Dopants behavior in polycrystallization of heavily doped Ge\textsubscript{1-x}Sn\textsubscript{x} layer using pulsed laser annealing in water

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Abstract
We have investigated dopant dependence of heavy doping behavior for poly-Ge\textsubscript{1-x}Sn\textsubscript{x} layer formed on insulator using pulsed laser annealing in water. We found that the resistivity of poly-Ge\textsubscript{1-x}Sn\textsubscript{x} layer clearly depends on kind of dopants. It is also observed that the reduction of the dopant density after the annealing depends on kind of dopants. We consider that out-diffusion behavior from Ge\textsubscript{1-x}Sn\textsubscript{x} layer during laser annealing is different among dopants, which means differences of the diffusion coefficient in melting Ge\textsubscript{1-x}Sn\textsubscript{x}.

1. Introduction
Polycrystalline-Ge (poly-Ge) layer on insulator is one of the most attractive semiconductor materials for advanced three-dimensional integrated circuits (3D-ICs) because of its high carrier mobility and low crystallization temperature compared with poly-Si [1]. To fabricate high performance CMOS circuits with poly-Ge on insulators, heavy doping technique for both n- and p-type poly-Ge with low thermal budget process is required to enhance a driving current of MOSFETs.

Recently, we are focusing on the pulsed laser annealing (PLA) in water for this requirement. Our group previously found that using this method for a 2% Sn-incorporated amorphous Ge (a-Ge) layer effectively suppresses the ablation of layers even for the high-energy-density laser, and as a result, large grain growth was achieved [2]. We also achieved high-quality heavy n- and p-type doping for poly-Ge\textsubscript{1-x}Sn\textsubscript{x} layers with Sb and Ga, respectively, using this method [3].

In this study, we investigated the dopant dependence of heavily doping behavior for poly-Ge\textsubscript{1-x}Sn\textsubscript{x} layer prepared with PLA in water. It is well known that equilibrium segregation coefficient ($k$) and maximum solubility limit depend on kind of dopants [4]. On the other hand, we found that, in the case of PLA in water for poly-Ge\textsubscript{1-x}Sn\textsubscript{x} layer, out-diffusion of dopants form melted Ge\textsubscript{1-x}Sn\textsubscript{x} is an important factor to achieve heavy doping without the reduction of dopant density.

2. Experiment
N-type Si(001) wafer covered with a 1-µm-thick SiO\textsubscript{2} layer was used as substrate. A 50-nm-thick a-Ge\textsubscript{0.98}Sn\textsubscript{0.02} layer was deposited on the substrate at room temperature (RT) using molecular beam deposition system. We introduced various dopants into a-Ge\textsubscript{0.98}Sn\textsubscript{0.02} layer by ion-implantation technique or in-situ doping during a-Ge\textsubscript{0.98}Sn\textsubscript{0.02} deposition. Details of the dopant introduction are summarized in Table I. The a-Ge\textsubscript{0.98}Sn\textsubscript{0.02} layers were crystalized with the irradiation of a KrF excimer laser (pulse duration: 55 ns, wavelength: 248 nm) in pure water at RT. The laser energy density ($E$) was set in range of 90–320 mJ/cm\textsuperscript{2}, and the laser beam was pulsed 20 times at an irradiated area.

3. Results and discussion
Figures 1(a) and (b) shows the resistivity of poly-Ge\textsubscript{1-x}Sn\textsubscript{x} layer with n- and p-type dopants, respectively, as a function of the laser energy density. In the n-type doping case, at $E \leq 110$ mJ/cm\textsuperscript{2}, the resistivity is higher than that of the undoped poly-Ge\textsubscript{1-x}Sn\textsubscript{x} layer, which suggests the carrier compensation of electrons from activated n-type dopants and holes from electrically activated vacancies. Increasing $E$, the resistivity of As- and Sb-doped samples decreases, which indicates that the electron density and/or mobility is increased by PLA with a high $E$. Actually, we already found that the Hall electron density and mobility increase with irradiation of high-energy-density laser for a Sb-doped a-Ge\textsubscript{0.98}Sn\textsubscript{0.02} layer [3]. In contrast, the resistivity of P-doped sample increases at $E > 190$ mJ/cm\textsuperscript{2} and it is similar to that of an undoped poly-Ge\textsubscript{1-x}Sn\textsubscript{x} layer, which suggests that P atoms introduced into a a-Ge\textsubscript{0.98}Sn\textsubscript{0.02} layer don’t contribute to electrical properties of the polycrystallized Ge\textsubscript{1-x}Sn\textsubscript{x} layer. As shown in Fig. 1(b), the resistivity of all poly-Ge\textsubscript{1-x}Sn\textsubscript{x} layers with p-type dopant at $E \leq 190$ mJ/cm\textsuperscript{2} is lower than that of the undoped poly-Ge\textsubscript{1-x}Sn\textsubscript{x} layer, which suggests that there are additional holes related to p-type dopants. Increasing $E$, the resistivity of Al- and In-doped samples increases like the P-doped sample.

To clarify the reason of the dopant dependence of the resistivity, we carried out hard x-ray photoelectron spectroscopy (HAXPES; SPring-8 BL47XU and BL09XU) and SIMS measurements to investigate the dopant density in poly-Ge\textsubscript{1-x}Sn\textsubscript{x} layers. Figure 2(a) shows the ratio of the dopant density after PLA with various energies and that
before PLA. As, Ga, and Sb densities don’t depend on the laser-energy density. In contrast, Al and P densities are drastically reduced by PLA with a high-energy density of E > 170 mJ/cm². Thus, it can be considered that the dopant reduction affects the resistivity increase. Because the equilibrium segregation coefficients of As and Sb are lower than those of P and Al and the maximum solubility limits of Al and P are also higher than that of Sb [4], it is difficult to explain the dopant reduction by the segregation phenomena or differences of the maximum solubility limit. We consider that one of the possible reasons is out-diffusion of dopant atom from melting Ge₁ₓSnₓ layer. Figure 2(b) shows the schematic illustration of dopant distributions with different diffusion coefficients (D) after annealing. As shown in Fig. 2(b), in the case of a large D, out-diffusion reduces the dopant density at not only surface but also deep region of Ge₁ₓSnₓ layer. Thus, it is suggested that Al and P atoms in a melting Ge₁ₓSnₓ layer has a higher D than Ga, Sb, and As atoms. It is noted that, in the case of melting Si, the similar trend of D has been reported [5]. These results suggest that the diffusion coefficient in melting Ge₁ₓSnₓ is one of the keys for achieving heavy doping using PLA in water.

### 4. Conclusions

We examined the heavy doping for poly-Ge₁ₓSnₓ layer with various dopants using PLA in water. We found that Al and P densities after PLA are drastically reduced compared with other dopants. This result suggests that out-diffusion occur by large diffusion coefficient in Al and P cases compared with other dopants.

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### References


### Table 1 Summary of dopant introduction method and density.

<table>
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<tr>
<th>Dopant</th>
<th>Method, energy, dose</th>
<th>Average density (e/cm²)</th>
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<tr>
<td>Phosphorus</td>
<td>ion-implantation, 25 keV, 6x10¹⁴ cm⁻²</td>
<td>1x10²⁰</td>
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<td>Arsenide</td>
<td>ion-implantation, 50 keV, 6x10¹⁴ cm⁻²</td>
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<td>Aluminum</td>
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<tr>
<td>Gallium</td>
<td>in-situ</td>
<td>3x10¹⁹</td>
</tr>
<tr>
<td>Indium</td>
<td>ion-implantation, 55 keV, 5x10¹⁴ cm⁻²</td>
<td>1x10²⁰</td>
</tr>
</tbody>
</table>

### Fig. 1 The resistivity of poly-Ge₁ₓSnₓ layer with (a) n- and (b) p-type dopants as a function of the laser energy density.

### Fig. 2 (a) The ratio of the dopant density after and before PLA as a function of the laser energy density. (b) The schematic illustration of dopant distribution with different diffusion coefficients in Ge₁ₓSnₓ layer.