Large grain growth of poly-GeSn on insulator by pulsed laser annealing in water
Masashi Kurosawa1,2, Noriyuki Taoka1, Hiroshi Ikkenoue1, Osamu Nakatsuka1, and Shigeki Zaima1

1 Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan
2 JSPS Research Fellow, 5-3-1 Kojimachi, Chiyoda-ku, Tokyo 102-0083, Japan

Department of Electronics, Kyushu University, 744 Motooka, Fukuoka 819-0395, Japan

Abstract
Amorphous Ge1-xSnx films on insulators are crystallized by using a pulsed laser annealing (PLA) in air and water. Even the melt process, Sn precipitation hardly occurs for the case of 2%-Sn incorporation. Also, we found that a combination of the Sn incorporation and the PLA in water provides us improvement of the grain size up to ~800 nm and a good flatness of the intra grains.

1. Introduction
Poly-GeSn is a promising material for realizing advanced thin film transistors with high mobility and 3D integrated circuits without the bonding process.[1-3] Recently, we clarified that Sn incorporation of 2% is effective for reducing crystallization temperature of a GeSn layer on SiO2 layer, and that the GeSn layer has a relatively high Hall mobility of ~1000 cm2/Vs.[4,5] However, grain size of the GeSn layer is much smaller than that for poly-Si formed by a pulsed laser annealing (PLA).[6] In order to further improve the mobility, formation of the GeSn layer with large grain size is required.

Recently, PLA in water was proposed by Machida et al. as a low temperature crystallization method for amorphous Si layers, which can provide to form poly-Si layers with a large grain of ~1.5 µm on a SiO2 layer.[6] Since PLA is a melting growth, it should be clarified that Sn precipitation occurs or not for the Ge-Sn system because the solubility limit of Sn in Ge is around 1.1%. In this study, we comprehensively examine the effect of laser irradiation atmosphere, laser energy density, and Sn content on the growth features of the poly-GeSn layer.

2. Experimental Procedure
The laser annealing system and the sample structure is schematically shown in Fig. 1. A Si(100) wafer covered with a 1-µm-thick SiO2 layers was used as the substrate. A 50-nm-thick amorphous Ge layer with a Sn content of 2% was deposited on the substrate at room temperature (RT) by a solid source MBE. Then, these samples were crystallized using the PLA in air or water, where a pulsed KrF excimer laser with duration of 55 ns (λ=248 nm, Gigaphoton Inc.) was irradiated at RT. The beam size on the substrate surface is around 360×850 µm². The laser energy (E) was changed to 50-310 mJ/cm², and the number of laser beam pulses was set to 100 pulse/location.

3. Results and Discussion
Since laser annealing with high energy typically induces surface roughness, impact of PLA in water on the surface roughness was firstly investigated. Figure 2 shows irradiation atmosphere (air or water) dependence of the average surface roughness (Rq) of the Ge layers with the Sn incorporation. It is found that Rq for the air irradiation was drastically increases more than 130 nm/cm². On the other hand, in the case of the water, the increment of Rq is smaller than that for the air irradiation, indicating that PLA in water is effective for reduction of the surface roughness at the high E. This is attributed to a homogenization of the temperature distribution within these layers[6]. In addition, although, in the case of the water, the roughness increases at around 200 µm/cm², the roughness hardly changes at more than 250 µm/cm². This reason will be discussed later. Also, a laser with high energy typically induces ablation of a layer. As shown in Fig. 3(a), the Ge layer without the Sn incorporation was partially ablated at 95 nm/cm² as indicated the white arrow. On the other hand, the Ge layer with the Sn incorporation has a uniform surface even after PLA at 100 nm/cm² (Fig. 3(b)). These results clearly indicate that the Sn incorporation has a role to prevent the ablation of the Ge layers by PLA.

The crystallization of the Ge layers with and without the Sn incorporation after PLA at various E was confirmed by Raman scattering spectroscopy. At less than E occurring the ablation, the Ge layers with and without the Sn incorporation are crystallized (Fig.4). Also, the peak associated with the Ge-Sn vibration GeSn-Sn shifts toward higher energy when Sn incorporation is shifted from that for the Ge layer without the Sn incorporation. The shifted value is identical to 1.6 cm⁻¹ without depending on E at more than 100 mJ/cm². This suggests the formation of the GeSn layer with the Sn content of 2% without significant precipitation. The crystallinitiies of the Ge and GeSn layers were evaluated from the ratio of the area of the intensity associated with amorphous and crystal components of the Raman peaks. The crystallinity of the Ge layer increases with increasing E up to 85 mJ/cm² (Fig. 5(a)). Then, at higher than 85 mJ/cm², the ablation occurs as previously mentioned. Furthermore, the crystallinity is still 85%. On the other hand, the crystallinitiies of the GeSn layers reach to 100% at more than 190 mJ/cm². Also, the full widths at half maximum (FWHM) of the Raman peaks for the both layers monotonically decrease with increasing E (Fig. 5(b)), suggesting that the formation of the Ge and GeSn layers with the high crystalline quality at high E.

Grain sizes of the GeSn layers crystallized by PLA in water at 130 (Fig. 6) and 310 (Fig. 7) mJ/cm² are confirmed by TEM. Incorporation of small grains is observed in Fig. 6. On the other hand, in Fig. 7, there is no contrast for the small grains, indicating large grain growth. Also, the smooth surface of the GeSn layer is observed. Taking into account the smooth surface, the degradation and saturation of Rq from 200 mJ/cm² to 300 mJ/cm² shown in Fig. 2 may be attributed to the large grain growth and the roughness at the grain boundaries. Furthermore, EBSD reveals that the grains size increases from ~20 nm to ~800 nm with increasing E from 130 (Fig. 8(a)) to 310 (Fig. 8(b)) mJ/cm². It should be noted that the maximum grain size of ~800 nm obtained in our experiment is at least seven times larger than that for the conventional PLA of a-Ge in air.[7]

Consequently, in order to obtain the poly-Ge layer with large grain size and the high crystalline quality, PLA with more than 250 mJ/cm² is needed. Therefore, the combination of PLA in water and the Sn incorporation is quite important.

4. Conclusions
Large grain poly-Ge0.98Sn0.02 layers without any Sn precipitation have been successfully realized on a SiO2 layer combined with the Sn incorporation of 2% and PLA in water. This method is a promising technique for high quality crystallization of thin semiconductor films such as Si and Ge even on flexible substrates and Si platforms.

Acknowledgements
We would like to thank Dr. S. Arai for providing the opportunity to use the TEM observations. M.K. acknowledges JSPS Research Fellowships for Young Scientists. This work was partly supported by a Grant-in-Aid for Scientific Research of MEXT, Japan.

References
Fig. 1. (a) Laser annealing system and (b) initial sample structure used in this experiment.

Fig. 2. PLA irradiation atmosphere dependence of average surface roughness (R_a) measured by AFM.

Fig. 3. Surface morphologies after PLA in water for (a) Ge layer at 95 mJ/cm² and (b) GeSn layer with the Sn content of 2% at 100 mJ/cm².

Fig. 4. Raman spectra for Ge layer and GeSn layer with the Sn content of 2%. These layers were crystallized by PLA in water.

Fig. 5. Sn content dependences of (a) crystallinity and (b) FWHM of Ge-Ge peaks in Ge_{1-x}Sn_{x} layer measured by Raman spectra. These layers were crystallized by PLA in water.

Fig. 6. TEM images of GeSn layers with the Sn content of 2% after PLA in water at 130 mJ/cm².

Fig. 7. TEM images of GeSn layers with the Sn content of 2% after PLA in water at 310 mJ/cm².

Fig. 8. EBSD images of GeSn layers with the Sn content of 2% after PLA in water at (a) 130 mJ/cm² and (b) 310 mJ/cm².