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主論文の要旨

論文題目　**Study on Heavily *n*-type Doping for Ge and $Ge_{1-x}Sn_x$ Epitaxial Layers**
(GeおよびGe$_{1-x}$Sn$_x$エピタキシャル層への高濃度*n*型ドーピング技術に関する研究)

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論文内容の要旨

Chapter 1 introduces about this study. Firstly, the limitation of conventional Si-CMOS is briefly mentioned follow up with the introduction of new higher-mobility channel material Ge and embedded S/D stressor structure to overcome the limitation. For Ge-CMOS, the reduction of a high parasitic resistance of metal/*n*-Ge contact due to the limitation of *n*-type dopant concentration in Ge is the most significant issue according to the 2018 International Roadmap for Devices and Systems. The recent statue of the contact resistivity of metal/*n*-Ge interface with the reason of difficulty in heavy *n*-doping on Ge is explained follow up with the breakthrough point used in this study.

The sample preparation procedures and characterization methods of this study are presented in Chapter 2. The growth of heavily Sb-doped Ge and $Ge_{1-x}Sn_x$ epitaxial layers by molecular beam epitaxy (MBE) system is explained with describing the working principle of MBE deposition method and the detailed sample preparation parameters of epitaxial layer growth. Similarly, the deposition of Ni layer by the electron beam evaporation method and Ni (stano)germanidation are followed with the working principle of the deposition method and the detailed sample preparation parameters of layer growth. The following is the deposition of Al electrode and circular transmission line model (C-TLM) patterning procedure for the measurement of contact resistivity. The characterization of the crystalline structure, electrical property, and chemical bonding state of the heavily *n*-doped Ge and $Ge_{1-x}Sn_x$ layer is presented by explaining the measurement principle of used equipment and relevant equations for evaluation.

In Chapter 3, the epitaxial growth and *in-situ* Sb doping on Ge and $Ge_{1-x}Sn_x$ layers are investigated and discussed. The growth of Sb-doped Ge and $Ge_{1-x}Sn_x$ epitaxial layers was performed by *in-situ* Sb doping under the non-thermal equilibrium condition in MBE with a temperature as low as 150 °C to realize the heavy doping of Sb. The pseudomorphically grown $Ge_{1-x}Sn_x$ layer with an Sn content around 6% is confirmed. The improvement of the crystallinity of the Ge and $Ge_{1-x}Sn_x$ epitaxial layers is observed with increasing the Sb doping concentration. The high electron concentration over the range of 10^{20} cm^{-3} is observed in not only Ge and but also $Ge_{1-x}Sn_x$ samples.

Interestingly, the enhancement of the Hall electron mobility along with the electron concentration is evaluated. This is due to the crystallinity improvement of the Sb-doped epitaxial layers due to the Sb surfactant effect and the parallel conduction through both in L and Γ valleys due to the heavily *n*-type doping and thus shifted Fermi level over the Γ valley.

In Chapter 4, the thermal stability of the heavily *n*-doped Ge and $Ge_{0.94}Sn_{0.06}$ epitaxial layers is investigated and discussed to clarify the upper limit of the formation temperature of metal/*n*-$Ge_{1-x}Sn_x$ contact. The Sb-doped Ge and $Ge_{0.94}Sn_{0.06}$ layers were annealed in a rapid thermal annealing system up to the temperature of 400 °C for 1 min in a pure N_2 atmosphere.

In the aspect of the crystalline structure, the thermal stability was higher than the temperature of 400 °C, since the pseudomorphically grown Sb-doped

$Ge_{1-x}Sn_x$ layers maintained the strain on the layer and suppressed dopant segregation or/and precipitation on the surface.

However, in the aspect of the electrical property and chemical bonding state of dopant, the upper limit of the thermal stability was lower than the temperature of 400 °C since the electron concentration and Sb^{1+} concentration decreased near to the thermal equilibrium solid solubility of Sb at the annealing temperature of 400 °C, which recommends the metal contact formation temperature lower than 400 °C to realize a low contact resistivity at metal/*n*-Ge and metal/*n*-$Ge_{1-x}Sn_x$ contacts.

Interestingly, it is found that there is no correlation between the presence of Sn and thermal stability of the electron and Sb concentration despite of the higher possibility of not only dopant segregation, but also strain relaxation and crystallinity degradation.

Furthermore, the $Ge_{0.94}Sn_{0.06}$ sample formed at higher Sb K-cell temperature; 280 °C eventually had superior thermal stability by maintaining higher electron and Sb^{1+} concentration. This is due to the strong surfactant effect of Sb and thus the superior crystallinity at the as-grown Ge and $Ge_{1-x}Sn_x$ epitaxial layers, maintaining its crystallinity after annealing.

In Chapter 5, metal/*n*-doped $Ge_{1-x}Sn_x$ contacts with various doping conditions and those contact resistivity are investigated and discussed. Here, not only Sb-doped epitaxial layers prepared by MBE but also *P*-doped epitaxial layers prepared by metal-organic chemical vapor deposition method are shown for comparison. The $Ni(Ge_{1-x}Sn_x)$, which has the formation temperature of 350 °C, was selected as the metal material, considering the thermal stability limit of heavily *n*-doped Ge and $Ge_{1-x}Sn_x$ layer; 400 °C. The formation of the $Ni(Ge_{1-x}Sn_x)$ layer was confirmed by grazing angle 2θ XRD measurement. Fully maintained strain and crystallinity in the Sb-doped $Ge_{1-x}Sn_x$ layer were found without serious dopant segregation after Ni (stano)germanidation.

The ultra-low contact resistivity as low as 10^{-9} $\Omega \cdot cm^2$ was achieved at both

NiGe/Sb-doped Ge/Ge and Ni($Ge_{1-x}Sn_x$)/Sb-doped $Ge_{0.935}Sn_{0.065}$/Ge structures at the Sb-doped samples with an electron concentration range as high as 10^{20} cm^{-3}. The contact resistivity of Sb-doped $Ge_{1-x}Sn_x$ samples is a lower value than the P-doped sample, in spite of higher Sn contents by maintaining the high doping concentrations.

The Schottky barrier heights Φ_B deduced from the estimated contact resistivity with respect to the electron concentration was lower than the experimentally reported values of metal/n-Ge contact; 0.6 eV. It is considered that the dominant portion of this is due to the heavy doping, and thus image-force lowering on SBH.

Finally, the research achievements and remaining issues of this study, and the future tasks are presented in Chapter 6 for the establishment of a further decrease in contact resistivity of metal/n-$Ge_{1-x}Sn_x$ interface. In this study, significantly low contact resistivity at NiGe/n^+-Ge and Ni($Ge_{1-x}Sn_x$)/n^+-$Ge_{1-x}Sn_x$ contacts is achieved which promises the improvement of the performance of n-type Ge and $Ge_{1-x}Sn_x$ MOSFET devices.

Furthermore, the achievements of this study by using low-temperature process ($\leq$ 400 °C) are also valuable for future monolithic integration of the surrounding electronic devices and for the photoelectric fusion using Group-IV semiconductor since a low resistivity at metal/semiconductor is one of the crucial issues for all these devices, and it should be achieved using a low-temperature process.

One of the remaining issues of this study is investigating the interfaces of Ni($Ge_{1-x}Sn_x$)/n^+-$Ge_{1-x}Sn_x$/p-Ge structure. In the future, the contact resistivity evaluation using a multi-ring CTLM pattern which is an upgraded model to evaluate contact resistivity, P- and Sb- co-doping or delta doping on the epitaxial layer, and the issue of junction leakage should be worked as a future task.