

Large photoresponsivity in semiconducting BaSi₂ epitaxial films grown on Si(0 0 1) substrates by molecular beam epitaxy

著者別名	都甲 薫, 末益 崇
journal or publication title	Journal of crystal growth
volume	378
page range	198-200
year	2013-09
権利	(C) 2013 Elsevier B.V. NOTICE: this is the author ' s version of a work that was accepted for publication in Journal of crystal growth. Changes resulting from the publishing process, such as peer review, editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version was subsequently published in Journal of crystal growth, 378, 2013 http://dx.doi.org/10.1016/j.jcrysgro.2012.12.052
URL	http://hdl.handle.net/2241/119788

doi: 10.1016/j.jcrysgro.2012.12.052

1 **Large photoresponsivity in semiconducting BaSi₂ epitaxial films grown**
2 **on Si(001) substrates by molecular beam epitaxy**

3 S. Koike^a, K. Toh^a, M. Baba^a, K. Toko^a, K. O. Hara^b, N. Usami^{b,c}, N. Saito^d,

4 N. Yoshizawa^d, T. Suemasu^{a,c}

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

6 ^b*Institute for Materials Research, Tohoku University, Sendai, Miyagi 980-8577,*

7 *Japan*

8 ^c*Japan Science and Technology Agency, CREST, Chiyoda, Tokyo 102-0075, Japan*

9 ^d*National Institute of Advanced Industrial Science and Technology, Tsukuba,*

10 *Ibaraki 305-8568, Japan*

11

12 **Corresponding author:** T. Suemasu

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

14 Japan

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

16

17 Approximately 900- and 400-nm-thick BaSi₂ epitaxial films were grown on Si(111)
18 and Si(001) substrates, respectively, by molecular beam epitaxy, and their
19 photoresponse properties were compared at room temperature. When the bias
20 voltage V_{bias} applied between the 1.5-mm-spacing stripe-shaped electrodes on the
21 BaSi₂ surfaces increased, photocurrents were clearly observed for photon energies
22 greater than the band gap for both samples. However, the photoresponsivity for
23 BaSi₂ on Si(001) was more than 8 times larger than that for BaSi₂ on Si(111);
24 reaching approximately 50 and 5 mA/W at 1.6 eV, respectively, when V_{bias} was 1.0
25 V. This is attributed to the difference in the grain size of BaSi₂ films confirmed by
26 plan-view transmission electron microscopy.

27

28

29 PACS: 78.40.Fy

30 **Keywords:** B1. Semiconducting silicides; B2. BaSi₂; B3. Solar cell; A3. MBE; A1.

31 Large grain

32

33

34 1. Introduction

35 It is important for solar cell materials to have a large absorption coefficient
36 and a suitable band gap that matches the solar spectrum to yield high conversion
37 efficiency. Among such materials, we have focused on semiconducting
38 orthorhombic BaSi₂. The band gap of BaSi₂ is approximately 1.3 eV and can be
39 increased up to 1.4 eV in Ba_{1-x}Sr_xSi₂ [1,2], which matches the ideal solar spectrum
40 much better than crystalline Si. In addition, BaSi₂ has a very large absorption coefficient
41 α of approximately $3 \times 10^4 \text{ cm}^{-1}$ at 1.5 eV [2]. A large value of α and expansion of the
42 band gap in Ba_{1-x}Sr_xSi₂ were theoretically expected [3,4]. BaSi₂ can be grown
43 epitaxially on a Si(111) substrate with the orientation alignment of
44 BaSi₂(100)//Si(111), with a small lattice mismatch of 1.0% for BaSi₂[010]//Si[112]
45 [5]. Therefore, lots of studies have been done on BaSi₂ epitaxial films grown on
46 Si(111) by molecular beam epitaxy (MBE). Recently, we have achieved large
47 photoresponsivity in undoped *n*-type BaSi₂ epitaxial layers on Si(111) and
48 polycrystalline BaSi₂ layers on (111)-oriented polycrystalline Si layers on SiO₂
49 [6-8]. With respect to the lattice mismatch, we have considered that the (111) facet
50 of a Si substrate is best for BaSi₂ growth, although the grain size of BaSi₂ is as
51 small as approximately 0.2 μm [9]. This is because of three epitaxial variants, due

52 to the sixfold symmetry of Si(111) [10], rotating around each other by 120° in the
53 surface normal. Many grain boundaries and other defects in a film would deteriorate
54 the optical and electrical properties. Thus, it is important to increase the grain size
55 of BaSi₂ films. Note that *a*-axis oriented BaSi₂ was surprisingly grown on the
56 Si(001) substrate, despite the large lattice mismatch of 0.1% for
57 BaSi₂[001]//Si[110] and 12.5% for BaSi₂[010]//Si[110] [5]. Very recently, we
58 found that the grain size of *a*-axis-oriented BaSi₂ epitaxial layers on Si(001) is more
59 than 1 μm, much larger than that on Si(111) [11]. However, we have not yet
60 measured photoresponse properties of BaSi₂ epitaxial films on Si(001). In this paper,
61 we aimed to compare the photoresponsivity of BaSi₂ grown on Si(001) with that on
62 Si(001), already reported in Ref. [7].

63

64 **2. Experimental**

65 An ion-pumped MBE system equipped with standard Knudsen cells for Ba
66 and Sb, and an electron-beam evaporation source for Si was used. After cleaning
67 Czochralski n-Si(111) ($\rho=0.015 \Omega\cdot\text{cm}$) and n-Si(001) ($\rho=0.07 \Omega\cdot\text{cm}$) substrates at
68 850 °C for 30 min in ultrahigh vacuum, approximately 850- and 350-nm-thick
69 undoped *n*-BaSi₂ epitaxial films were grown on Si(111) and Si(001) substrates,

70 respectively, by reactive deposition epitaxy (RDE; Ba deposition on hot Si) for
71 BaSi₂ template layers, and subsequent MBE (codeposition of Ba and Si on Si) to
72 form thick BaSi₂ films. Details of the growth procedure have been previously
73 described [7,11]. Finally, approximately 50-nm-thick Sb-doped n⁺-BaSi₂ (~10²⁰
74 cm⁻³) layer was formed for ohmic contacts [12]. For photoresponse measurements,
75 Cr and Au were evaporated on the surface to form 1.5-mm-spacing stripe-shaped
76 electrodes. The photocurrent flowing in the lateral direction between the electrodes was
77 evaluated by a lock-in technique using a 150 W Xenon lamp (5 mW/cm² at 470 nm)
78 with a 25-cm focal-length single monochromator (Bunkoukeiki SM-1700A). The light
79 intensity was calibrated by a pyroelectric sensor (MELLES GRIOT 13PEM001/J). The
80 crystalline quality of the grown films was characterized by reflection high-energy
81 electron diffraction (RHEED), X-ray diffraction (XRD), and transmission electron
82 microscopy (TEM).

83

84 **3. Results and discussion**

85 Figure 1 show the RHEED patterns of BaSi₂ films after (a) RDE at 550 °C
86 and (a') MBE at 600 °C on Si(111), and after (b) RDE at 530 °C and (b') MBE at
87 580 °C on Si(001) substrates. The RHEED patterns were observed along the Si[11-2]

88 and Si[110], respectively. We can see clear streaky RHEED patterns for BaSi₂ films
89 on Si(111), which is typical for *a*-axis-oriented BaSi₂ epitaxial films [13]. On the
90 other hand, two clear sets of streaky patterns with different spacings are seen for
91 BaSi₂ on Si(001), in Figs. 1(b) and 1(b'). The ratio of wide streaky spacing to
92 narrow spacing is approximately 1.7, which is explained by the ratio of $1/b$ to $1/c$.
93 Taking into account that the electron beam was incident along the Si[110] azimuth,
94 these two streaky patterns with different spacings indicate the existence of two epitaxial
95 variants rotating 90° to each other in the surface normal; BaSi₂(100)//Si(001) with
96 BaSi₂[010]//Si[110] and BaSi₂[001]//Si[110] [11].

97 Figures 2(a) and 2(b) present the θ - 2θ XRD patterns of BaSi₂ films on
98 Si(111) and Si(001) substrates, respectively. The diffraction peaks at $2\theta = 20^\circ, 41^\circ,$
99 63° correspond to BaSi₂(200), (400), and (600) planes, respectively, indicating that
100 highly *a*-axis-oriented BaSi₂ films were grown.

101 Figures 3(a) and 3(b) shows the plan-view bright-field (BF) TEM images of
102 BaSi₂ films on (a) Si(111) and (b) Si(001) substrates. The incident electron beam was
103 almost parallel to the BaSi₂[100] zone axis, but was slightly tilted for the grain
104 boundaries (GBs) to be seen clearly. We can easily see that the grain size of the BaSi₂
105 film on Si(111) is approximately 0.2 μm . In contrast, the grains of more than 1 μm in

106 diameters exist in the BaSi₂ film on Si(001) in Fig. 3(b). We speculate that the large
107 grain of BaSi₂ on Si(001) is partly due to the reduced number of epitaxial variants from
108 three for BaSi₂ on Si(111) to two for BaSi₂ on Si(001). However, the difference in grain
109 size is significantly larger than expected. Thus, further studies are required to clarify the
110 mechanism that explains this difference.

111 Figures 4(a) and 4(b) show the photoresponse spectra measured at RT under
112 various bias voltages applied between the 1.5-mm-spacing stripe-shaped Au/Cr
113 electrodes on the surface of BaSi₂ films on (a) Si(111) and (b) Si(001) substrates. In
114 both samples, photocurrents increased sharply with increasing bias voltages V_{bias} for
115 photon energies greater than the band gap. However, the magnitude of
116 photoresponsivity differed significantly between them. The photoresponsivity
117 reached 13 mA/W at 1.6 eV for BaSi₂ on Si(111) when V_{bias} was 2.5 V on Si(111),
118 while it marked approximately 100 mA/W for BaSi₂ on Si(001). This difference is
119 attributed to the difference in the grain size of BaSi₂ films. It should be noted that in
120 the photoresponse spectra, peaks become pronounced at 1.46 eV. This is due to the
121 non-linear property of the photocurrent caused by the intense line-shaped spectrum
122 of the Xenon light at this photon energy. On the basis of these results, we concluded
123 that the further improvement of photoresponsivity in BaSi₂ epitaxial films is

124 expected with much larger grains. In this sense, a Si(001) face is more preferable
125 for BaSi₂ than a Si(111) surface.

126

127 4. **Summary**

128 Approximately 900- and 400-nm-thick BaSi₂ epitaxial films were grown on
129 Si(111) and Si(001) substrates, respectively, by MBE. Plan-view BF TEM images
130 revealed that the grain size of BaSi₂ on Si(001) was more than 1 μm, while that on
131 Si(111) was approximately 0.2 μm. When the bias voltage V_{bias} was 2.5 V, the
132 photoresponsivity reached 100 mA/W for BaSi₂ on Si(001) at 1.6 eV. On the other
133 hand, it was only 13 mA/W for BaSi₂ on Si(111).

134

135 **Reference**

- 136 [1] K. Morita, M. Kobayashi, T. Suemasu, *Jpn. J. Appl. Phys.* 45 (2006) L390.
- 137 [2] K. Toh, T. Saito, T. Suemasu, *Jpn. J. Appl. Phys.* 50 (2011) 068001.
- 138 [3] D. B. Migas, V. L. Shaposhnikov, V. E. Borisenko, *Phys. Status Solidi B* 244 (2007)
- 139 2611.
- 140 [4] Y. Imai, A. Watanabe, *Thin Solid Films* 515 (2007) 8219.
- 141 [5] R. A. Mckee, F. J. Walker, *Appl. Phys. Lett.* 63 (1993) 2818.
- 142 [6] W. Du, M. Suzuno, M. A Khan, K. Toh, M. Baba, K. Nakamura, K. Toko, N. Usami,
- 143 T. Suemasu, *Appl. Phys. Lett.* 100 (2012) 152114.
- 144 [7] Y. Matsumoto, D. Tsukada, R. Sasaki, M. Takeishi, T. Suemasu, *Appl. Phys. Express*
- 145 2 (2009) 021101.
- 146 [8] D. Tsukada, Y. Matsumoto, R. Sasaki, M. Takeishi, T. Saito, N. Usami, T. Suemasu,
- 147 *Appl. Phys. Express* 2 (2009) 051601.
- 148 [9] M. Baba, K. Toh, K. Toko, N. Saito, N. Yoshizawa, K. Jiptner, T. Sekiguchi, K.
- 149 O. Hara, N. Usami, T. Suemasu, *J. Cryst. Growth* 348 (2012) 75.
- 150 [10] Y. Inomata, T. Nakamura, T. Suemasu, F. Hasegawa, *Jpn. J. Appl. Phys.* 43
- 151 (2004) L478.
- 152 [11] K. Toh, K. O. Hara, N. Usami, N. Saito, N. Yoshizawa, K. Toko, T. Suemasu, *J.*

- 153 Cryst. Growth 345 (2012) 16.
- 154 [12] M. Kobayashi, Y. Matsumoto, Y. Ichikawa, D. Tsukada, T. Suemasu, Appl.
155 Phys. Express 1 (2008) 051403.
- 156 [13] T. Suemasu, M. Sasase, Y. Ichikawa, M. Kobayashi, D. Tsukada, J. Cryst.
157 Growth 310 (2008) 1250.

Fig. 1 RHEED patterns of BaSi₂ films after (a) RDE at 550 °C and (a') MBE at 600 °C on Si(111), and after (b) RDE at 530 °C and (b') MBE at 580 °C on Si(001) substrates, observed along Si [110] and Si[11-2], respectively. The arrows show the existence of two sets of streaky patterns with different spacings for BaSi₂ on Si(001).

Fig. 2 θ - 2θ XRD patterns of BaSi₂ films on (a) Si(111) and (b) Si(001) substrates. The forbidden diffraction peaks caused by the Si substrates are indicated by asterisks.

Fig. 3 Plan-view BF TEM images of BaSi₂ films on (a) Si(111) and (b) Si(001) substrates. The incident electron beam was almost parallel to the BaSi₂[100] zone axis, but was slightly tilted for the GBs to be seen clearly.

Fig. 4 Photoresponse spectra measured at RT under various bias voltages applied between the 1.5-mm-spacing stripe-shaped Au/Cr electrodes on the surface of BaSi₂ films on (a) Si(111) and (b) Si(001) substrate

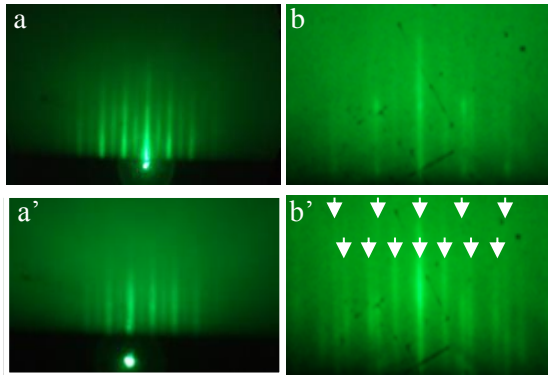


Fig. 1

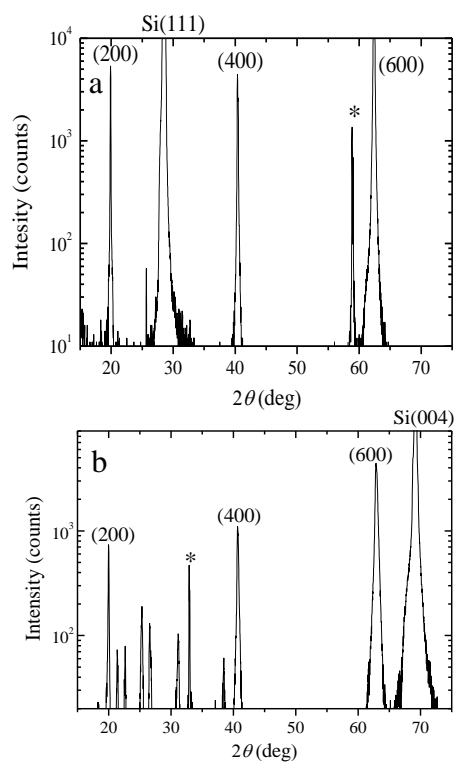


Fig. 2

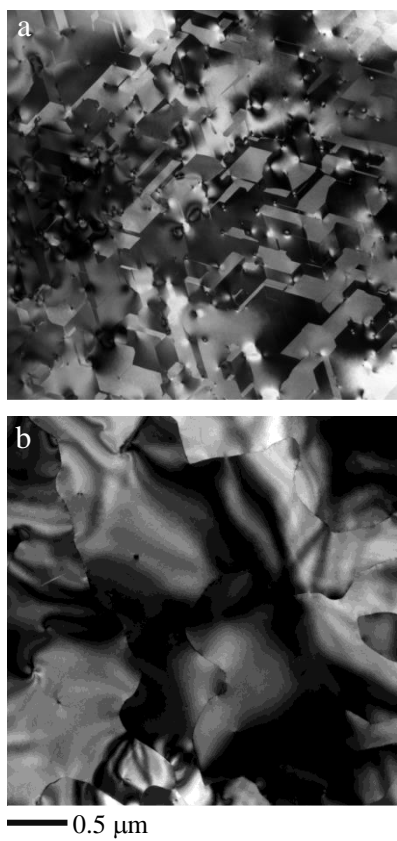


Fig. 3

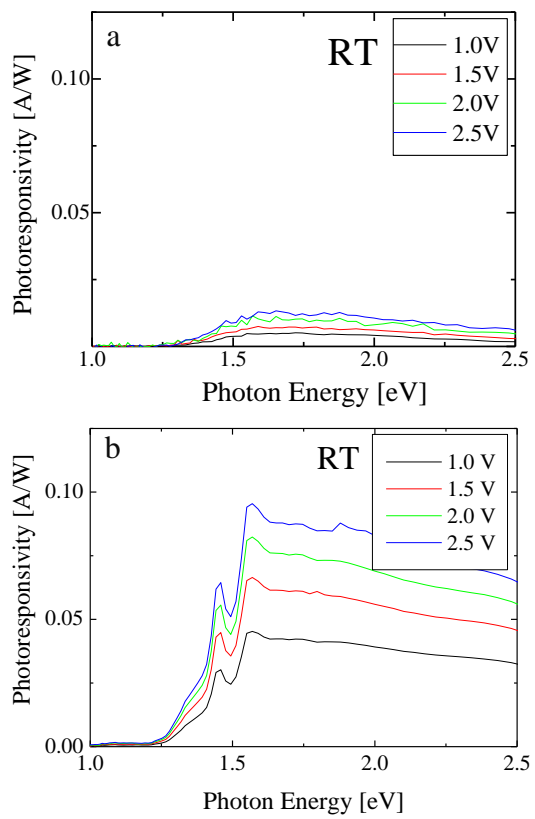


Fig. 4