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1 **Growth promotion of Al-induced crystallized Ge films on insulators by**
2 **insertion of a Ge membrane below the Al layer**

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18

19 **Abstract**

20 Al-induced crystallization (AIC) enables low-temperature crystallization of
21 amorphous Ge thin films on insulators. We investigated growth promotion of Ge thin
22 films using Ge membranes (1-10 nm thickness) that are initially inserted below the Al
23 layer. These Ge insertion layers enhanced supersaturation of Al with Ge, which results
24 in low-temperature AIC (275°C). However, thick (≥ 3 nm) insertion layers result in
25 small grains because of the high nucleation frequency. A 1-nm-thick insertion layer
26 accomplished a growth promotion and yielded large grains of over 100 μm in diameter.
27 Moreover, electron backscatter diffraction measurement revealed that the AIC-Ge layer
28 was highly (111) oriented. This low-temperature crystallization technique opens up the
29 possibility for developing Ge-based electronic devices on inexpensive glass substrates,
30 as well as on flexible polymer substrates.

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34 *Keywords:* A1.Crystal orientation, A2.Solid phase crystallization, B1.Polycrystalline
35 films; B2.Semiconducting germanium

36

37 **1. Introduction**

38 Germanium is useful for fabricating high-speed metal-oxide-semiconductor
39 field-effect transistors (MOSFETs) and high-efficiency tandem solar cells [1-3]. In
40 particular, (111) oriented Ge provides the highest mobility for MOSFETs [1, 2], and is
41 used as an epitaxial template for several advanced functional materials [4-6]. Because a
42 bulk Ge substrate is extremely expensive, substituting the Ge substrate with a crystalline
43 Ge (c-Ge) film on an inexpensive substrate, such as a glass or a polymer, is desired. In
44 line with this, many researchers have investigated techniques for forming c-Ge films on
45 insulators at low temperatures [7-14], because the softening temperature of the
46 abovementioned substrates is low: approximately 550 °C for glasses and 300 °C for
47 polymers. However, the resulting Ge layers consist of randomly oriented small grains (<
48 1 μm).

49 Study of Al-induced crystallization (AIC) of amorphous Si and Ge films on
50 insulators has recently accelerated [15-28]. The AIC technique yields large-grained
51 (diameters: 10-100 μm) polycrystalline Si films on insulators at low temperatures
52 (420-550 °C) through exchange between the Al and Si layers [15-16]. The driving force
53 behind the low-temperature crystallization in AIC-Si is the supersaturation of Al with Si
54 atoms [15, 18]. In addition, the crystal orientation of the AIC-Si can be controlled to

55 either (100) or (111), by modulating the growth conditions: the thickness of the Al and
56 Si layers, the thickness of the interlayer between the Al and Si layers, and the annealing
57 temperature [17-22].

58 The AIC technique enables the formation of polycrystalline Ge (poly-Ge) films on
59 insulators at low temperatures ($< 250^{\circ}\text{C}$) [23-28]. However, the AIC-Ge films result in
60 Ge-Al mixed structures composed of small grains ($< 100\text{ nm}$) [23-28] because of an the
61 absence of layer exchange. Kurosawa *et al.* achieved a layer exchange growth in AIC of
62 Ge at an annealing temperature of 410°C , which resulted in relatively large grains
63 (approx. $5\ \mu\text{m}$) with (111) orientation (70-% area fraction) [29]. Recently, we
64 accomplished highly (111) oriented Ge films with large grains ($>100\ \mu\text{m}$) by optimizing
65 the interfacial AlO_x formation process and the annealing conditions (325°C , 100 h) [30,
66 31]. If the annealing temperature can be reduced to below 300°C , certain flexible
67 polymer sheets can be used as a substrate. In line with this, we developed a growth
68 promotion technique for AIC-Ge where a Ge membrane is inserted between the Al and
69 substrate. The Ge insertion layer causes an increase in the initial Ge concentration in the
70 Al. This paper investigates the effect of the Ge insertion layer. A 1-nm-thick Ge
71 insertion layer exhibits low temperature crystallization at 275°C and yields large grains
72 of over $100\text{-}\mu\text{m}$ in diameter.

73

74 **2. Experimental details**

75 Amorphous Ge membranes, that is, Ge insertion layers for promoting AIC, were
76 prepared on SiO₂ glass substrates. The thicknesses of the Ge insertion layers (defined as
77 t_i) were 0 nm, 1 nm, 3 nm, and 10 nm. The Al layers (each being 50-nm thick) were
78 prepared on the a-Ge membranes and then exposed to air for 10 minutes to form native
79 Al oxide layers (AlO_x). After that, second a-Ge layers were prepared on the AlO_x layers.
80 The total thickness of the first and second a-Ge layers was fixed to be 50 nm. All the
81 depositions were carried out at room temperature using a radio-frequency (RF)
82 magnetron sputtering method. The deposition rate was 23 nm/min for Ge and 25
83 nm/min for Al. The degree of purity for the sputtering targets was 99.99% for Ge and
84 99.9% for Al. Argon pressure during the sputtering was 0.2 Pa, and the RF power was
85 set to 100 W. The samples were annealed at 275-325°C for 0.5-100 h in a N₂ ambient to
86 induce layer exchange growth. The growth morphologies of the samples were observed
87 using Nomarski optical microscopy. The actual grain size and crystal orientation were
88 evaluated using electron backscattered diffraction (EBSD) measurement. Prior to the
89 EBSD measurement, the aluminum and oxide layers on the Ge layers were etched for
90 one minute in an HF solution (HF: 1.5%).

91

92 **3. Results and discussion**

93 Fig. 2(a)-(d) show a typical growth evolution of the AIC-Ge, observed using
94 Nomarski optical microscopy. These micrographs show the back surface of the sample
95 observed through the transparent SiO₂ substrate. The thickness of the Ge insertion layer
96 (t_i) is 1 nm and the annealing temperature (T_a) is 325°C. The dark area indicates
97 crystallized Ge and the bright-colored area indicates Al. The micrographs suggest that,
98 during annealing, the Ge atoms diffuse to the back surface, grow laterally, and cover the
99 entire surface of the substrate.

100 We calculated the coverage ratio of AIC-Ge to substrate for samples with and
101 without Ge insertion (t_i : 1, 3, 10 nm) from the micrographs. The results are summarized
102 in Fig. 2(e) as a function of the annealing time. For all samples, Ge coverage increases
103 as the annealing time increases, and finally reaches approximately 100%. It is worth
104 noting that a thicker Ge insertion layer corresponds to a shorter annealing time for
105 completing AIC. This result proves that the Ge insertion layers enhance Ge
106 supersaturation of the Al and promote growth in AIC.

107 Next, the nucleation time, growth velocity, grain density, and eventual grain
108 radius were compared between samples with $t_i = 0$ nm, 1 nm, 3 nm, and 10 nm; and

109 with $T_a = 275^\circ\text{C}$, 300°C , and 325°C . The grain size was evaluated from the micrographs
110 as a function of annealing time. Fig. 3(a) shows the result for the sample with $t_i = 1$ nm
111 and $T_a = 325^\circ\text{C}$. Grain growth starts after a certain incubation time, and then stop after
112 several hours because of grain collisions. From Fig. 3(a), the nucleation time is
113 estimated to be 0.9 h, the growth velocity $104 \mu\text{m/h}$, and the eventual grain radius 267
114 μm . The grain density was calculated to be 450 cm^{-2} using the value of the eventual
115 grain radius. These parameters were obtained in the same way for the other samples,
116 and are summarized in Fig. 2(b)-(d). Fig. 2(b) clearly indicates that the nucleation time
117 shortens with increasing t_i . We could not observe Ge nucleation for the sample annealed
118 at 275°C for 100 h. These results prove that the Ge insertion layer promoted Ge
119 nucleation. On the other hand, Fig. 3(c) indicates that the growth velocity decreases
120 with increasing t_i . The reason for this is explained later. Additionally, a higher annealing
121 temperature provided a shorter nucleation time and a higher growth velocity for all the
122 samples. This is simply because the Ge diffusion rate increases with an increase in the
123 annealing temperature. Fig. 3(d) indicates that the eventual grain radius decreases with
124 an increase in the thickness of the Ge insertion layer, while the grain density has
125 opposite tendency. Consequently, the sample with $t_i = 1$ nm is optimum for
126 simultaneously achieving growth promotion and a large grain size.

127 On the basis of the layer exchange mechanism, the effect of the Ge insertion is
128 explained as follows. The expected growth mechanism is schematically shown in Fig.
129 3(a)-(d). Figure 3(a) shows the structure of the prepared samples. During annealing, Ge
130 atoms in the Ge insertion layer uniformly diffuse into the Al layer, as shown in Fig. 3(b).
131 Ge nucleation occurs as a result of supersaturation of the Al with Ge [15, 18]. Hence, a
132 thicker t_i provides greater concentration of Ge in the Al, which results in faster
133 nucleation because of faster supersaturation of the Al with Ge, as shown in Fig. 2(b).
134 However, when t_i is thicker than 1 nm, the nucleation frequency is too high, as shown in
135 Fig. 2(d). Therefore, the thickness of the Ge insertion layer has an optimum value.

136 After nucleation, lateral growth is induced by Ge diffusion from the top Ge layer,
137 as shown in Fig. 3(c) [15-22, 25]. In contrast to the nucleation rate, the lateral growth
138 rate decreased with increasing t_i , as shown in Fig. 3(c). This behavior can be explained
139 as follows. Ge atoms diffusing from the top layer into the Al are shared by Ge crystals
140 for lateral growth [18, 20]. Hence, the growth velocity of each grain becomes low when
141 the grain density is high because of the thick t_i . Therefore, a role of the Ge insertion
142 layer is to enhance Ge nucleation rather than lateral growth; the Ge insertion layer is
143 consumed only by nucleation. A continuous supply of Ge atoms from the top Ge layer
144 induces the completion of layer exchange through the pushing up of Al, as

145 schematically shown in Fig 3(c) and (d) [20].

146 The crystal orientation was evaluated using EBSD measurement for the sample
147 with $t_i = 1$ nm and $T_a = 275^\circ\text{C}$. Fig. 4(a) and (b) show crystal orientation maps in the
148 normal direction (ND) and the transverse direction (TD) relative to the sample surface,
149 respectively. The black solid lines indicate random grain boundaries, which were drawn
150 based on EBSD analysis results. Fig. 4(a) indicates that the AIC-Ge layer is highly (111)
151 oriented over the entire region. The area fraction of the (111) orientation was calculated
152 using EBSD analysis and was found to be as high as 99%. As shown in Fig. 4(b), EBSD
153 analysis reveals that a grain observed using Nomarski optical microscopy is divided into
154 several different orientations. The net grain size is estimated from the TD map and is
155 found to be over 100- μm in diameter. This value is larger than the 325°C annealed
156 AIC-Ge without a Ge insertion layer. Because the net grain size increases with
157 decreasing annealing temperature [31], the enlargement of the net grain size is likely
158 due to the low-temperature annealing (275°C), which was accomplished by growth
159 promotion using the Ge insertion layer.

160

161 **4. Conclusions**

162 We investigated the effects of Ge insertion below the Al layer in AIC-Ge. The Ge

163 insertion layer promoted AIC by enhancing supersaturation of the Al with Ge, which
164 resulted in low-temperature growth (275°C). However, thick (≥ 3 nm) Ge insertion
165 layers provided a high nucleation frequency and a small eventual grain size. A
166 1-nm-thick Ge insertion layer achieved both growth promotion and large grains of over
167 100 μm in diameter. Moreover, the AIC-Ge was highly (111) oriented. This
168 low-temperature formation technique of large grained Ge (111) thin films on amorphous
169 substrates opens up the possibility for advanced Ge-based devices on inexpensive
170 flexible substrates.

171

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234

235

236 **Figure captions**

237 **Fig. 1.** Nomarski optical micrographs of the sample with $t_i = 1$ nm and $T_a = 325^\circ\text{C}$. The
238 annealing times are (a) 0.5 h, (b) 2 h, (c) 3 h, and (d) 5 h. (e) Ratio of Ge coverage to
239 substrate as a function of annealing time, where $t_i = 0$ nm, 1 nm, 3 nm, and 10 nm.

240

241 **Fig. 2.** (a) Annealing time dependence of the sample grain radii with $t_i = 1$ nm and $T_a =$
242 325°C . Insertion layer thickness (t_i) dependence of (b) nucleation time, (c) growth
243 velocity, and (d) eventual grain radius and grain density, where $T_a = 275^\circ\text{C}$, 300°C , and
244 325°C .

245

246 **Fig. 3.** Schematics of the layer exchange process in AIC-Ge with a Ge insertion layer.
247 (a) Sample structure before annealing. (b) Ge diffusion from the Ge insertion layer into
248 the Al. (c) Ge nucleation and lateral growth induced by Ge diffusion from the top a-Ge
249 layer, which pushes Al up into the top a-Ge layer. (d) Completion of the layer exchange.

250

251 **Fig. 4.** Crystal orientation of the AIC-Ge layer with $t_i = 1$ nm and $T_a = 275^\circ\text{C}$. EBSD
252 images in the (a) normal direction (ND) and (b) transverse direction (TD) relative to the
253 sample surface. The colors indicate the crystal orientation according to the inserted

254 color key.

255

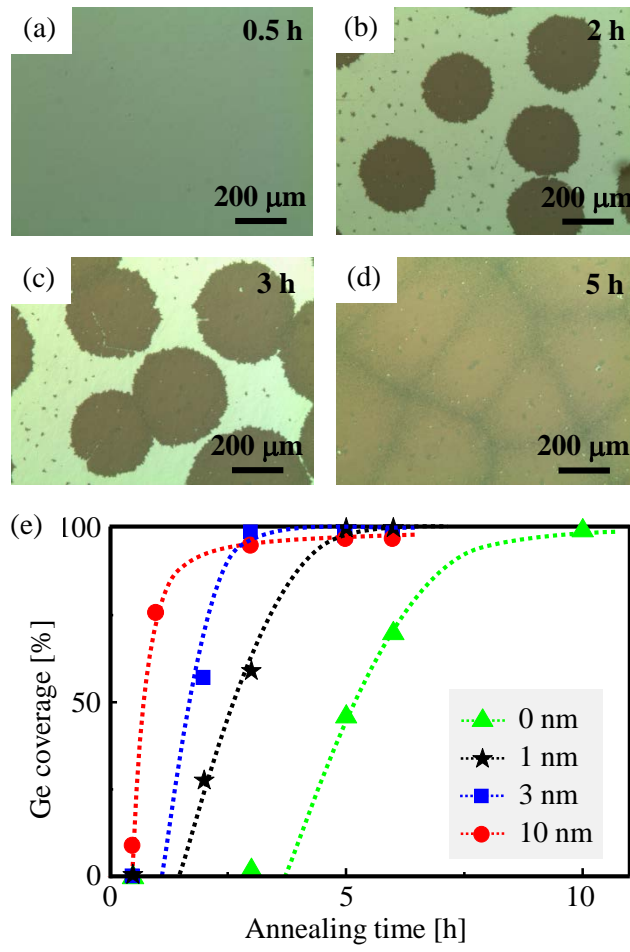


Fig. 1

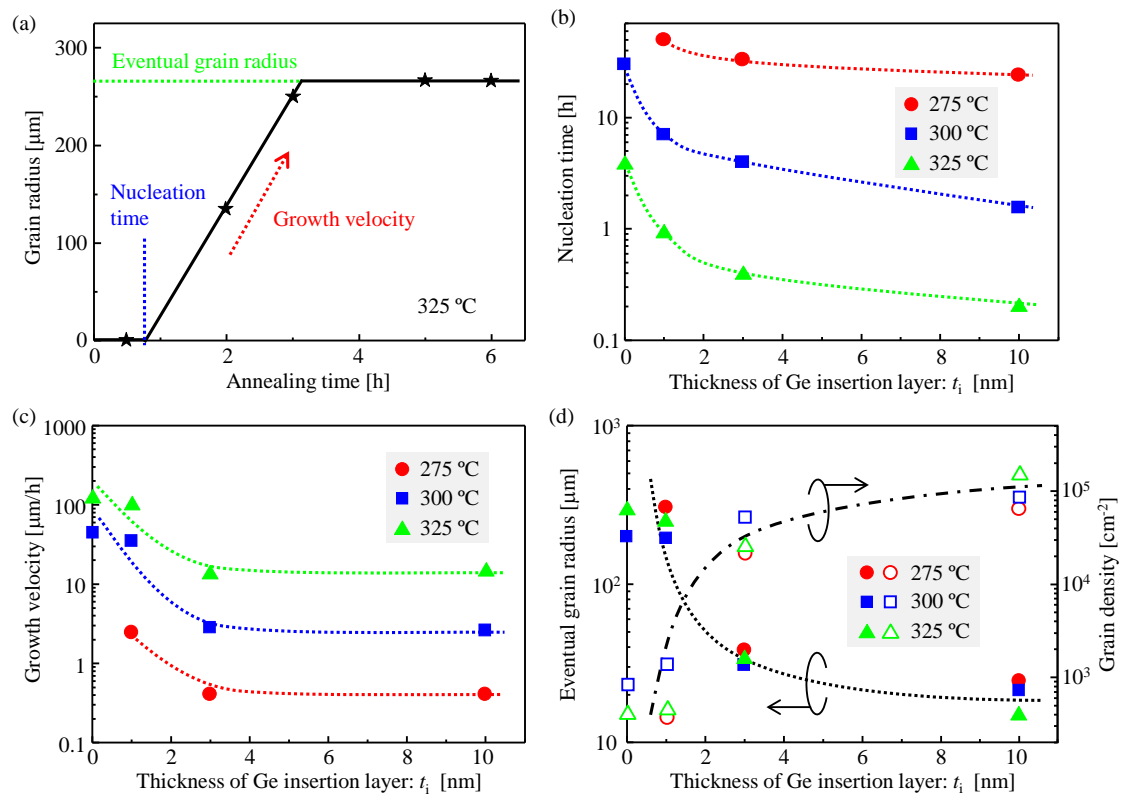


Fig. 2

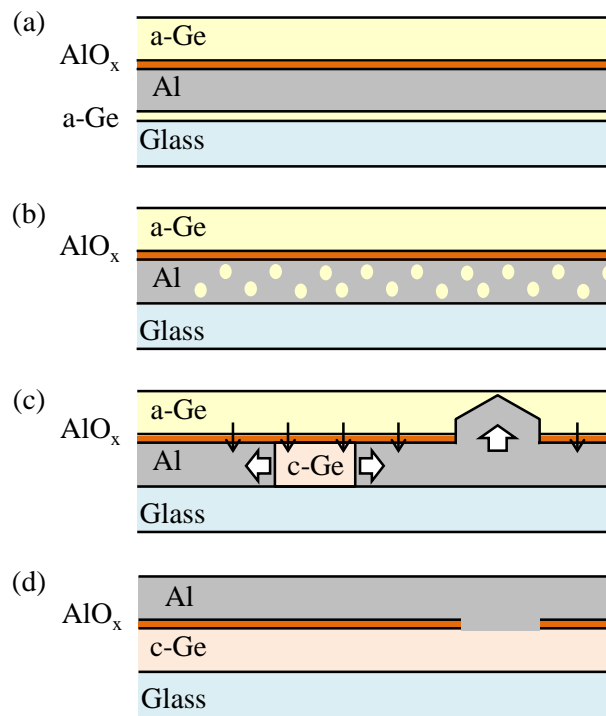


Fig. 3

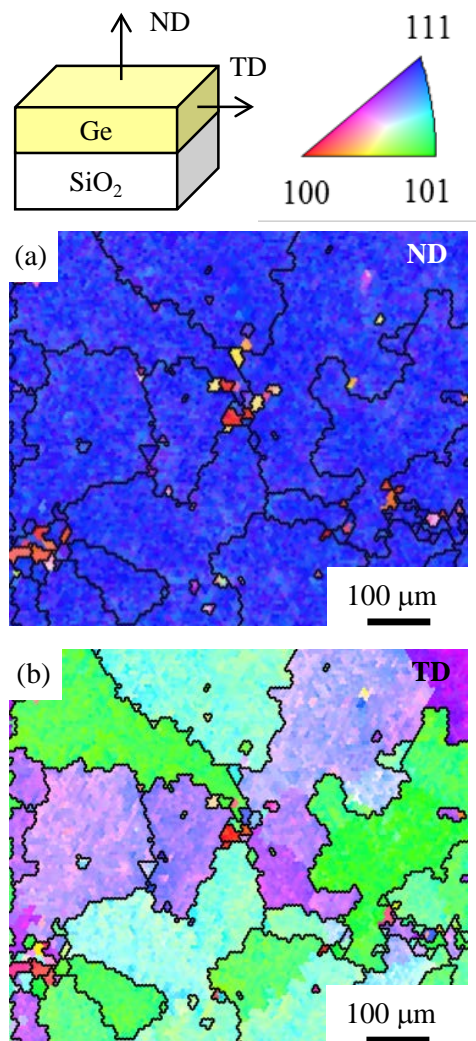


Fig. 4