

1 **Fabrication of (111)-oriented Si layers on SiO₂ substrates by an**
2 **aluminum-induced crystallization method and subsequent growth of**
3 **semiconducting BaSi₂ layers for photovoltaic application**

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5 Dai Tsukada^a, Yuta Matsumoto^a, Ryo Sasaki^a, Michitoshi Takeishi^a, Takanobu Saito^a, Noritaka
6 Usami^b and Takashi Suemasu^{a,c}

7 *Institute of Applied Physics, University of Tsukuba, 1-1-1 Tennohdai, Tsukuba, Ibaraki*
8 *305-8573, Japan*

9 ^a*Institute of Applied Physics, University of Tsukuba, 1-1-1 Tennohdai, Tsukuba, Ibaraki*
10 *305-8573, Japan*

11 ^b*Institute for Materials Research (IMR), Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai*
12 *980-8577, Japan*

13 ^c*PRESTO, Japan Science and Technology Agency, Chiyoda-ku, Tokyo 102-0075, Japan*

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16 **Corresponding author:** Takashi Suemasu

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

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

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20 We have prepared (111)-oriented Si layers on SiO₂ (fused silica) substrates from
21 amorphous-Si(a-Si)/Al or Al/a-Si stacked layers using an aluminum-induced crystallization
22 (AIC) method. The X-ray diffraction (XRD) intensity from the (111) planes of Si was found
23 to depend significantly on growth conditions such as the thicknesses of Si and Al, deposition
24 order (a-Si/Al or Al/a-Si on SiO₂), deposition technique (sputtering or vacuum evaporation)
25 and exposure time of the Al layer to air before the deposition of Si. The crystal orientation of
26 the Si layers was confirmed by θ -2 θ , 2 θ XRD and electron backscatter diffraction (EBSD).
27 The photoresponse properties of semiconducting BaSi₂ films formed on the (111)-oriented Si
28 layers by the AIC method were measured at room temperature. Photocurrents were clearly
29 observed for photon energies greater than 1.25 eV. The external quantum efficiencies of the
30 BaSi₂ were also evaluated.

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37 compounds

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39 1. Introduction

40 Novel Si-based materials are of great interest for high-efficiency solar cells. At
41 present, most solar cells produced are bulk silicon based. However, the band gap of Si is only
42 1.1 eV, which is approximately 0.3 eV smaller than the ideal band gap for solar cells from the
43 viewpoint of the solar spectrum [1]. In addition, the optical absorption coefficient (α) of Si is
44 much smaller than that of GaAs and CdTe. Thus, a Si thickness of at least 100 μm is required
45 to form crystalline Si solar cells. For this reason, we have focused on orthorhombic barium
46 disilicide (BaSi_2) as an interesting and useful alternative material to Si. Both experimental and
47 theoretical studies have revealed that BaSi_2 has a very large α value of over 10^5 cm^{-1} at 1.5
48 eV [2,3]. This value is more than two orders of magnitude larger than that of crystalline Si. In
49 addition, by replacing half of the Ba atoms with isoelectric Sr atoms, the band gap of BaSi_2
50 was found to reach the ideal value of approximately 1.4 eV, matching the solar spectrum [2,4].
51 Thus, BaSi_2 has attracted significant attention for use in solar cells. The purpose of the present
52 study was to fabricate BaSi_2 layers on SiO_2 (fused silica) and to investigate its photoresponse
53 properties with regard to application to inexpensive solar cells. For this purpose, the
54 aluminum-induced crystallization (AIC) was employed [5-7]. AIC is a metal induced
55 crystallization (MIC) [8] technique that enables low-temperature crystallization of amorphous
56 Si (a-Si) below the eutectic temperature of 577 $^\circ\text{C}$, and leads to large grained poly-Si layers.
57 Recently, Knaepen *et al.* have studied the crystallization kinetics of the MIC process in detail

58 for 20 different metals [9]. A preferential (111) orientation of the Si layers was reported [10].
59 This is favorable for the subsequent growth of BaSi₂ layers, because *a*-axis-oriented BaSi₂
60 films can be epitaxially grown on Si(111) with a lattice mismatch of approximately 1%
61 [11-15]. However, the growth of (100)-oriented Si layers has been also reported [16-18].

62 In this study, the influence of the layer thicknesses of Si and Al, deposition order
63 (a-Si/Al or Al/a-Si on SiO₂), deposition technique (sputtering or vacuum evaporation) and
64 exposure time of the Al layer to air before the deposition of Si on the crystalline quality of the
65 Si layers was investigated. The photoresponse properties of polycrystalline BaSi₂ films grown
66 on (111)-oriented poly-Si layers prepared by the AIC method on SiO₂ substrates were also
67 studied. There have been no reports on the photoresponse properties of BaSi₂ until very
68 recently; these properties are very important when we discuss quantum efficiency in BaSi₂. In
69 a previous paper [19], we reported the external quantum efficiency in 900-nm-thick BaSi₂
70 epitaxial films for the first time.

71

72 **2. Experimental procedure**

73 First, the influence of the layer thicknesses and deposition order of Al and Si on the
74 crystallization behavior of AIC-Si layers was investigated. The AIC process was performed as
75 follows. Al layers were deposited on SiO₂ by radio-frequency (RF) magnetron sputtering,
76 followed by breaking of the vacuum to form a native Al oxide layer for 50 h, and the

77 subsequent deposition of a-Si layers by RF magnetron sputtering. The thickness of Al was
78 varied from 50 to 300 nm. The thickness of the Si was almost the same as that of the Al. The
79 vacuum level was 1.0 Pa and the RF power was 100 W. The deposition rates of Al and Si by
80 RF magnetron sputtering were approximately 50 and 25 nm/min, respectively. The deposition
81 order of Al and Si was inverted for sample E. Samples were annealed in a dry N₂ ambient
82 atmosphere at 500 °C for 10 h. During annealing, a-Si was transformed to the crystal phase by
83 exchange between the Al and a-Si layers. The preparation method for samples A-E is
84 summarized in Table 1. We next investigated the influence of the deposition technique
85 (sputtering or vacuum evaporation) on the crystalline quality of the AIC-Si layers. First, a 100
86 nm-thick Al layer was deposited, followed by breaking of the vacuum to form a native Al
87 oxide layer for 10 min, and the subsequent deposition of a 100-nm-thick a-Si layer. For the
88 vacuum evaporation of Al, conventional resistive heating using a tungsten filament was
89 employed, and the deposition rate of Al was approximately 100 nm/min. For the vacuum
90 evaporation of Si, an electron-beam evaporation was used, and the deposition rate was
91 approximately 3 nm/min. The samples were annealed in a dry N₂ ambient atmosphere at
92 500 °C for 10 h. As described later, the crystalline quality of AIC-Si layers depends on
93 exposure time of the Al layer to air. The exposure time of 10 min was chosen here just to
94 shorten the time necessary for this experiment. The preparation method for samples F-J is
95 summarized in Table 2. BaSi₂ layers for photoresponse measurements were prepared as

96 follows. After the Al layers were etched away, the wafers were dipped in a hydrofluoric acid
97 to remove native oxide layers of Si, followed by heating at 550 °C for 5 min in ultra high
98 vacuum. Then, approximately 30-nm-thick Si layers were grown by molecular beam epitaxy
99 (MBE), and approximately 300-nm-thick undoped BaSi₂ layers were subsequently grown.
100 The growth procedure employed for the preparation of the BaSi₂ layers was almost the same
101 as that adopted previously [19]. Finally, Al was evaporated on the surface to form
102 1.5-mm-spacing striped electrodes. The ohmic nature of the contacts was confirmed from the
103 current-voltage characteristics. The samples were not covered with anti-reflection coatings.

104 The crystalline quality of the films was characterized by θ - 2θ and 2θ X-ray
105 diffraction (XRD) using a Cu $K\alpha$ source, atomic force microscopy (AFM) and scanning
106 electron microscopy (SEM). Electron backscatter diffraction (EBSD) was performed in order
107 to analyze the preferential orientation of the film. The X-ray beam was incident at an angle of
108 2° in the 2θ XRD measurement. Both the θ - 2θ and 2θ XRD measurements help us
109 understand what lattice plane in the crystal is parallel to the substrate plane. The photocurrent
110 in the lateral direction between the electrodes was evaluated at RT by a lock-in technique
111 using a xenon lamp with a 25-cm focal-length single monochromator (Bunko Keiki,
112 SM-1700A). The light intensity was calibrated using a pyroelectric sensor (Melles Griot,
113 13PEM001/J).

114

115 **3. Results and discussion**

116 *3.1 Formation of (111)-oriented Si layers on SiO₂ by AIC*

117 Figure 1 shows the θ - 2θ and 2θ XRD patterns of samples A-E. The Al layers were
118 not etched for these measurements. The (111) peaks of Si were observed in the θ - 2θ XRD
119 patterns for samples A-C, but were not found in the 2θ XRD patterns. Thus, these results
120 show that (111)-oriented Si layers were fabricated in samples A-C. The peak intensity of
121 Si(111) was found to increase with increasing thickness of the Si layers. However, layer
122 exchange, and hence the crystallization of Si, was not observed for sample D. We believe that
123 much longer annealing times are required for sample D because of the thicker Si layer. In
124 sample E, prepared by inverted AIC, the layer exchange occurred and a poly-Si layer was
125 formed on the top surface and a metallic Al layer was formed between the poly-Si layer and
126 the SiO₂ substrate, which can act as a back electrode for solar cells. In addition, a very flat
127 surface was obtained in this sample. The root-mean-square (RMS) roughness of sample E was
128 much smaller than that of sample B, prepared by the standard AIC method, as shown in Fig. 2.
129 However, the peak intensity of the Si(111) plane was much smaller in sample E, at about 100
130 counts. We believe that whether the crystallization of Si occurs or not is much more important
131 than the RMS roughness value of the AIC-Si surface, because a flat surface can be produced
132 later by epitaxial thickening of the AIC layers. Thus, we chose to use the standard AIC
133 process from here on.

134 Next, we investigated the influence of the deposition method on the crystalline
135 quality. Figure 3 shows the θ - 2θ and 2θ XRD patterns of samples F-J, where the Al and Si
136 layers were deposited by either RF magnetron sputtering or vacuum evaporation. The
137 thicknesses of the Al and Si layers were kept constant at 100 nm. The sample preparation
138 method is summarized in Table 2. Layer exchange was found to occur in all of the samples.
139 As shown in Fig. 3, intense peaks from Si(111) and Al(111) planes were observed for samples
140 H-J, with the peak intensity being much larger in sample J. These results show that the
141 vacuum evaporation of Al layers significantly improves the crystalline quality of Al-Si
142 layers. To further investigate the influence of the Al deposition method, AFM observations
143 were performed just after Al deposition and after 50 h exposure to air for sample B, and just
144 after Al deposition and after 48 h exposure to air for sample J. As shown in Fig. 4, it was
145 found that the Al had a much smoother surface and its grain size was much smaller in the
146 vacuum-evaporated Al layer. In the case of vacuum evaporation, the kinetic energy of Al
147 atoms is approximately $k_B T$ (< 1 eV), where k_B and T are the Boltzmann constant and the
148 absolute temperature, respectively. In contrast, the kinetic energy of Al atoms sputtered is on
149 the order of 10 eV [20]. We think that this difference is attributed to the difference in surface
150 roughness shown in Fig. 4. It is well known that the presence of native Al oxide at the a-Si/Al
151 interface plays an essential role in the final crystal quality of poly-Si layers [5-7, 21-24]. We
152 believe that the rough surface of the Al layers produced by sputtering gave rise to

153 non-uniform Al oxide layers, which influenced the crystallization of the AIC-Si layers. Figure
154 5 shows the dependence of the XRD peak intensity of the Si(111) plane on the air-exposure
155 time of the vacuum-evaporated Al layers. The AIC process conditions were the same as those
156 of sample J except for the exposure time. The peak intensity tended to increase with
157 increasing exposure time, although there is a lack of values in the intermediate time range. On
158 the basis of these results, we adopted the AIC process of sample J, on which BaSi₂ films were
159 grown by MBE.

160 Figures 6(a) and 6(b) show examples of an SEM image and EBSD mapping of
161 sample J observed along the normal direction, respectively. It was found from the SEM image
162 that the Si layer was continuous. The EBSD measurement was carried out at intervals of 2 μm
163 within an area of 200×200 μm². In Fig. 6(b), regions of (111)-oriented Si grains are colored
164 blue, and regions of (001)-oriented Si grains are colored red. In the present study,
165 (111)-oriented grains were defined as grains whose misorientation from the ideal (111) plane
166 was less than 10 °. Figure 6(b) reveals that approximately 94% of the film surface area had a
167 preferential orientation of (111). The RMS roughness value of the poly-Si layer was relatively
168 large, at 14.72 nm.

169

170 *3.2 Formation and photoresponsivity of BaSi₂ film on AIC-Si/SiO₂*

171 Figure 7(a) shows the θ - 2θ and 2θ XRD patterns from the samples after the growth

172 of a 300-nm-thick BaSi₂ film by MBE on the Si layers formed by the AIC process of sample J.
173 The diffraction peaks of the (211), (301) and (411) planes of BaSi₂ were observed instead of
174 *a*-axis-oriented diffraction peaks which dominate in the BaSi₂ epitaxial films grown on
175 single-crystalline Si(111) substrates [12]. We think that this can be attributed to the rough
176 surface of the AIC-Si layers, as mentioned above. Epitaxial thickening by chemical vapor
177 deposition utilizing the AIC poly-Si layers as seed crystals might lead to a flat surface of the
178 poly-Si layers, thereby yielding *a*-axis-oriented high-quality BaSi₂ layers. Figure 7(b) shows
179 the external quantum efficiency (η) versus photon energy measured at RT under various bias
180 voltages. Light absorption produces electron-hole pairs that are separated by the electric field
181 between the electrodes, leading to current flow in the external circuit as the photoexcited
182 carriers drift before recombination. Photocurrents were observed for photon energies greater
183 than 1.25 eV, and increased sharply with increasing photon energy to reach a maximum at
184 approximately 1.60 eV. For comparison, the η versus photon energy plot measured for the
185 AIC-Si layers in sample J was inserted in Fig. 7(b). The η value was more than two orders of
186 magnitude smaller than that for the BaSi₂ sample. Thus, the contribution of photoexcited
187 carriers originating from the AIC-Si layers to the measured photoresponse can be excluded.
188 This is because the α value of BaSi₂ exceeds 10^5 cm^{-1} at around 1.60 eV [2,3], and therefore
189 almost all the photons around 1.60 eV are absorbed within the 300-nm-thick BaSi₂ film. η
190 was found to reach a value as large as approximately 8% at a bias voltage of 5 V. This value

191 corresponds to that obtained in 900-nm-thick BaSi₂ epitaxial films on single-crystalline
192 Si(111) substrates [19]. In this study, photoexcited carriers drifted in the lateral direction, and
193 therefore the carriers likely encountered grain boundaries. With increasing drift velocity, the
194 number of carriers that reached the electrodes before recombination increased, resulting in an
195 increase in the external quantum efficiency with increasing bias voltage, as shown in Fig. 7(b).
196 In the case of a BaSi₂ *pn* junction, an enhanced external quantum efficiency can be expected,
197 because a much larger built-in electric field ($\sim 10^4$ V/cm) exists around the junction, and also
198 the distance that photoexcited carriers must travel is much shorter (~ 1 μm) than that in the
199 present case (1.5 mm). The highest temperature used in this study was 600 °C, and that is the
200 temperature when BaSi₂ films were grown by MBE. Thus, the whole process can be carried
201 out for cheaper substrates than fused silica substrates in the near future.

202

203 **4. Conclusions**

204 We have prepared (111)-oriented Si layers on fused silica substrates by the AIC
205 method. The dependence of the crystallinity on the thicknesses of the Si and Al layers,
206 deposition order and deposition technique, and air-exposure time after Al deposition was
207 studied. It was found that vacuum evaporation of Al and subsequent exposure to air
208 significantly improved the crystallinity of AIC-Si layers. EBSD mapping revealed that
209 approximately 94% of the AIC-Si surface area had a preferential (111) orientation.

210 300-nm-thick undoped-BaSi₂ films were grown by MBE on (111)-oriented Si layers produced
211 on SiO₂ by the AIC method. Photoresponse spectra for photons with energies greater than
212 1.25 eV were clearly observed. The external quantum efficiency at 1.60 eV increased with the
213 bias voltage applied between the electrodes, and reached a value of approximately 8% at 5 V.
214

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247 **Figure captions**

248

249 Figure 1 θ - 2θ and 2θ XRD patterns of samples A-E. The X-ray beam was incident at
250 an angle of 2° in the 2θ XRD measurement. Sample preparation is summarized in Table 1.
251 The Al layers were not etched for these measurements.

252

253 Figure 2 AFM images of samples B and E. In the case of sample B, the Al layer was
254 etched before measurement.

255

256 Figure 3 θ - 2θ and 2θ XRD patterns of samples F-J. θ - 2θ and 2θ XRD patterns of
257 samples A-E. The X-ray beam was incident at an angle of 2° in the 2θ XRD measurement.
258 Sample preparation is summarized in Table 2. The Al layers were not etched for these
259 measurements.

260

261 Figure 4 AFM images of samples B and J taken just after Al deposition by RF
262 magnetron sputtering (a) and by vacuum evaporation (c), and after 50-h-exposure to air (b)
263 and after 48-h-exposure to air (d), respectively.

264

265 Figure 5 Dependence of XRD peak intensity of Si(111) plane on exposure time to

266 air after Al deposition. The experimental conditions were the same as those for sample J
267 except for the exposure time. The solid line is a guide only.

268

269 Figure 6 (a) SEM image and (b) EBSD mapping of the AIC-Si layer in sample J.
270 observed along the normal direction. (111)-oriented grains were defined as grains whose
271 misorientation from the ideal (111) plane was less than 10° .

272

273 Figure 7 (a) θ - 2θ and 2θ XRD patterns of BaSi₂ on SiO₂ and (b) external quantum
274 efficiency vs. photon energy for BaSi₂ layers measured at RT. The quantum efficiency for the
275 AIC-Si layer (sample J) multiplied by 10 under the bias voltage of 2 V is inserted for
276 comparison.

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