Charge neutrality level shift in the Bardeen limit of Fermi-level pinning at atomically flat Ge/metal interface

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Abstract
In this work, we investigated the Fermi level pinning (FLP) at metal/Ge interface formed on atomically flat Ge(111) surface. The effective charge neutrality level $\phi_{NL}$ is shifted by 0.1 eV from that of metal/Ge interface formed on rough surface. The $\phi_{NL}$ shift associated with interface Ge structure should be considered to discuss the FLP at metal/Ge interface in addition to S parameter.

1. Introduction
Fermi level pinning (FLP) at the metal/semiconductor interface is generally described as follows,
$$ q\phi_{bn} = S (q\phi_{m} - q\chi) + (1 - S) (q\phi_{CNL} - q\chi), $$
where $q\phi_{bn}$ is the Schottky barrier height (SBH) to conduction band edge of semiconductor, $q\phi_{m}$ is the work function of metal, $q\chi$ is electron affinity of semiconductor, $S$ is $\phi_{bn}/\phi_{m}$, and $q\phi_{CNL}$ is effective charge neutrality level. Therefore, S and $q\phi_{CNL}$ are critical for understanding the FLP. In the case of Ge, strong FLP ($S \approx 0$ (Bardeen limit)) close to valence band edge of Ge ($q\phi_{CNL} \approx q\chi + E_{v}$) has been reported at metal/Ge interface [1,2]. The origin of strong FLP has not been identified, because it is inferred that the metal/Ge interface still includes extrinsic FLP factors (ex. defects [3] and/or disorder induced gap states [4]).

Recently, we successfully formed the atomically flat Ge(111) surface by H$_2$ annealing process [5]. It is expected that the extrinsic FLP factors might be well eliminated by forming the well-defined structure. Then, the objective of this work is to study the FLP of metal/Ge interface employing the atomically flat surface.

2. Experimental
We prepared two kinds of surface structures on n-type Ge (111) substrates. One was chemically cleaned surface, and the other was atomically flat surface formed by H$_2$ annealing after chemical cleaning. The step & terrace structure was formed by annealing in H$_2$ ambient at 650°C for 15 min. The detail of H$_2$ annealing is described elsewhere [5]. Fig. 1 shows the AFM images of chemically cleaned Ge(111) surface and H$_2$ annealed one. The step & terrace on H$_2$ annealed Ge(111) surface are clearly observed.

The Ge Schottky diodes were fabricated by thermal evaporation of several metals (Ag, Al, Cu, Co, Au and Ni) on both chemically-cleaned Ge(111) substrate and H$_2$ annealed one. Both electrode area and peripheral length was changed from 1.2 to 8.6 x 10$^{-2}$ cm and from 4.5 to 11 x 10$^{-2}$ cm respectively to eliminate the peripheral leakage current.

3. Results and Discussion
All n-Ge/metal junctions fabricated in this work showed Schottky characteristics irrespective of the work function of metals. However, in most metal cases, the off-leakage current of H$_2$ annealed sample was definitely improved.
larger than chemically cleaned one (Fig. 1(a)). The SBH value of metal/n-Ge interface was estimated from the I-V characteristics. Saturation current $I_s$ in each diode was estimated by extrapolating the off-leakage current to $V = 0$, and then the saturation current density $J_s$ was evaluated from the peripheral length dependence of electrode on $I_s$ to eliminate the peripheral leakage. Then, the exact $q\phi_{bn}$ was calculated from the $J_s$ with the following equation,

$$q\phi_{bn} = kT \ln \left( \frac{AT^2}{J_s} \right),$$

where $A$ is the Richardson constant (67 A/cm²/K² for n-Ge). 

Figure 2(b) shows the evaluated $q\phi_{bn}$ in various metals. Here, the work functions reported in the literature was assumed[6]. Although the Bardeen limit is still observed even on the H₂ annealed samples, it should be noted that its $q\phi_{CNL}$ is shifted by 0.1 eV from that of metal/Ge interface formed on chemically cleaned Ge(111) one. Since the H₂ annealed Ge(111) surface consists of the step and terrace as shown in Fig. 1(a), it is concerned that the step edge might induce a local leakage path and cause apparent $q\phi_{bn}$ lowering. We investigated the step density dependence of Ge(111) substrate on $q\phi_{bn}$ by changing the off-angle of Ge(111) substrate. On the H₂ annealed Ge (111) surface with off-angle of 0.07°, 0.10° and 0.16°, the step density was estimated to be 3.7, 5.2 and 8.3 step/μm by AFM measurement, respectively, which implies the step density is simply determined by the off-angle of substrate at 650°C without the step bunching formation observed on Si(111). However, possible $q\phi_{bn}$ lowering caused by an increase of leakage current at step edge was not observed as shown in Fig. 3. Namely, it is suggested that the $q\phi_{bn}$ is determined on the terrace, and that $q\phi_{CNL}$ of metal/Ge interface formed on H₂ annealed Ge(111) is actually different that on chemically cleaned one.

Finally, $q\phi_{CNL}$ at metal/Ge interface is discussed. Tersoff has proposed that $q\phi_{CNL}$ at metal/semiconductor interface is close to the charge neutrality level defined in bulk semiconductor [7]. The charge neutrality level of bulk Ge are theoretically estimated to be 4.48 [8] and 4.63eV [9], which are in a good agreement with the previous results obtained experimentally [1,2]. However, thanks to the small S parameter of metal/Ge interface, it is clarified that $q\phi_{CNL}$ at metal/Ge interface is definitely shifted on atomically flat Ge surface as schematically shown in Fig. 4. Namely, $q\phi_{CNL}$ at metal/Ge interface is determined not only by bulk characteristics of semiconductor but also by surface microstructure.

It is recently reported that $q\phi_{bn}$ at epitaxial Fe₃Si/Ge interface is reduced down to 0.46 eV [10]. They speculated that the FLP is alleviated by the passivation of extrinsic FLP factors (defect and dangling bond) due to the epitaxial interface formation [11]. However, considering the result of this work, it is possible that the reduction of $q\phi_{bn}$ at epitaxial metal/Ge interface is also explained by $q\phi_{CNL}$ shift associated with the interface microstructure of Ge. Therefore, we should take care of both S parameter and $q\phi_{CNL}$ to discuss the SBH modulation even in the case of metal/Ge interface.

4. Conclusion

It has been found for the first time that $q\phi_{CNL}$ at metal/Ge interface is shifted by 0.1 eV in Berdeen limit of FLP on atomically flat Ge (111) surface. This fact clearly indicates that $q\phi_{CNL}$ is determined not only by the bulk characteristics of Ge but also by the interface structure. Therefore, to discuss the SBH modulation at metal/Ge interface from the viewpoint of FLP, $q\phi_{CNL}$ in addition to S parameter should be carefully taken into account.

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References