Investigation of Schottky diodes on germanium using mercury probe
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I. Introduction
Ge is a promising alternative to Si as a material for MOSFET channel, because of the higher bulk mobilities of electron and hole in Ge than those in Si; however, higher mobility has yet to be shown in nMOSFETs. This is due to the high contact resistance at metal/nGe in the Source/Drain regions, which originates mainly from insufficient electrical activation of nGe layer [1] and the Fermi level pinning (FLP) at the charge neutral level (CNL) of Ge, close to the valence band maximum (e.g., [2]). Although the origin of the FLP has been explained in terms of the metal-induced gap states (MIGS) model [2], it does not constitute proof. In this study, we focused on the FLP of Ge to find a key to the fabrication of the ideal metal/nGe, and therefore investigated various metal/Ge Schottky characteristics. In particular, we used Hg/Ge diodes with mercury (Hg) probe to measure Ge diodes without the reaction between electrodes and Ge, and to clarify the effect of the interfacial Ge oxides (GeO₂) layers on the Schottky properties.

II. Experimental
We fabricated various metal/Ge Schottky diodes. p- and n-type Ge(100) wafers were used as the substrates, and Si(100) wafers were used as the reference. Those wafers were treated with halogen acids (20% HF, 35% HCl, or 30% HBr). By thermal evaporation, Au or Al was formed on the substrate surface through a shadow mask as the electrode, and Al was formed on the backside as the contact to reduce the resistance. The J-V characteristics of those diodes were measured. Furthermore, the J-Vs of those Ge substrates treated with the halogen acid were measured by using mercury (Hg) probe [Figs. 1(a) and (b)], which can suppress the reaction on the substrates [3].

III. Results and Discussion
Figure 3 shows typical characteristics of the metal/Ge diodes fabricated by thermal evaporation. Those J-Vs showed ohmic characteristics in both Au/pGe and Al/pGe, and rectifying characteristics in both Au/nGe and Al/nGe [Figs. 3(a) and (b)], even though the work function (WF) difference between Au and Al is about 1 eV (Fig. 2), which should cause great differences in those J-Vs. In the case of metal/Si diodes, on the other hand, those J-Vs showed a reasonable tendency corresponding to the WF difference, i.e., nearly ohmic characteristics in Au/pSi and Al/nSi, and rectifying characteristics in Au/nSi and Al/pSi (data not shown). Furthermore, we have confirmed that neither forming gas annealing (FGA) nor other treatments (HCl and HBr) for the Ge diodes had any effect on the J-V characteristics. This originates from the Fermi level pinning (FLP); Fermi levels of various metals are pinned at the CNL of Ge [2].

Next, we measured J-V characteristics of Hg/nGe and Hg/pSi using Hg probe (Fig. 1). Figure 4 shows the J-V characteristics of Hg/nSi(100) and Hg/pSi(100) treated with HF. Each J-V showed rectifying behavior, though both Au/pSi(100) and Al/nSi(100) showed almost ohmic behavior. This corresponds to the WF differences (Fig. 2), leading to the Schottky barrier height (SBH) difference. The SBHs of Hg/nSi(100) and Hg/pSi(100) were estimated to be ~0.50 and ~0.77 eV, respectively, the sum of which is almost the same value as the band-gap of Si. The J-Vs for Hg/Ge with various halogen acid treatments (HF, HCl, and HBr) showed completely different characteristics than those for metal/Ge(100); in the order of HBr, HCl, and HF, the J-Vs for pGe tended to change from ohmic to rectifying characteristics, and those for nGe tended to change from rectifying to ohmic characteristics. This is probably related to GeO₂ existing at the interface between Hg and Ge(100). According to the XPS results for those Ge, peaks indicating very thin GeO₂ appeared in Ge 3d (Fig. 7). In the order of HBr, HCl, and HF, the peaks became large, i.e., the average thicknesses of GeO₂ become thick, which is the same as in a previous study about Ge nanowires [4]. We confirmed the effect of halogen acids on bonding states of the Ge surfaces. HBr- and HCl-treated Ge surfaces showed Br 3d and Cl 2p peaks, respectively [Figs. 6 (a) and (b)], and the intensity of Cl 2p was relatively weaker than that of Br 3d. On the other hand, no F 1s peak was observed in HF-treated Ge surface [Fig. 6 (c)]. Thus, the dependence of the halogen acids on the GeO₂ thickness can be explained by the tendency that better surface passivation of the Ge is performed by the halogen acid with heavier halogen atoms.

It has previously been reported that Al/GeO₂ (2-2.2nm)/Ge diode showed quasi-ohmic behavior for nGe and clear Schottky characteristics for pGe [2], which is similar to our results. The authors concluded that GeO₂ suppressed the wave function penetration and therefore the origin of the FLP was MIGS [2]. If this is the case, however, Hg/pGe and Hg/nGe diodes should show ohmic and rectifying characteristics, respectively, because E₀ of Hg is located at the vicinity of the CNL of Ge (Fig. 8). Although there were halogen atoms on the Ge surfaces, they would not affect the Schottky properties. Since the electronegativities of F, Cl, Br, and Ge are 4, 3, 2.8, and 1.8, respectively [6], F, Cl, and Br are negatively charged and Ge is positively charged, when halogen atom and Ge are bonded. Those bonds may generate dipoles, which shift the position of the FLP; however, it is the opposite direction of the case of the metal electrodes. Those bonds may generate dipoles, which shift the position of the FLP; however, it is the opposite direction of the case of other metal electrodes. In this study, we consider that the GeO₂ layer shifted E₀ of Hg from the CNL (Fig. 8) or changed the CNL itself, and the MIGS model cannot be proved by their experiment alone. GeO₂ insertion at Al/Ge interfaces.

IV. Conclusions
The characteristics of Schottky diodes on Ge were investigated to examine the origin of high contact resistance for metal/nGe. In the case of metal electrodes fabricated by thermal evaporation, the diodes showed ohmic characteristics for pGe, and rectifying characteristics for nGe, originating from the FLP at the CNL of Ge. In the case of Hg, on the other hand, the diodes showed different characteristics compared to the case of the metal electrodes. Those J-Vs approached the ohmic behavior for nGe, and the rectifying behavior for pGe, owing to the GeO₂ layer at the interface of the diodes.

References
Fig. 1: Schematic view of mercury (Hg) probe.

Fig. 2: Work function, electron affinity, and band-gap for various metals (Au, Al, and Hg [5]) and semiconductors (Ge and Si [6]).

Fig. 3: J-V characteristics of (a) Al/pGe(100) and Au/pGe(100) and (b) Al/nGe(100) and Au/nGe(100).

Fig. 4: J-V characteristics of Hg/pSi(100) and Hg/nSi(100).

Fig. 5: J-V characteristics of (a) Hg/pGe(100) and (b) Hg/nGe(100) substrates with HF, HCl, and HBr treatments.

Fig. 6: XPS spectra of (a) Br 3d, (b) Cl 2p, and (c) F 1s from the Ge(100) substrates, which were treated with HBr, HCl, and HF, respectively.

Fig. 7: XPS spectra of Ge 3d from Ge(100) substrates with HF, HCl and HBr treatments.

Fig. 8: Band diagram of Hg/Ge with and without GeOx interfacial layer.