Orientation-Controlled Large-Grain SiGe on Flexible Substrate by Nucleation-Controlled Gold-Induced Crystallization

Jong-Hyeok Park^{1,2}, Masanobu Miyao¹, and Taizoh Sadoh¹

¹ Department of Electronics, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan ² JSPS Research Fellow, 5-3-1 Kojimachi, Chiyoda-ku, Tokyo 102-0083, Japan

Phone: +81-92-802-3737 Fax: +81-92-802-3724 E-mail: j_park@nano.ed.kyushu-u.ac.jp

Abstract

Low-temperature gold-induced crystallization of SiGe is investigated. By annealing (~250°C) of a-SiGe/Au/insulator stacked structures, positions of SiGe and Au layers are inverted, and SiGe crystals are obtained on insulator. Combined with nucleation control through modulation of SiGe/Au mixing by diffusion barriers and anisotropic interface energy of SiGe/substrates, (111)- or (100)-oriented large (\geq 20 µm) crystals are obtained. Moreover, direct formation onto flexible plastic substrates is realized. This technique will facilitate high-performance flexible electronics.

1. Introduction

Low-temperature ($\leq 250^{\circ}$ C) formation of orientationcontrolled large-grain (>10 µm) SiGe on insulator is essential to realize flexible electronics, where various functional devices are integrated on flexible plastic substrates (softening temperature: ~300°C). This is because SiGe provides higher carrier mobility and superior optical properties compared with Si.

Recently, Al-induced crystallization (AIC) of Si, SiGe, and Ge are intensively investigated, where a-Si/Al, a-SiGe/Al, and a-Ge/Al stacked structures are employed [1-4]. In these AIC processes, layer-exchange of the stacked structures results in formation of poly-crystal films on insulator. Owing to bond-modulation by catalysis, AIC of Ge proceeds at $\sim 200^{\circ}$ C [8]. However, high-temperature annealing (400-450°C) is necessary to induce crystallization of Si and SiGe. Thus, the crystallization temperatures should be further decreased to employ flexible plastic substrates. For this purpose, a new catalyst should be developed.

In the present study, we investigate gold-induced crystallization [5-7]. This enables growth of $Si_{1-x}Ge_x$ ($0 \le x \le 1$) at a low-temperature (~250°C). Moreover, by controlling the nucleation process, orientation-controlled large-grain crystals are achieved.

2. Experiments and Results

Au films (50-100 nm thickness) were deposited on quartz substrates. Subsequently, $a-Si_{1-x}Ge_x$ films ($0 \le x \le 1$) (50-100 nm thickness) were deposited on the Au layers. The samples were annealed in N₂ to induce crystallization, as shown in Fig. 1(a).

The composition profiles in samples before and after annealing were evaluated by AES. The profiles of Au and Si in Si/Au samples before and after annealing (250°C, 20 h) are shown in Figs. 1(b) and 1(c), respectively. The sample consists of Si-top- and Au-bottom-layers before annealing. After annealing, positions of Si and Au layers are inverted. This indicates that layer-exchange occurs at 250°C. Similar results were obtained for samples with the whole Ge fractions after annealing (250°C).

The crystallinity of grown layers was investigated by Raman spectroscopy. Fig. 2(a) shows the Raman spectra of annealed samples with various initial Ge fractions (30, 50, and 80%). In all spectra, three peaks due to Ge-Ge, Si-Ge, and Si-Si modes of c-SiGe are clearly observed. Ge fractions of the grown layers evaluated from the spectra are almost the same as those of the initial a-SiGe layers, as shown in Fig. 2(b). This indicates no segregation of Si or Ge atoms during the growth. Thus, formation of SiGe crystals with controlled Ge fractions becomes possible at a low temperature (~250°C).

To obtain orientation-controlled large-grain crystals, randomly-oriented bulk nucleation in Au layers should be suppressed and instead, preferentially-oriented nucleation at Au/substrate interfaces should be dominated. This domination of interface nucleation can be achieved through controlling Si, Ge atomic supply into Au layers, because interface nucleation is energetically favorable compared to bulk nucleation. Based on this idea, we examine diffusion control technique. Here, amorphous Al_2O_3 diffusion barriers (~7 nm thickness) were introduced between a-SiGe and Au layers. These samples were annealed at 250°C.

Crystal structures of the grown layers are studied by EBSD after selective removal of Au and Al₂O₃ layers. EBSD images for the samples without or with Al₂O₃ layer are shown in Figs. 3(a) and 3(b), respectively. For the sample without Al₂O₃ layer, grain sizes are very small $(2-3 \mu m)$, and the crystal orientations are random. On the other hand, (111)-oriented large-grains (20-50 µm) are obtained for the sample with Al₂O₃ layer. The result for the samples having Al₂O₃ layers are attributed to that nucleation at Au/SiO₂ interface becomes dominant, as shown in Fig. 3(c). The free energy on SiO_2 shows the for (111)-oriented crystal minimum [8], thus (111)-oriented nuclei should be dominantly generated. Growth from these low-density (111)-oriented nuclei results in (111)-oriented large-grain Ge.

This result triggered an idea to obtain (100)-oriented large-grain Ge by introducing Al_2O_3 layers between Au and substrates, because (100)-oriented nucleation is the most energetically favorable on Al_2O_3 layers [9]. To examine this, a-Ge (100 nm)/Al_2O_3 (7 nm)/Au (100nm) stacked-structures were formed on quartz substrates

covered with Al_2O_3 layers (thickness: 30 nm). Fig. 4(a) shows an EBSD image after annealing (250°C, 100 h). As expected, (100)-oriented large-grain Ge is obtained. These phenomena are attributed to preferential (100)-oriented nucleation on Al_2O_3 bottom-layers, as shown in Fig. 4(b).

Moreover, we investigate growth on plastic substrates [Fig. 5(a)]. An EBSD image of the annealed sample is shown in Fig. 5(b). Interestingly, (111)-oriented large-grain (~50 μ m) crystals are obtained directly on the plastic substrate. This result is attributed to preferential (111)-oriented nucleation on plastic substrates due to interface-energy minimization, as shown in Fig. 5(c).

3. Conclusion

Nucleation-controlled gold-induced crystallization technique has been developed. Through domination of interface nucleation by introduction of interface-layers, i.e., diffusion barriers, and orientation control of nuclei using anisotropic free energy on substrates, formation of orientation-controlled large-grain ($\geq 20 \ \mu m$) crystals on flexible plastic becomes possible at 250°C. This technique is very useful to realize advanced thin-film devices for flexible electronics.

References

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Fig.1. Sample structure (a), and Si and Al concentration profiles before (b) and after annealing (250°C, 20h) (c).







Fig.3. EBSD images for Ge samples without (a) and with Al_2O_3 diffusion barrier (b), and schematic explanation of (111)-oriented nucleation on SiO₂ (c).



Fig.4. EBSD image of gown layer (a) and schematics of (100)-oriented nucleation on $\rm Al_2O_3$ (b).

Fig.5. Sample photo (a), EBSD image of gown layer (b) and schematics of (111)-oriented nucleation on plastic (c).