at 1.5 eV
39 [1-3]. In our previous works, we have achieved large photoresponsivities in undoped *n*-type
40 BaSi_2 epitaxial layers on Si(111) and polycrystalline BaSi_2 layers on SiO_2 [4-6]. BaSi_2 can be
41 grown epitaxially on both Si(111) and Si(001) [7,8]. Very recently, we have found a large
42 minority-carrier diffusion length of over 9 μm in undoped *n*-type BaSi_2 epitaxial layers [9].
43 Thus, BaSi_2 is considered to be a promising material for solar cell applications. However, the
44 grain size of BaSi_2 epitaxial films is typically as small as approximately 0.2 μm [9], due to
45 three epitaxial variants rotated by 120° about the surface normal [10]. Grain boundaries (GBs)
46 often function as recombination centers for minority carriers [11,12]; therefore, improved
47 photoresponsivity in BaSi_2 epitaxial films is expected with much larger grains. Thus, the
48 formation of large grains is important for solar cell applications. We have previously
49 succeeded in the expansion of BaSi_2 grains in films using vicinal Si(001) and Si(111)

50 substrates [13,14]. In this paper, we aimed to form large-grain-sized BaSi₂ exceeding 1 μm on
51 exact Si(111) substrates by adjusting the growth conditions and post-annealing.

52

53 **2. Experimental**

54 A two-step growth method was adopted that included reactive deposition epitaxy
55 (RDE; Ba deposition on hot Si) for BaSi₂ template layers [15], and subsequent molecular
56 beam epitaxy (MBE; codeposition of Ba and Si on Si) to form thick BaSi₂ films. Details of
57 the growth procedure have been previously described [9,13]. Prior to growth, exact Si(111)
58 substrates were cleaned by RCA washing, followed by thermal cleaning in ultrahigh vacuum.

59 A 7×7 streaky reflection high-energy electron diffraction (RHEED) pattern indicated that a
60 clean Si surface was obtained. The sample preparation details are summarized in Table 1. The
61 substrate temperature T_{RDE} , was set to 500 or 600 °C, and the Ba deposition rate R_{Ba} , was
62 varied from 0.25 to 1.0 nm/min to form BaSi₂ template layers by RDE. Also the duration of
63 growth by RDE t_{RDE} , was increased from 5 to 120 min, while R_{Ba} was decreased from 1 to
64 0.25 nm/min to enhance migration of Ba atoms on the surface. t_{RDE} was determined so that the
65 entire Si surface was covered sufficiently with BaSi₂ template layers by atomic force
66 microscopy (AFM). Both Ba and Si were then deposited on these template layers to form
67 BaSi₂ by MBE. The substrate temperature T_{MBE} was set to 580 °C, and the MBE growth
68 duration t_{MBE} was 60 min for 100-nm-thick BaSi₂ in samples A-D, and 240 min for

69 500-nm-thick BaSi₂ in sample E. Post annealing was performed for samples D and E at
70 760 °C for 10 min after MBE. This temperature was chosen because the desorption of Ba
71 atoms from grown BaSi₂ films occurs around 800 °C. The crystalline quality of the films was
72 evaluated using RHEED, θ -2 θ X-ray diffraction (XRD) and the crystal-plane direction was
73 observed using electron backscatter diffraction (EBSD). The EBSD measurement was carried
74 out at intervals of 0.1 μ m. Transmission electron microscopy (TEM; Topcon EM-002B,
75 operated at 120 kV) of film surfaces after mechanical polishing and ion milling was employed
76 to investigate the grain size of BaSi₂.

77

78 **3. Results and discussion**

79 Sharp streaky RHEED patterns were obtained for samples A-D, observed along the
80 Si[1-10] azimuth, and θ -2 θ XRD peaks of only (100)-oriented BaSi₂ planes, such as the (200),
81 (400) and (600) planes were obtained, as previously reported [9]. These results indicate the
82 successful growth of highly *a*-axis-oriented BaSi₂ epitaxial films.

83 Figures 1(a)-1(c) show the AFM images taken after RDE growth for samples A-C,
84 respectively. Many island domains of approximately 0.3 μ m in size are evident in Fig. 1(a).
85 As R_{Ba} is decreased, and both t_{RDE} and T_{RDE} are increased, step-and-terrace structures become
86 dominant, as shown in Figs. 1(b) and 1(c). The step height is approximately 0.9 nm, which
87 corresponds to *a*-axis lattice parameter in BaSi₂ [16,17]. This is attributed to enhanced lateral

88 migration of Ba atoms on the surface.

89 Figures 2(a)-2(d) show dark-field (DF) plan-view TEM observations for samples
90 A-D, taken under a two-beam diffraction condition to clarify the grain size of BaSi₂.
91 Selected-area diffraction (SAED) patterns are also shown. The diffraction vector \mathbf{g} was set to
92 be $\langle 004 \rangle$. Under these conditions, the diffraction spot corresponding to the (004) plane
93 becomes bright in the SAED patterns, while other spots denoted by (00n) ($n = \pm 1, \pm 2, \pm 3, \dots$)
94 are also evident. Note that those BaSi₂ grains that satisfy Bragg's condition of diffraction
95 become bright; one of the three BaSi₂ epitaxial variants becomes bright, which provides
96 information regarding the grain size. A detailed discussion of the grain boundaries (GBs) in
97 BaSi₂ was given in our previous report [9]. Figure 2(a) shows that the grain size of BaSi₂ is
98 approximately 0.2 μm in sample A, which is typical for BaSi₂ layers [9]. The grains in
99 samples B and C are significantly expanded, showing that the grains of the RDE-grown BaSi₂
100 template layers significantly affect those of MBE-grown BaSi₂ films. Regarding sample D,
101 the curvature of the sample made it difficult to investigate the grain size of BaSi₂ by TEM,
102 but the grain size in sample D became apparently larger than that in sample A. This means
103 that the post-annealing is a very effective means to enhance the grain size of BaSi₂. The
104 difference in growth conditions between samples A and D is that the post-annealing was
105 performed on sample D. Thus, it is considered that the 0.2- μm -sized BaSi₂ grains in sample A
106 coalesced with each other during the post-annealing, growing in much larger grains.

107 In order to observe the BaSi₂ grains in the wider range, EBSD mappings were
108 performed. Figures 3(a)-3(d) show EBSD images obtained along the transverse direction (TD)
109 for samples A-C and E, respectively. We can see three colors represented by red, green, and
110 blue, indicating three epitaxial variants of *a*-axis-oriented BaSi₂ on Si(111) [9,10]. The grain
111 size can be roughly determined from the areas of regions with the same color. As shown in
112 Fig. 3 (b), the grains in sample B are the largest among the four, extending to more than 4 μm,
113 and this is the largest grain we have ever achieved. In Fig. 3(b), green area dominates. But we
114 don't think that there is a mechanism which makes one of the three domains larger than the
115 others. Observation of EBSD mappings in a much wider area will give us correct EBSD
116 mappings. The grain size of BaSi₂ in sample C is approximately 2.0 μm, which is also much
117 larger than that in sample A, but smaller than that in sample B, indicating that there is an
118 optimum condition for RDE to expand the grains of BaSi₂. As for the effect of post-annealing,
119 the grains in sample E are much larger than that in sample A. As discussed in Fig. 2(d),
120 post-annealing also increased the grains of 100-nm-thick BaSi₂ in sample D. On the basis of
121 these results, we concluded that the optimization of RDE growth conditions for large-grained
122 BaSi₂ templates and the post-annealing are both effective to enlarge the grains of BaSi₂
123 epitaxial films on Si(111).

124

125 **4. Summary**

126 We attempted to grow BaSi₂ epitaxial layers with large grains by adjusting the RDE
127 growth conditions and the post-annealing, and successfully achieved a grain size of over 4.0
128 μm by decreasing R_{Ba} and increasing t_{RDE} . The grain size was confirmed by plan-view TEM
129 observations and EBSD maps. We also found that post-annealing at 760 °C for 10 min
130 extended the grains of BaSi₂.

131

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138 **References**

- 139 [1] K. Morita, Y. Inomata, T. Suemasu, *Thin Solid Films* 508 (2006) 363.
- 140 [2] D. B. Migas, V. L. Shaposhnikov, V.E. Borisenko, *Phys. Status Solidi B* 244 (2007) 2611.
- 141 [3] K. Toh, T. Saito, T. Suemasu, *Jpn. J. Appl. Phys.* 50 (2011) 068001.
- 142 [4] W. Du, M. Suzuno, M. A Khan, K. Toh, M. Baba, K. Nakamura, K. Toko, N. Usami, T.
- 143 Suemasu, *Appl. Phys. Lett.* 100 (2012) 152114.
- 144 [5] Y. Matsumoto, D. Tsukada, R. Sasaki, M. Takeishi, T. Suemasu, *Appl. Phys. Express* 2
- 145 (2009) 021101.
- 146 [6] D. Tsukada, Y. Matsumoto, R. Sasaki, M. Takeishi, T. Saito, N. Usami, T. Suemasu, *Appl.*
- 147 *Phys. Express* 2 (2009) 051601.
- 148 [7] R. A. Mckee, F. J. Walker, J. R. Conner, E. D. Specht, D. E. Zelmon, *Appl. Phys. Lett.* 59
- 149 (1991) 782.
- 150 [8] R. A. Mckee, F. J. Walker, *Appl. Phys. Lett.* 63 (1993) 2818.
- 151 [9] M. Baba, K. Toh, K. Toko, N. Saito, N. Yoshizawa, K. Jiptner, T. Sekiguchi, K. O Hara, N.
- 152 Usami, T. Suemasu, *J. Cryst. Growth* 348 (2012) 75.
- 153 [10] Y. Inomata, T. Nakamura, T. Suemasu, F. Hasegawa, *Jpn. J. Appl. Phys.* 43 (2004) L478.
- 154 [11] J. Chen, T. Sekiguchi, D. Yang, F. Yin, K. Kido, S. Tsurekawa, *J. Appl. Phys.* 96 (2004)
- 155 5490.
- 156 [12] I. Gordon, L. Cernel, D. Van Gestel, G. Beaucarne, J. Poortmans, *Thin Solid Films* 516

157 (2008) 6984.

158 [13] K. Toh, K. O. Hara, N. Usami, N. Saito, N. Yoshizawa, K. Toko, T. Suemasu, *J. Cryst.*

159 *Growth* 345 (2012) 16.

160 [14] K. O. Hara, N. Usami, K. Toh, K. Toko, T. Suemasu, *Jpn. J. Appl. Phys.* 51 (2012)

161 10NB06.

162 [15] Y. Inomata, T. Nakamura, T. Suemasu, F. Hasegawa, *Jpn. J. Appl. Phys.* 43 (2004) 4155.

163 [16] J. Evers, G. Oehlinger, A. Weiss, *Angew. Chem., Int. Ed.* 16 (1977) 659.

164 [17] M. Imai, T. Hirano, *Phys. Rev. B* 58 (1998) 11922.

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171 Fig. 1. (a)-(c) AFM images after RDE growth for samples A-C, respectively.

172

173 Fig. 2. DF TEM images for (a) sample A, (b) sample B, (c) sample C, and (d) sample D

174 obtained under a two-beam diffraction condition using the diffraction vector $\mathbf{g} = \langle 004 \rangle$ for

175 one of the three epitaxial variants.

176

177 Fig. 3. TD EBSD images for (a) sample A, (b) sample B, (c) sample C, and (d) sample E. The

178 relationship between the three epitaxial variants (red, green, and blue) are also shown.

Table 1: Growth conditions for samples A-E.

Sample	R_{Ba}	T_{RDE}	t_{RDE}	T_{MBE}	t_{MBE}	Annealing
	(nm/min)	(°C)	(min)	(°C)	(min)	
A	1.0	500	5	580	60	w/o
B	0.5	600	60	580	60	w/o
C	0.25	600	120	580	60	w/o
D	1.0	500	5	580	60	760 °C, 10 min
E	1.0	500	5	580	240	760 °C, 10 min

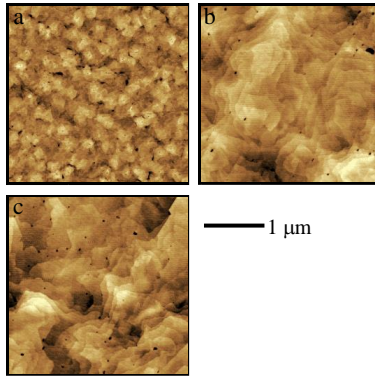


Fig. 1

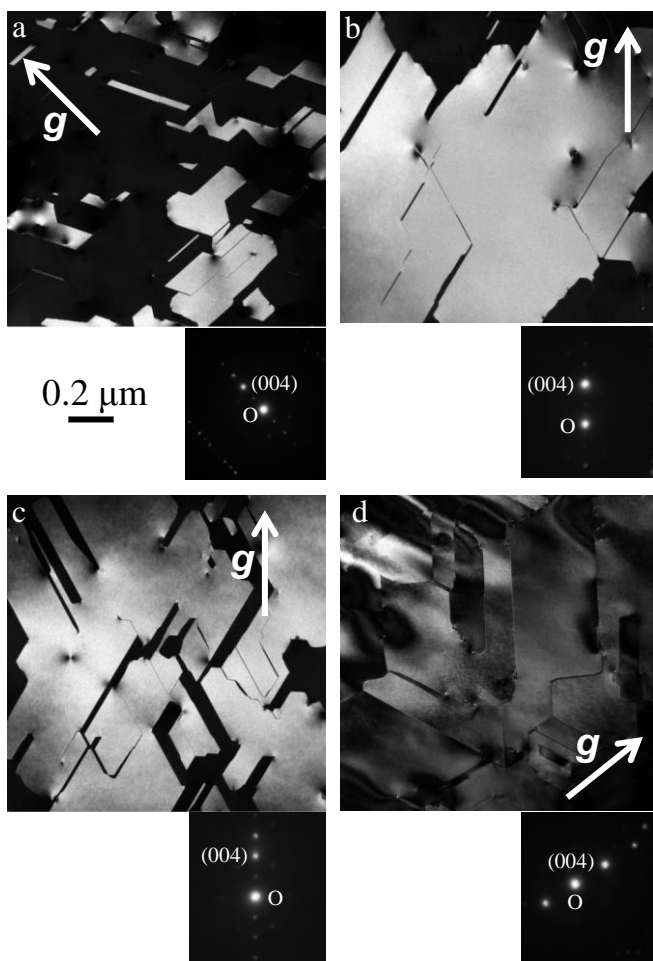


Fig. 2

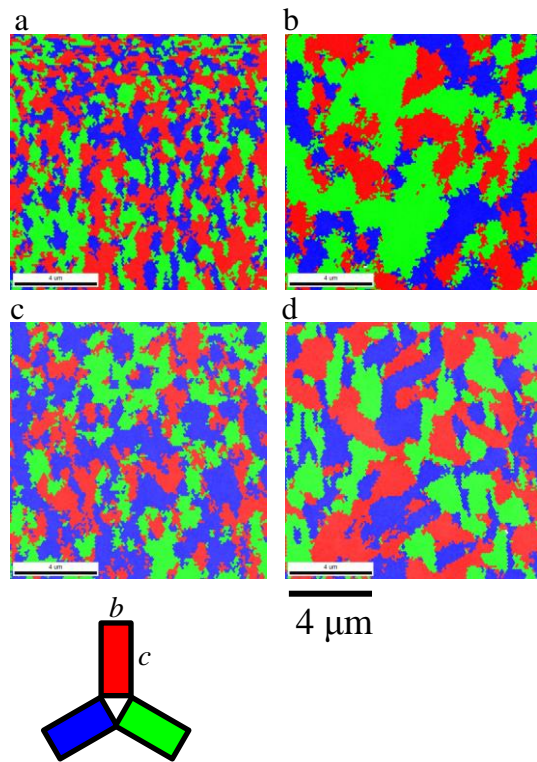


Fig. 3