# Effects of Al grain size on metal-induced layer exchange growth of amorphous Ge thin film on glass substrate

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### ABSTRACT

Metal-induced layer exchange (MILE) has attracted increasing attention as a way to lower the crystallization temperature of amorphous semiconductor thin films on insulating substrates. This paper demonstrates that the quality of the catalytic Al layer strongly influences the growth properties in the MILE of amorphous Ge. The growth velocity of the MILE significantly decreases with increasing the deposition temperature of Al ($T_{Al}$: RT–200 °C), while the grain size of crystallized Ge becomes maximum (28 μm) at $T_{Al} = 100$ °C. This behavior is attributed to the Al grain size depending on $T_{Al}$, which influences both the nucleation frequency and the lateral growth velocity of Ge in Al. These findings give new insight into MILE for fabricating high-quality semiconductor thin films at low temperatures on inexpensive substrates.

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## 1. Introduction

Semiconductor thin film technology has been progressing rapidly for fabricating next-generation electronic devices with resource saving. Germanium is a promising candidate for a thin-film material because it has higher carrier mobilities than Si [1] and large light-absorbing capacity in the near-infrared [2]. Additionally, amorphous Ge (a-Ge) crystallizes at lower temperatures than the softening temperature of commonly-used glass (~550 °C) [3–5]. (111)-Oriented Ge is particularly attractive because it provides a high carrier mobility for metal-oxide-semiconductor transistors [6,7] and acts as an epitaxial template for group III–V compound semiconductors [8,9], aligned nanowires [10, 11], and spintronics materials [12]. These properties have motivated many researchers to synthesize orientation-controlled, large-grained Ge on glass for fabricating high-speed thin-film transistors, high-efficiency thin-film tandem solar cells, and multi-functional devices [13–17].

Highly (111)-oriented Ge layers have been recently achieved on glass [18–24] and plastic substrates [25–27] owing to the development of metal-induced layer exchange (MILE), that is, crystallization via the layer exchange between a-Ge and metals. The MILE is a powerful technique to fabricate high-speed thin-film transistors [28] or vertically aligned nanowires [29,30] on amorphous substrates including plastics. The layer exchange phenomenon was originally found in the reaction between Al and Si [31–48]. The mechanism has been investigated over a decade from the perspective of both technological and scientific

points, which is summarized as follows. The driving force of the MILE process is the difference in Gibbs energy between amorphous and crystalline Si [34,43–45]. First, Si atoms diffuse from metastable amorphous Si into Al through the Al grain boundaries (GBs) during annealing [42, 43]. When the Si concentration in Al is supersaturated, Si nucleates in Al GBs [43,44]. After that, Si atoms dissolving in Al contact with the Si nuclei, which induces the lateral growth of Si crystals. The Si lateral growth stresses Al and pushing it to the upper layer [42,43]. Eventually, Si forms a bottom layer while Al forms an upper layer. The crystal quality of the resulting Si layer depends on the growth rate, i.e., the Si diffusion rate into Al [47,48].

The abovementioned mechanism is applicable to MILE between Ge and Al. Because the MILE begins with the diffusion of Ge atoms into Al GBs, the Al grain size should influence the MILE process and also the crystal quality of the resulting poly-Ge layer. In the present study, we therefore focus on the effects of the initial Al grain size on the MILE process of a-Ge. We demonstrate that the Al grain size has an optimum value for providing Ge of good crystal quality.

## 2. Experimental details

Fig. 1 presents a schematic of the sample preparation process. We prepared 50-nm-thick Al layers on $SiO_2$ glass substrates where the substrate temperatures ($T_{Al}$) were room temperature (RT), 50 °C, 100 °C, and 200 °C. After natural cooling, the Al layers were exposed to air for 5 min to form native $AlO_x$ membranes as diffusion-limiting layers. Because the MILE progresses with the diffusion of Ge into Al as mentioned above, the diffusion-limiting layer significantly influences the growth properties of the MILE [19,22,37]. Then, 40-nm-thick a-Ge layers were
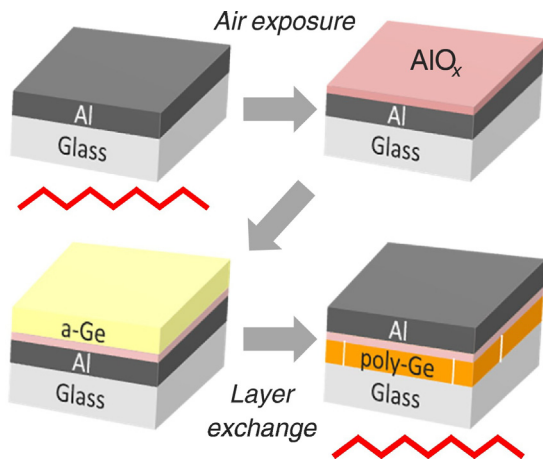
Fig. 1. Illustration of the process of Al-induced layer exchange growth of a-Ge on a glass substrate.

prepared on the $AlO_x$ at RT. Here, the thickness of the a-Ge layers is thinner than that of the Al layers in order to clarify growth domains [21]. All of the depositions were performed using radio frequency (RF) magnetron sputtering (Sanyu Electron SVC-700RF, base pressure: $3.0 \times 10^{-4}$ Pa) with an Ar pressure of 0.2 Pa and an RF power of 50 W. The deposition rate was 28 nm min$^{-1}$ for Ge and 31 nm min$^{-1}$ for Al. Finally, the samples were annealed at 385 °C in $N_2$ for 1–100 h to induce layer exchange between Ge and Al. The semiconductor layer grown by MILE does not contain N atoms after annealing [19,40]. The samples were evaluated using Nomarski optical microscopy (Leica DM 2500 M), atomic force microscopy (AFM, SHIMADZU SPM-9600), and electron backscatter diffraction (EBSD, TSL OIM analysis).

## 3. Results and discussion

The grain size of the as-deposited Al layers were roughly evaluated using AFM. The results are shown in Fig. 2. As shown in the AFM images, the surface of the Al layers takes on different forms depending on $T_{Al}$. The average grain size of Al, estimated from the AFM images, clearly increases with increasing $T_{Al}$. This behavior is common in sputtering deposition [49].

We evaluated the growth velocity of crystalline Ge in the MILE process as a function of $T_{Al}$ using Nomarski optical microscopy observing the back surface of the samples. The growth evolution for the sample with $T_{Al} = 100$ °C is shown in Fig. 3(a)–(c), where the dark-colored
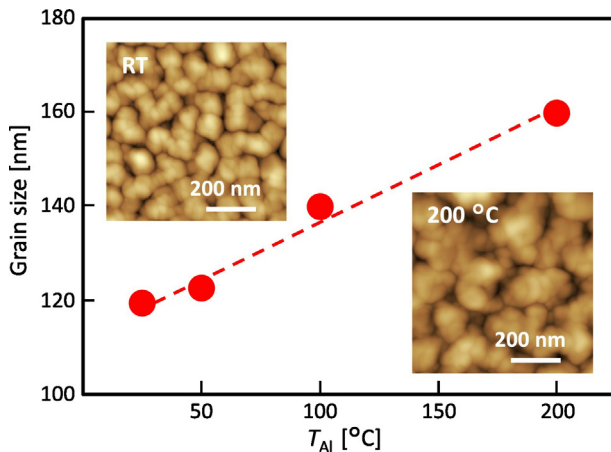


Fig. 2. Average grain size of the as-deposited Al layers as a function of $T_{Al}$. The grain size was estimated from AFM images, as typical shown for the samples with $T_{Al} = $ RT and 200 °C.
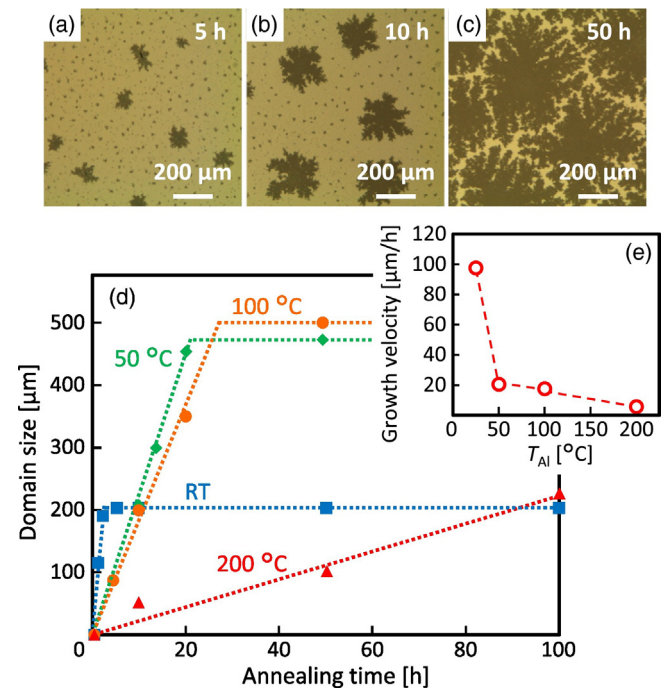


Fig. 3. (a–c) Nomarski optical micrographs showing the back surface of the sample with $T_{Al} = 100$ °C through the transparent substrate, where the sample was annealed at 385 °C for (a) 5 h, (b) 10 h, and (c) 50 h. (d) Annealing time dependence of the size (diameter) of crystalline Ge domains, estimated from Nomarski optical micrographs, for the samples with $T_{Al} = $ RT, 50, 100, and 200 °C. (e) Lateral growth velocity of the Ge domains as a function of $T_{Al}$.

area indicates crystallized Ge and the bright-colored area indicates Al. The micrographs indicate that crystal Ge domains laterally grow with increasing annealing time. As shown in Fig. 3(c), the lateral growth stops before the growth fronts collide with each other because the initial Ge is thinner than Al [21].

We measured the Ge domain sizes (diameters) from Nomarski optical micrographs for the samples with $T_{Al} = $ RT, 50 °C, 100 °C and 200 °C. The results are summarized in Fig. 3(d) as a function of the annealing time. For all samples except $T_{Al} = 200$ °C, the domain size increases as the annealing time increases and becomes saturated. We note that the higher $T_{Al}$ provided the larger saturated domain size. For the sample with $T_{Al} = 200$ °C, the domain growth was not saturated within 100 h. The lateral growth velocity of the Ge domains can be derived from the slopes in Fig. 3(d) because the lateral growth velocity in MILE is almost consistent with annealing time [47,48]. Fig. 3(e) shows the lateral growth velocity of the Ge domains as a function of $T_{Al}$. It is found that the growth velocity clearly decreases with an increase of $T_{Al}$. This behavior will be discussed later together with the crystal quality of Ge.

In MILE, a growth domain is generally divided into several grains [19, 27]. The actual grain sizes of the resulting Ge layers were evaluated using EBSD analysis. Before EBSD, top Al layers were removed using an HF solution (HF: 1.5%) for 1 min. Fig. 4(a)–(d) show that the crystal orientation of Ge strongly depends on $T_{Al}$: the (111) orientation fraction is maximum for the sample with $T_{Al} = 100$ °C. Such (111) orientation can be explained from the perspective of the appearance of the energetically stable plane [18,44]. In MILE, the lower growth rate leads to the higher (111) fraction [19,40,47,48]. On the other hand, the (111) fraction decreases with increasing the surface roughness of Al [46,48]. The sample with $T_{Al} = 100$ °C presented the highest (111) fraction among the samples in this study likely owing to the good balance between the growth rate and the surface roughness of Al. The grain size of Ge was defined as the diameter of the regions surrounded by the black solid lines in Fig. 4(a)–(d). Fig. 4(e) shows the grain size of Ge