

Investigation of grainboundaries in BaSi₂epitaxialfilms on Si(1 1 1) substrates using transmissionelectronmicroscopy and electron-beam-induced current technique

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journal or publication title	Journal of crystal growth
volume	348
number	1
page range	75-79
year	2012-06
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URL	http://hdl.handle.net/2241/117289

doi: 10.1016/j.jcrysgr.2012.03.044

1 **Investigation of grain boundaries in BaSi₂ epitaxial films on Si(111)**
2 **substrates using transmission electron microscopy and**
3 **electron-beam-induced current technique**

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18 *Keywords:* A3. Molecular beam epitaxy; B2. Semiconductor silicon compounds

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22 *a*-Axis-oriented undoped *n*-BaSi₂ epitaxial films were grown on Si(111) substrates by
23 molecular beam epitaxy, and the crystalline quality and grain boundaries were investigated by
24 means of reflection high-energy electron diffraction, X-ray diffraction, and transmission
25 electron microscopy (TEM). The grain size of the BaSi₂ films was estimated to be
26 approximately 0.1-0.3 μm, and straight grain boundaries (GBs) were observed in the
27 plan-view TEM images. Dark-field TEM images under two-beam diffraction conditions
28 showed that these GBs consist mostly of BaSi₂ {011} planes. The diffusion length of minority
29 carriers in *n*-BaSi₂ was found to be approximately 10 μm by an electron-beam-induced
30 current technique.

31

32 **1. Introduction**

33 Solar cells have recently been receiving considerable interest as a next-generation
34 energy source to replace conventional sources such as oil and coal. Approximately 90% of
35 solar cells are made from silicon owing to its abundance in the earth's crust, its well-known
36 semiconducting properties and established handling technologies. The production of Si solar
37 cells has been increasing year over year, and this trend is anticipated to continue in the future.
38 However, it is difficult to realize high-efficiency thin-film solar cells using crystalline Si
39 because the absorption coefficient is as small as approximately 10^3 cm^{-1} at 1.5 eV and the
40 band gap is 1.1 eV. These properties are not suitable for high-efficiency thin-film solar cells
41 [1]. Therefore, other novel Si-based materials are of great interest for solar cells. We have
42 specifically targeted realizing *pn* junction solar cells using semiconducting barium disilicide
43 (BaSi_2). Composed of the abundant Ba and Si, BaSi_2 has a very large absorption coefficient of
44 $3 \times 10^4 \text{ cm}^{-1}$ at 1.5 eV, and a band gap of 1.3 eV, matching the solar spectrum [2-4]. Thus,
45 BaSi_2 is considered to be an alternative new material to Si. Recent achievements of large
46 photoresponsivity of BaSi_2 epitaxial layers formed on Si(111) substrates and polycrystalline
47 BaSi_2 layers on SiO_2 substrates have spurred interest in this material [5-7]. Orthorhombic
48 BaSi_2 is stable under ambient conditions and room temperature (RT), with lattice constants of
49 $a=0.891$, $b=0.672$, and $c=1.153$ nm [8-10]. This material can be grown epitaxially on a
50 Si(111) substrate with the orientation alignment of $\text{BaSi}_2(100)//\text{Si}(111)$, with a small lattice

51 mismatch of 1.0% for BaSi₂[010]//Si[112] and 0.1% for BaSi₂[001]//Si[110] [11]. The grain
52 size of BaSi₂ can be as small as approximately 0.1 μm [12], due to three epitaxial variants
53 rotating around each other by 120° with respect to the surface normal [13,14]. Many grain
54 boundaries (GBs) and other defects in a film typically deteriorate optical and electrical
55 properties of the film. Thus, it is very important to investigate the GBs character in BaSi₂. In
56 the case of polycrystalline Si, GBs enhance carrier recombination due to their high defect
57 densities [15], however this recombination activity depends significantly on the GB character
58 due to the difference in the ability of gettering impurities. For example, low-Σ GBs such as Σ3
59 do not act as defect centers of minority carriers [16]. On the other hand, it is thought that
60 recombination of carriers is suppressed by the local built-in potential at the GBs in the case of
61 GBs in Cu(InGa)Se₂ [17]. However, there have been no reports thus far on GBs in BaSi₂
62 epitaxial films. The diffusion length of minority carriers, a key parameter determining the
63 performance of solar cells, has yet to be evaluated in BaSi₂. The electron-beam-induced
64 current (EBIC) technique is considered to be a powerful method for investigating the
65 electrical properties of various semiconductor materials [18].

66 In this study, we grew *a*-axis-oriented BaSi₂ epitaxial films on Si(111) substrates by
67 molecular beam epitaxy (MBE) and examined the GBs by transmission electron microscopy
68 (TEM). It was found, from plan-view TEM images and selected-area electron diffraction
69 (SAED) patterns, that the GBs in these BaSi₂ epitaxial films are composed mostly of

70 BaSi₂{011} planes. We also evaluated the minority-carrier (holes) diffusion length in *n*-type
71 BaSi₂ epitaxial layers using the EBIC technique.

72

73 **2. Experimental procedures**

74 A two-stage growth method was adopted, which included reactive deposition epitaxy
75 (RDE; Ba deposition on hot Si) and molecular beam epitaxy (MBE; co-deposition of Ba and
76 Si) to form thick BaSi₂ films [10]. The RDE process was carried out for deposition of a
77 template layer as a BaSi₂ precursor prior to the subsequent MBE process [13,14]. The same
78 growth method was successfully utilized for the epitaxial growth of semiconducting β-FeSi₂
79 films on both Si(001) and Si(111) substrates [19,20]. An ultrahigh vacuum (UHV) chamber
80 equipped with a Knudsen cell for Ba and an electron beam gun for Si was employed. Before
81 the growth, the *n*-Si substrates ($\rho = 0.1 \text{ } \Omega \cdot \text{cm}$) were prepared by subjecting them to the
82 following treatment. The substrates were washed using RCA clean steps, which removed
83 organic and metallic contaminants. The substrates were then annealed at 830 °C for 30 min in
84 the UHV ($1 \times 10^{-6} \text{ Pa}$) chamber to remove the protective SiO₂ layers. After annealing, a 7×7
85 streaky reflection high-energy electron diffraction (RHEED) pattern was observed, indicating
86 a clean Si surface.

87 We fabricated 300-nm-thick undoped *n*-BaSi₂ films by RDE at 550 °C for 5 min,
88 followed by MBE at 600 °C for 120 min. Undoped BaSi₂ shows *n*-type conductivity with

89 electron concentrations of approximately 10^{16} cm^{-3} [2]. The crystalline quality of the films
90 was evaluated using RHEED and θ - 2θ X-ray diffraction (XRD) measurements. In order to
91 investigate the grain size of BaSi₂ and GBs, plan-view TEM samples prepared by mechanical
92 polishing and ion milling were observed using TOPCON EM-002B operated at 120 kV. For
93 EBIC measurements, Al/n-BaSi₂ Schottky diode was formed. Front-side Schottky contacts
94 were formed with Al on the BaSi₂ surface via wire bonding, and the back-side ohmic contact
95 was made with Al by sputtering. EBIC observations were carried out in the edge-scan
96 configuration with a Hitachi S4300 field-emission scanning electron microscope (SEM) in the
97 EBIC mode at RT [16]. The acceleration voltage of the electron beam, V_{ac} , was set at 5 kV to
98 avoid penetration of the beam into the Si substrate. The penetration depth of the electron
99 beam is estimated to be shorter than 300 nm, which is the thickness of the BaSi₂ layers, when
100 V_{ac} is 5 kV, with the density of BaSi₂ being 5.14 g/cm^3 .

101

102 **3. Results and discussion**

103 Figure 1(a) shows RHEED patterns of MBE-grown BaSi₂ observed along the Si
104 [1-10] azimuth. Sharp streaky patterns of BaSi₂ can be seen. Figure 1(b) shows the θ - 2θ XRD
105 patterns from the sample. Diffraction peaks can be seen only from (100)-oriented BaSi₂
106 planes, such as the (200), (400) and (600) planes. These results indicate that highly
107 *a*-axis-oriented BaSi₂ epitaxial films were grown.

108 Figure 2(a) shows a bright-field (BF) plan-view TEM image of the BaSi₂. The
109 incident electron beam direction was almost parallel to the BaSi₂ [100] zone axis, but was
110 slightly tilted for the GBs to be seen clearly. Because GBs are parallel to the surface normal,
111 their contrast vanishes in the exact [100] zone axis. The BaSi₂ grain size is approximately
112 0.1-0.3 μm. We should also note here that approximately 120° sharp GBs are present, and
113 these GBs tend to align along specific directions. Figure 2(b) presents the SAED pattern
114 obtained from the area including several BaSi₂ grains in the [100] zone axis. Considering that
115 the GBs are caused by three different *a*-axis-oriented BaSi₂ epitaxial variants rotated from
116 each other by 120° with respect to the surface normal [14], the (002), (011), and (020) spots
117 can be grouped into three, shown in red, green, and blue colors in Fig. 2(b). Considering the
118 green and blue epitaxial variants, for example, the green (011) plane is parallel to the blue
119 (002) plane. Thus, it can be stated that the grain boundary indicated by the white dotted line in
120 Fig. 2(a) is composed of the green (011) plane and/or blue (002) plane. It is difficult to
121 distinguish the green (011) plane from the blue (002) plane in the SAED pattern because their
122 lattice spacing, *d*, is almost the same, that is, $d_{(011)}=0.586$ nm, and $d_{(002)}=0.579$ nm,
123 respectively.

124 Figure 3(a) shows SAED patterns obtained from single grain regions under
125 two-beam diffraction conditions. The diffraction vectors **g** were set to be <004> for the three
126 epitaxial variants shown by blue, red and green in Fig. 2(b). Under these conditions, the

127 diffraction spot corresponding to the (004) plane becomes bright, as seen in Fig. 3(b), while
128 other spots denoted by (00n) ($n = \pm 1, \pm 2, \pm 3, \dots$) can also be seen. These facts can help to
129 distinguish (002) plane from (011) plane.

130 Figures 4(a)-4(c) show dark-field (DF) plan-view TEM images using $\langle 004 \rangle$ plane
131 reflections observed at the same sample region. The diffraction conditions of these DF images
132 are the same as those in Fig 3(a). Under these conditions, BaSi_2 grains satisfying Bragg's
133 condition of diffraction, indicated by the blue-, red-, or green-colored domain, are supposed to
134 be bright in these images; in other words, one of the three BaSi_2 epitaxial variants becomes
135 bright in each figure. It should be noted that the superposition of bright regions in Figs.
136 4(a)-4(c) covers the whole surface of BaSi_2 . In Figs. 4(a)-4(c), it can be seen that the GBs are
137 parallel to the dashed lines in the blue-, red-, and green-colored BaSi_2 variants, respectively.
138 On the basis of this discussion, we conclude that the GBs are formed mostly from BaSi_2
139 $\{011\}$ planes. Further discussion is mandatory to clarify why BaSi_2 $\{011\}$ planes are likely to
140 form GBs.

141 Figure 5(a) shows the current-voltage (I - V) characteristics of the $\text{Al}/n\text{-BaSi}_2$ Schottky
142 diode measured at RT. The bias voltage was applied to the front Al contact with respect to the
143 sputtered Al back contact. Rectifying properties can be clearly observed. More current flows
144 when a positive bias is applied to the Al wire with respect to the back contact. These results
145 indicate that the $\text{Al}/n\text{-BaSi}_2$ junction forms a Schottky diode.

146 Figures 6(a)(b) and 6(c)(d) show secondary-electron (SE) and EBIC images around
147 the Al contact, respectively, with $V_{ac} = 5$ kV. In the EBIC method, carriers generated within
148 the diffusion length in the n -type BaSi₂ are collected by the electric field under the Al contact
149 and sensed as a current in the external circuit. In Figs. 6(c)(d), the brighter regions show
150 higher collection of electron-beam-induced carriers in the BaSi₂. We cannot see defect-related
151 black lines. Figure 7 shows the EBIC line-scan data along dotted line AA' in Fig. 6(c). The
152 EBIC profile shows an exponential dependence of the distance from the Al contact. In this
153 work, the diffusion length of minority carriers was roughly estimated to be approximately 10
154 μm , assuming that the EBIC profile varies as $\exp(-x/L)$, where x is the distance from the Al
155 edge (point A) along the dotted line, and L is the diffusion length of holes for BaSi₂. The
156 obtained minority-carrier diffusion length is much larger than the grain size of the BaSi₂,
157 implying that the GBs do not work as defect centers for minority carriers in n -BaSi₂. The
158 contribution of carriers generated within the n -Si substrate to the measured EBIC signals can
159 be excluded, because the simulated penetration depth of the electron beam is shorter than 300
160 nm, the thickness of the BaSi₂ layers, when V_{ac} is 5 kV. Thus, it is reasonable to think that the
161 number of carriers generated within the Si substrate was negligibly small compared to those
162 generated in the BaSi₂ layers. To confirm the GBs character, an EBIC system with spatial
163 resolutions less than 0.1 μm may be necessary. We should also note here that the obtained
164 minority-carrier diffusion length is roughly 30 times larger than $1/\alpha$ ($=0.3$ μm) at 1.5 eV,

165 suggesting that this value is large enough for solar cell applications.

166

167 **4. Conclusions**

168 We investigated the crystalline quality and GBs in *a*-axis-oriented BaSi₂ epitaxial
169 films grown on Si(111) substrates by MBE using RHEED, XRD, and TEM. The grain size in
170 the BaSi₂ films was found to be approximately 0.1-0.3 μm. Detailed investigation of BF and
171 DF TEM images and SAED patterns showed that the GBs in the BaSi₂ epitaxial layers consist
172 mostly of BaSi₂ {011} planes. The EBIC techniques revealed that the diffusion length of
173 minority carriers was estimated to be approximately 10 μm, much larger than the grain size of
174 the BaSi₂.

175

176 **Acknowledgements**

177 This work was financially supported by the Japan Science and Technology Agency
178 (JST/CREST). TEM observations were conducted at the Electron Microscope Facility,
179 supported in the IBEC Innovation Platform, AIST, Japan.

180

181 **References**

- 182 [1] C. H. Henry, J. Appl. Phys. 51 (1980) 4494.
- 183 [2] K. Morita, Y. Inomata, T. Suemasu, Thin Solid Films 508 (2006) 363.
- 184 [3] D. B. Migas, V. L. Shaposhnikov, V. E. Borisenko, Phys. Status Solid B 244 (2007)
- 185 2611.
- 186 [4] K. Toh, T. Saito, T. Suemasu, Jpn. J. Appl. Phys. 50 (2011) 068001.
- 187 [5] Y. Matsumoto, D. Tsukada, R. Sasaki, M. Takeishi, T. Suemasu, Appl. Phys. Express 2
- 188 (2009) 021101.
- 189 [6] D. Tsukada, Y. Matsumoto, R. Sasaki, M. Takeishi, T. Saito, N. Usami, T. Suemasu, Appl.
- 190 Phys. Express 2 (2009) 051601.
- 191 [7] T. Saito, Y. Matsumoto, M. Suzuno, M. Takeishi, R. Sasaki, T. Suemasu, N. Usami, Appl.
- 192 Phys. Express 3 (2010) 021301.
- 193 [8] M. Imai, T. Hirano, Phys. Rev. B 58 (1998) 11922.
- 194 [9] J. Evers, J. Less Common Met. 69 (1980) 399.
- 195 [10] M. Imai, T. Hirano, J. Alloys Compd. 224 (1995) 111.
- 196 [11] R. A. Mckee, F. J. Walker, Appl. Phys. Lett. 63 (1993) 2818.
- 197 [12] K. Toh, K. O. Hara, N. Usami, N. Saito, N. Yoshizawa, K. Toko, T. Suemasu, J. Cryst.
- 198 Growth **345** (2012) 16.
- 199 [13] Y. Inomata, T. Nakamura, T. Suemasu, F. Hasegawa, Jpn. J. Appl. Phys. 43 (2004) 4155.

- 200 [14] Y. Inomata, T. Nakamura, T. Suemasu, F. Hasegawa, *Jpn. J. Appl. Phys.* 43 (2004) L478.
- 201 [15] I. Gordon, L. Cernel, D. Van Gestel, G. Beaucarne, J. Poortmans, *Thin Solid Films* 516
- 202 (2008) 6984.
- 203 [16] J. Chen, T. Sekiguchi, D. Yang, F. Yin, K. Kido, S. Tsurekawa, *J. Appl. Phys.* 96 (2004)
- 204 5490.
- 205 [17] S. Oonishi, M. Kawamura, N. Takano, D. Hashimoto, A. Yamada, M. Konagai, *Thin*
- 206 *Solid Films* 519 (2011) 7347.
- 207 [18] H. J. Leamy, *J. Appl. Phys.* 53 (1982) R51.
- 208 [19] M. Takauji, N. Seki, T. Suemasu, F. Hasegawa, M. Ichida, *J. Appl. Phys.* 96 (2004) 2561.
- 209 [20] N. Hiroi, T. Suemasu, K. Takakura, N. Seki, F. Hasegawa, *Jpn. J. Appl. Phys.* 40 (2001)
- 210 L1008.
- 211

212 Fig.1 (a) RHEED patterns of MBE-grown BaSi₂ observed along the Si[1-10] azimuth (b) θ - 2θ
213 XRD pattern.

214

215 Fig.2 (a) Plan-view BF TEM image near the [100] zone axis of BaSi₂, and (b) SAED pattern
216 (crystallographic orientation) obtained from the area including several BaSi₂ grains in the
217 exact [100] zone axis.

218

219 Fig. 3 (a) SAED patterns obtained from single grain regions under two-beam diffraction
220 conditions. The diffraction vectors \mathbf{g} were set to three different $\langle 004 \rangle$ directions. (b) Enlarged
221 SAED pattern.

222

223 Fig.4(a)-(c) DF TEM images under two-beam diffraction conditions. The diffraction vector \mathbf{g}
224 was set to be $\langle 004 \rangle$ for each epitaxial variant. The schematics of three epitaxial variants of
225 BaSi₂ are shown. The colored domains look bright in each DF TEM image. The dashed lines
226 correspond to $\{011\}$ planes.

227

228 Fig. 5 I - V characteristics of the Al/n-BaSi₂ Schottky diode at RT.

229

230 Fig. 6 (a)(b) SE and (b)(d) EBIC images around the Al contact.

231

232 Fig. 7 Experimental and simulated (solid line) EBIC line-scan profiles along the dotted line
233 from points A to A' in Fig. 6(c).

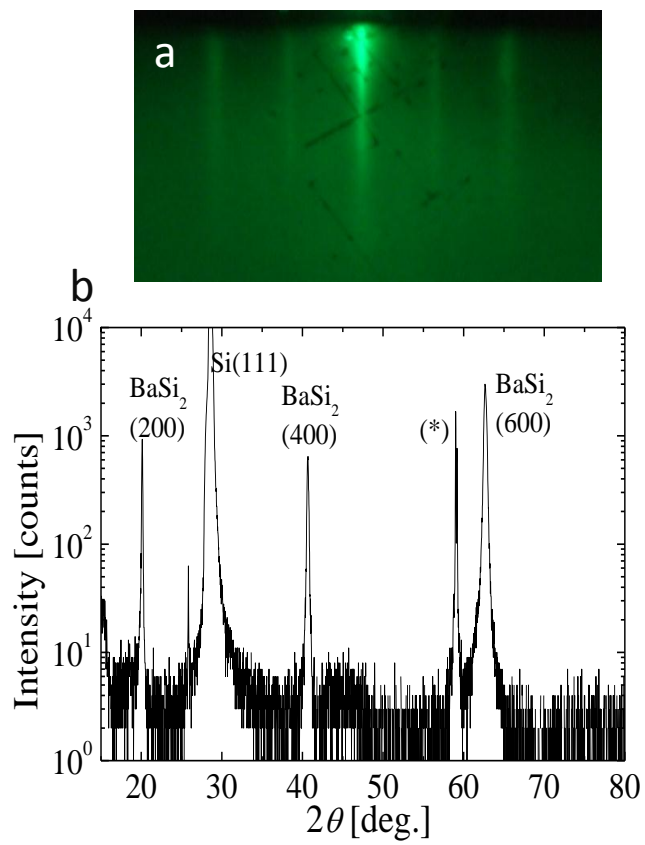


Fig. 1

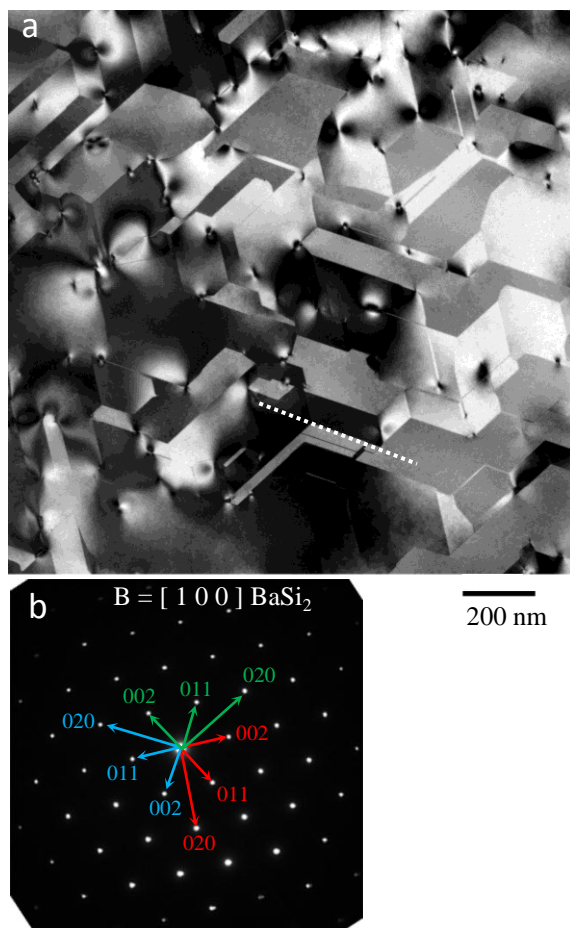


Fig. 2

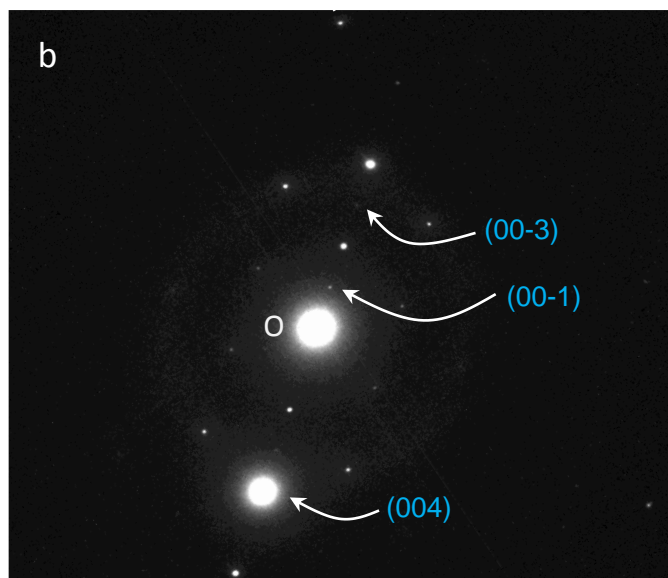
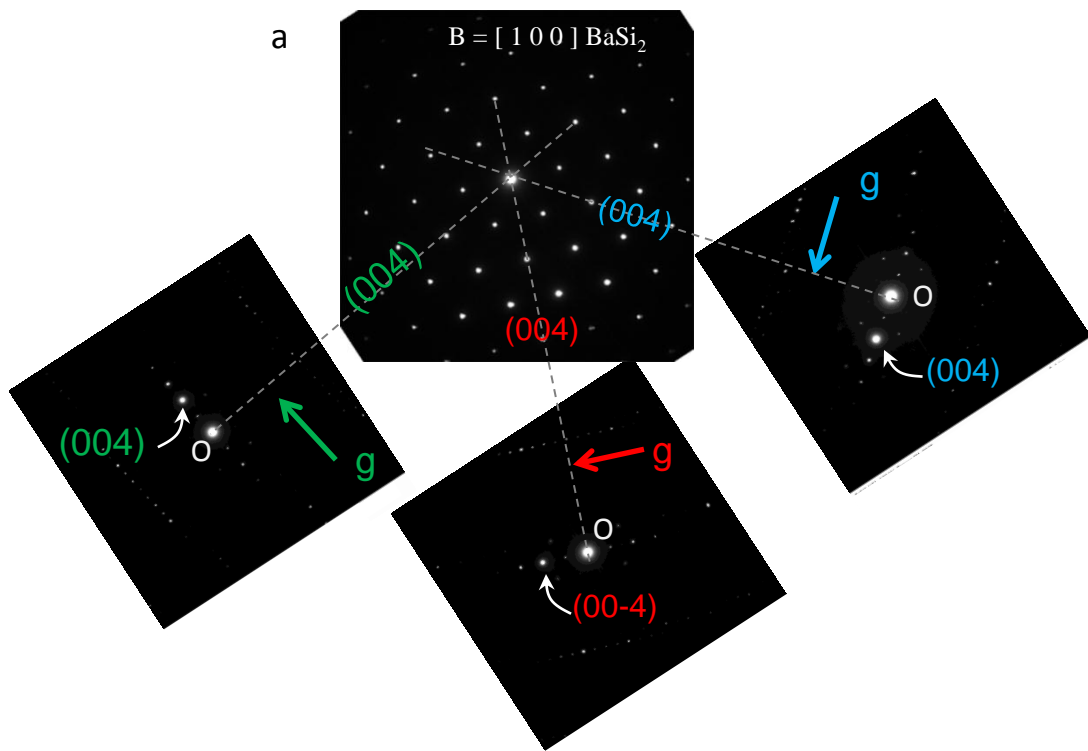


Fig. 3

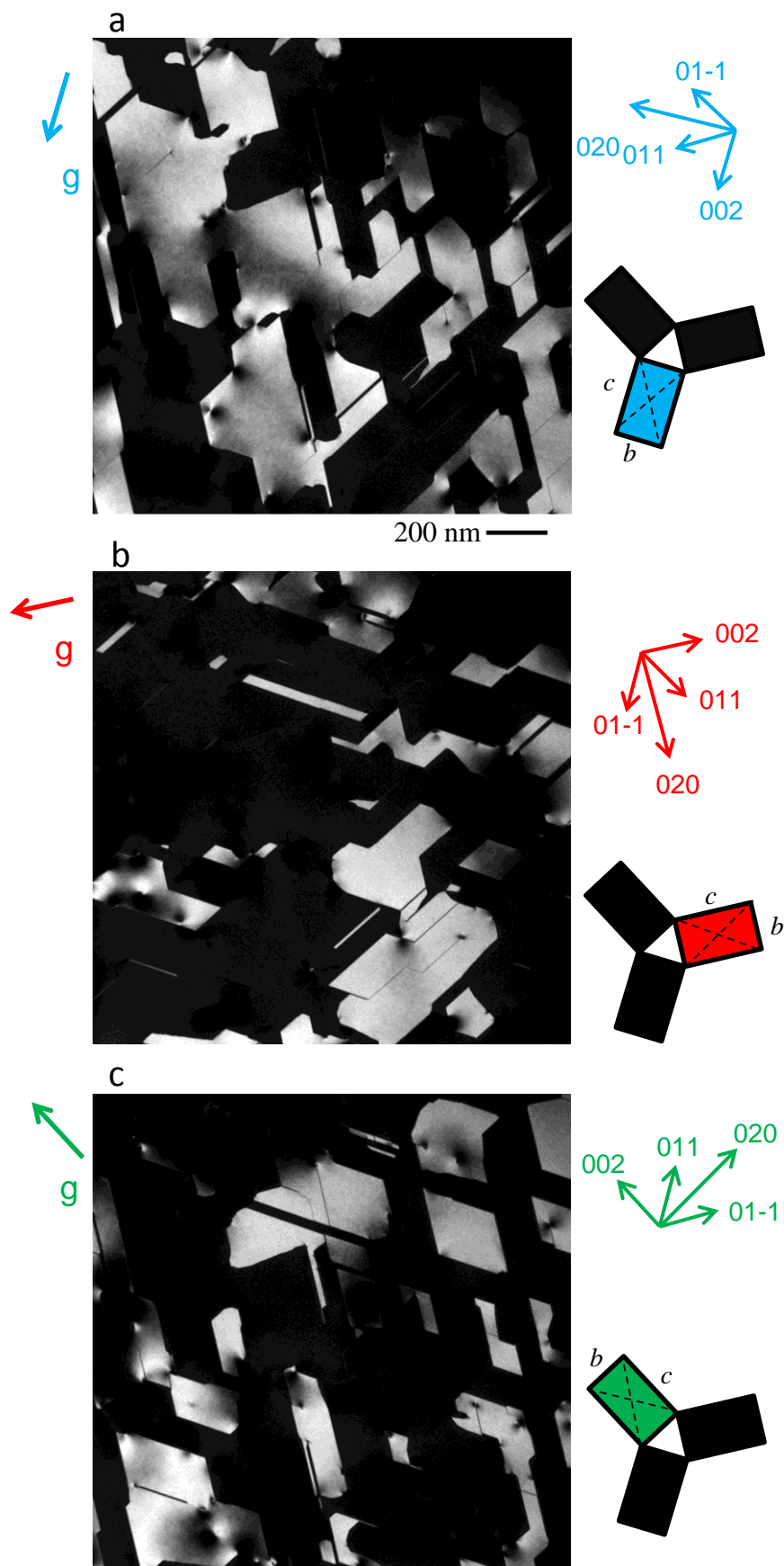


Fig. 4

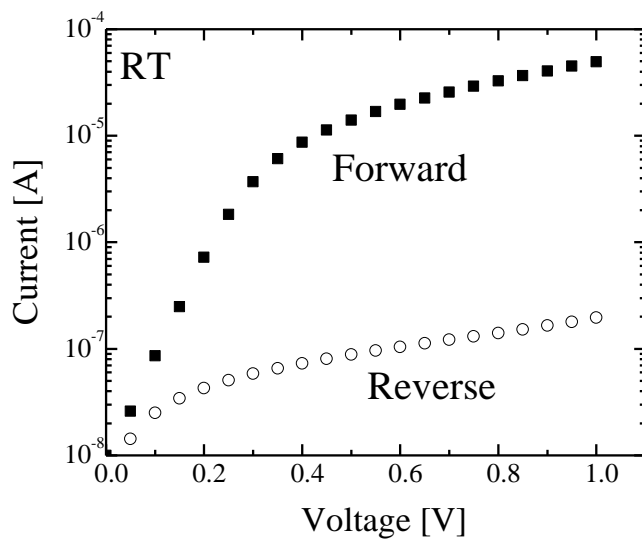


Fig. 5

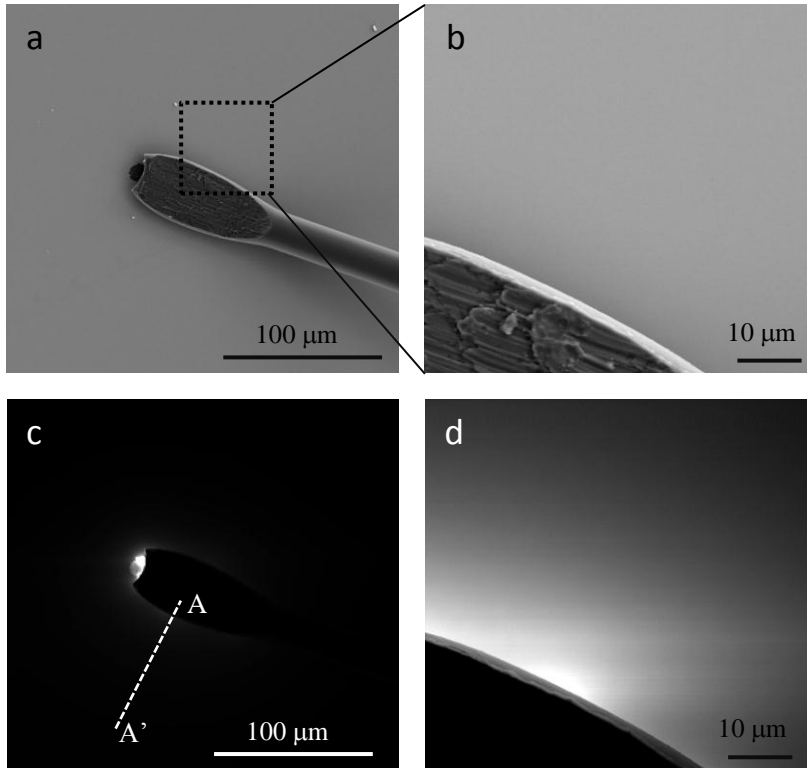


Fig. 6

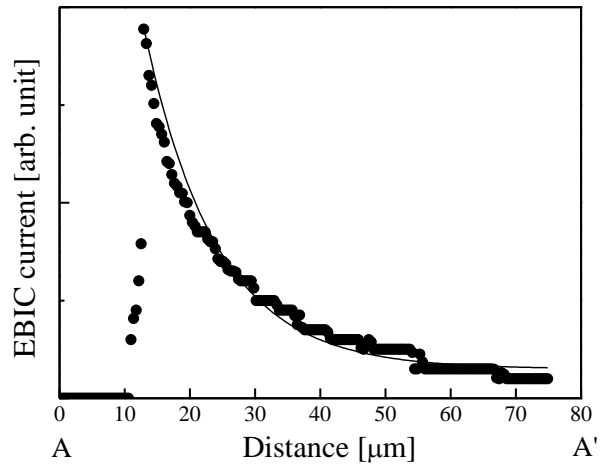


Fig. 7