Interface Structures and Electrical Properties of Micro-Fabricated Epitaxial Hf-Digermanide/n-Ge(001) Contacts

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ABSTRACT We investigated the interface crystalline structures and electrical conduction properties of epitaxial Hf-digermanide(HfGe2)/n-Ge(001) contacts with different electrode sizes of 20, 45, and 90 μm prepared via microfabrication. It was found that the microfabrication process improved the interface uniformity of the HfGe2/n-Ge(001) contacts. Detailed transmission electron microscopy analysis confirmed the growth of epitaxial HfGe2 on Ge(001) and implied that microfabrication suppressed the strain relaxation of HfGe2. These results imply that the applied strain of the epitaxial HfGe2, which was controlled via microfabrication in this study, is a possible parameter that may be used to improve the interface uniformity HfGe2/n-Ge(001) contacts. The Schottky barrier heights (SBHs) of the HfGe2/n-Ge(001) contacts estimated from the capacitance–voltage characteristics were small and in the range of 0.4 to 0.5 eV independent of the electrode size. Furthermore, considering the temperature dependence of the current density–voltage characteristics, we found that both the thermionic field emission current and the tunneling current through the interface dipole layer were possibly flowed in series and that the SBH for the 20 μm sample was 0.24 eV, whereas those for both the 45 and 90 μm samples were 0.31 eV.

INDEX TERMS Germanium, metal/semiconductor contact, epitaxy, Schottky barrier height.

I. INTRODUCTION

Germanium is a promising candidate material for the development of ultra-low power consumption integrated circuits, such as those found in advanced complementary metal–oxide–semiconductor (CMOS) and silicon photonics technologies, because of its higher mobility of both electrons and holes and lower energy bandgap compared to Si [1]. However, reducing the parasitic resistances in these systems, such as the source/drain and metal/Ge contact resistances, to realize the practical application of Ge poses significant challenges. As the contact resistivity of a metal/semiconductor interface increases exponentially on its Schottky barrier height (SBH) [1], SBH reduction is important for reducing the metal/semiconductor contact resistivity.

In theory, the SBH at a metal/semiconductor interface depends on the work function of the metal; in particular, this relationship should have a slope of unity in the case of the Schottky limit condition [1]. However, this is often not observed in practice, especially for Ge. The SBHs of various metal/n-Ge contacts are usually as high as 0.5 to 0.6 eV regardless of the metal [2], [3]. This difference in SBH results from Fermi-level pinning (FLP). In the case of metal/Ge contacts, the Fermi level of the metal is strongly pinned around the valence band edge of Ge, which corresponds to the charge neutrality of Ge.

In recent years, methods to reduce the SBH have been proposed. One is to insert a dielectric interlayer at the metal/Ge interface, such as Al2O3 [4], Si3N4 [5], TiO2 [6], [7], or ZnO [8], [9]. Another
method involves inserting a group-IV semiconductor or semimetal interlayer, such as Sn [10], Ge$_{1-x}$Sn$_x$ [11], or Si$_{1-x}$Ge$_x$Sn$_y$ [12], [13]. Although interlayer insertion is attractive for reducing the SBH by alleviating FLP or controlling the FLP position, it may increase the contact resistivity at the interface owing to the high resistivity of the inserted interlayer [14].

In contrast, recent studies have reported that a low-electron-density metal such as germanium suppresses metal-induced gap states (MIGS) in metal/n-Ge contacts [15]. Germanides and silicides have the following advantages for practical electronic device applications: (1) the fabrication process is simplified because germanides or silicides can be formed from metal/Ge or Si systems without any interlayers and (2) they enable self-aligned processes. In addition to suppressing the MIGS, it is important to further decrease the SBH, which may be achieved by the suppression of disorder-induced gap states (DIGS) caused by the reduced density of dangling bonds by achieving nearly complete atomic alignment at the interface [16], [17]

Previous studies have also proposed SBH reduction via epitaxial metal-germanide or -silicide contact formation, such as NiGe/Ge(110) [18], [19], Fe$_3$Si/Ge(111) [20], and Mn$_2$Ge$_3$/Ge(111) [21]; however, the use of Ge(001) for epitaxial contact formation has not been explored thus far, despite the importance of the <001> orientation for practical applications of Ge transistors.

Recently, we focused on HfGe$_2$ as a candidate epitaxial germanide that could lead to SBH reduction for n-Ge(001) due to its low work function [22], [23]. In addition, the mismatch between the lattice planes of HfGe$_2$(101) and Ge(100) (\(d_{Ge} = 0.5658 \text{ nm}\)) is as small as \(-5.7\%\) considering the lattice constants of orthorhombic HfGe$_2$ (Cmcm), wherein the constants of \(a\), \(b\), and \(c\) are equal to 0.3791, 1.4863, and 0.3754 nm, respectively [24]. Through experiments, we previously confirmed the formation of an epitaxial HfGe$_2$ layer on a Ge(001) substrate via post-deposition annealing (PDA) in a Hf/Ge(001) system [25]. However, many pits were observed at the micrometer scale after the formation of the epitaxial HfGe$_2$/n-Ge(001) contact, while the regime with no pits appeared to be relatively flat. Considering that no pits were observed before the epitaxial HfGe$_2$ formation, experimental parameters such as the PDA conditions and the device size, which possibly affects the strain applied to the Hf/Ge system, may be controlled to ensure epitaxial HfGe$_2$ formation, and improve its interface uniformity.

Furthermore, in a previous study, we also reported the electrical conduction properties of an Hf-germanide/n-Ge(001) contact formed via annealing [26]. However, only the current density–voltage (\(J-V\)) characteristics of this system was discussed, and further comprehensive analysis including the capacitance–voltage (\(C-V\)) characteristics is required to better understand the electrical conduction properties of this system.

In this study, we perform the microfabrication of an Hf/n-Ge(001) structure at a micrometer-scale, which is comparable to the size of the aforementioned pits, and investigate the effect of microfabrication on the interface structure and electrical conduction properties of epitaxial HfGe$_2$/n-Ge(001) contacts, which were partially reported in the 20th International Workshop on Junction Technology [27]. Additionally, we discuss the analysis results of the HfGe$_2$/n-Ge(001) interface structure and the possible effects that it may have on the electrical properties of this system.

II. EXPERIMENTAL PROCEDURE

We used an n-type Ge(001) wafer with a resistivity of 1 to 3 Ω cm as the substrate. After chemically cleaning the n-Ge(001) surface using a diluted HF (\(~1\%) solution and deionized water, the substrate was immediately introduced into an ultra-high-vacuum chamber. Approximately 20-nm-thick Hf and TiN layers were successively deposited using radio frequency sputtering at room temperature (RT). The Ar gas flow rate and pressure during sputtering process were maintained at 30 sccm and 0.12 Pa, respectively. Subsequently, photolithography and chemical selective etching were performed to form square-pattern electrodes with different lengths of a side (7, 20, 45, and 90 μm). As a reference, a blanket Hf/Ge sample without microfabrication was also prepared. Hereafter, this sample is denoted as the 1 cm sample. Finally, PDA at 500 °C for 5 min under a N$_2$ atmosphere using rapid thermal annealing (RTA) was carried out to form epitaxial HfGe$_2$/Ge contacts. Finally, an approximately 300-nm-thick backside Al electrode was formed using the vacuum evaporation method.

The epitaxial growth of HfGe$_2$ was confirmed by X-ray diffraction (XRD) measurements using a CuKα line (Rigaku RINT2000) and cross-sectional-view transmission electron microscope (TEM) measurements at an acceleration voltage of 200 kV (JEM-ARM200F), and the interface flatness was verified using a scanning electron microscope (SEM; Quanta200FEG). Furthermore, the \(J-V\) characteristics were measured at 200 to 300 K (Keysight B1500A Semiconductor Device Parameter Analyzer, Keysight Technologies), and the \(C-V\) characteristics at a frequency of 1 MHz (E4980A precision LCR meter, Agilent Technologies) were measured at 250 K to investigate the electrical conduction properties of these systems.

III. RESULT AND DISCUSSION

First, we characterized the effect of microfabrication on the interface uniformity and pit formation. Figure 1 shows SEM images obtained for each electrode size. Several pits were observed on the surface for all samples, regardless of the electrode size. It was also confirmed that the pits represent specific facet planes with typical angles (\(~32.7°\) and \(~55.3°\)) to the Ge(001) plane. The origin of this pits formation would be due to the reconstruction of Ge(001) surface along with <111> direction [28]. In fact, the observed angles are well consistent with reported angles between the Ge(001) plane and the reconstructed plane.

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and no diffraction peaks related to HfGe. However, it was also observed that the intensity of these diffraction peaks decreased with decreasing electrode size, which is consistent with the findings of our previous studies. The epitaxial growth achieved via PDA was verified for these three samples.

Figure 1 shows the out-of-plane XRD profiles for the samples with electrode sizes of 45 μm, 90 μm, and 1 cm. For these three samples, in addition to a diffraction peak related to the Ge 004 Bragg reflection, we observed four diffraction peaks at approximately 12.2°, 24.0°, 36.4°, and 48.3°, which are related to the HfGe b-planes 020, 040, 060, and 080 Bragg reflections, respectively. This result suggests that HfGe was epitaxially grown on a Ge(001) substrate, which is consistent with the findings of our previous studies. However, it was also observed that the intensity of these diffraction peaks decreased with decreasing electrode size, and no diffraction peaks related to HfGe were observed for the 7 and 20 μm samples. This is probably due to a decrease in the ratio of the electrode area relative to the sample size and the diffraction intensity would be less than the detection limit of XRD. To verify the epitaxial growth of HfGe for the 7 and 20 μm samples and characterize the HfGe/Ge(001) interface structure in greater detail, cross-sectional TEM analysis was performed for the 7, 20, and 90 μm samples.

Figures 3(a)–3(c) show cross-sectional TEM images of the epitaxial HfGe layer and Ge substrate by selecting rectangular regimes. Note that the rectangular sizes of HfGe and Ge are identical (40 nm × 5 nm). Figures 3(d)–3(f) show the FFT images of the Ge substrate clearly show regions related to Ge 002, 111, and 220, which are indicated by the white circles in Figs. 3(d)–3(f). In this study, we estimated the lattice spacing of HfGe using the 002, 111, and 220 regions of the Ge substrate as references. From the FFT images of the HfGe regime, we identified regions related to HfGe 040 and 060 in the out-of-plane direction, as well as the HfGe 200 region in the in-plane direction. This suggests the epitaxial growth of the HfGe layer on Ge(001) with a relationship of HfGe[010]/Ge[001] in the out-of-plane direction and HfGe[101]/Ge[100] in the in-plane direction, which is consistent with our previous findings. The lattice spacings of the HfGe(040) and (060) planes for each sample were estimated as 0.372 nm, 0.363 nm, and 0.344 nm for the HfGe(040) plane and 0.249 nm and 0.246 nm for the HfGe(060) plane. According to a powder diffraction file, the lattice spacings of the HfGe(040) and (060) planes are 0.3696 nm and 0.2492 nm, respectively. From these values, the
strain applied to HfGe$_2$ in the out-of-plane direction was estimated to be $-0.57\%$ to $-0.25\%$ for the 90 μm sample, $-2.0\%$ to $-1.7\%$ for the 20 μm sample, and $-8.8\%$ for the 7 μm sample. A negative value indicates that the compressive strain is applied in the out-of-plane direction of HfGe$_2$, namely, the tensile strain in the in-plane direction of HfGe$_2$. Here, the lattice mismatch between HfGe$_2$(101) and Ge(100) planes is $-5.7\%$, which is estimated from the lattice spacings of the HfGe$_2$(101) and Ge(100) planes of 0.5363 and 0.5658 nm, respectively. Therefore, the tensile strain in the in-plane direction is likely applied to the epitaxial HfGe$_2$ grown on Ge(001) when strain relaxation does not occur. The estimated strain results thereby suggest that strain relaxation occurred for the 90 μm sample, whereas it was suppressed as the electrode size decreased. This implies that the microfabrication of the Hf/Ge structure affects the strain applied to the epitaxial HfGe$_2$ even at the micrometer-scale.

Next, we discuss the electrical properties of HfGe$_2$/n-Ge(001) Schottky diodes subjected to microfabrication. Because the 7 μm sample could not be measured due to the limitations of microscope resolution in our measurement system, the C–V and J–V results for the 20, 45, and 90 μm samples are discussed. Figure 4 shows the $1/C^2$–V characteristics obtained with a measured frequency of 1 MHz for HfGe$_2$/n-Ge(001) Schottky diodes at 250 K. The C–V characteristic of the Schottky contact may be theoretically expressed as:

$$
\frac{1}{C^2} = -\frac{2}{q\varepsilon_S N_D} V + \frac{2V_i}{q\varepsilon_S N_D} \ln \left( \frac{N_D}{N_C} \right),
$$

and the SBH ($\phi_B$) is:

$$
\phi_B = V_i + \frac{k_B T}{q} \ln \left( \frac{N_D}{N_C} \right),
$$

where $q$ is the elementary charge, $\varepsilon_S$ is the permittivity, $N_D$ is the impurity concentration, $V$ is the applied voltage, $V_i$ is the built-in potential, $k_B$ is the Boltzmann constant, $T$ is the measurement temperature, and $N_C$ is the effective density of state [1]. $V_i$ was estimated from the intercept of the voltage axis of the approximately straight line of the $1/C^2$–V characteristics. The SBH and $N_D$ values were then estimated using Eqs. (1) and (2). The estimated SBH values for the 20, 45, and 90 μm samples were $0.37 \pm 0.03$, $0.47 \pm 0.02$, and $0.39 \pm 0.01$ eV, respectively. These SBH values are 0.1 to 0.2 eV lower than those previously reported for epitaxial-germanide and -silicide/n-Ge contacts [18]–[21]. Because the estimated SBH values are likely to reflect the average SBHs determined by the band bending of the depletion layer,
the obtained results can be well-fitted based on the TFE model in the forward current region.

Finally, we discuss the electrical conduction mechanisms of these systems. Figure 5(a) shows the $J$–$V$ characteristics measured at 200 to 300 K for the 20, 45, and 90 μm samples. It was found that the current density in the reverse bias condition for the 20 μm sample is larger than that for the 45 and 90 μm samples at each temperature. This implies that the 20 μm sample shows a lower SBH and/or a higher impurity concentration compared to the 45 and 90 μm samples. To clarify this further, we estimated the SBHs for the 20, 45, and 90 μm samples based on the thermionic emission (TE) current mechanism. In this model, when the forward bias is sufficiently large, the current density $J$ and saturation current density $J_S$ are expressed as follows:

$$ J = J_S \exp \left( \frac{q(V - IR_S)}{nk_BT} \right) , $$

$$ \frac{J_S}{T^2} = A^* \exp \left( -\frac{q\phi_B}{k_BT} \right), $$

where $n$ is the ideality factor and $A^*$ is the effective Richardson constant, which is related to the effective electrical conduction area [1]. From the current density in the forward bias region, $J_S$ was estimated based on Eqs. (3) and (4).

Figure 5(b) shows the Arrhenius plot of $J_S/T^2$ and $n$ estimated from the forward $J$–$V$ characteristics of the three samples with different electrode sizes. It was confirmed that the $n$ values were close to unity. From Eq. (4), SBH and $A^*$ were estimated using the slope and intercept of the Arrhenius plot, respectively. These values were 0.20 eV and $7.7 \times 10^{-3}$ A cm$^{-2}$ K$^{-2}$ for the 20 μm sample, 0.27 eV and $6.1 \times 10^{-3}$ A cm$^{-2}$ K$^{-2}$ for the 45 μm sample, and 0.27 eV and $7.9 \times 10^{-3}$ A cm$^{-2}$ K$^{-2}$ for the 90 μm sample, respectively. The SBH values were found to be approximately 0.1 eV lower than those estimated using the $C$–$V$ characteristics. However, the estimated $A^*$ values were much lower than the theoretical value of $n$-Ge(001), which is 143 A cm$^{-2}$ K$^{-2}$ [31]. The areas contributing to electrical conduction were only ~0.005% over the entire electrode area. This implies that the TE current flows in an extremely localized area. However, the TE current does likely not flow in this localized area, and another conduction mechanism likely exists.
Similar problems involving extremely local conductance and low SBH values obtained using the $J−E$ analysis based on the TE model have been reported for other metal/semiconductor contacts [32]. According to these reports, the possibility of a thermionic field emission (TFE) current, which is a tunneling process involving thermally excited electrons, was proposed even under lightly doped conditions. Therefore, we also considered the possibility of electrical conductance for the TFE current in the present case. The forward TFE current can be written as follows:

$$J_{\text{TFE}} = J_{S,\text{TFE}}(V) \exp \left( \frac{qV}{E_0} \right), \quad (5)$$

$$J_{S,\text{TFE}} = \frac{A^* T \sqrt{\pi E_{00} g(\phi_B - \Delta E_F - V)}}{k_B \cosh(E_{00}/k_BT)} \times \exp \left( -\frac{\Delta E_F k_BT}{q} - \frac{\phi_B - \Delta E_F}{E_0} \right), \quad (6)$$

$$E_{00} = \frac{gh}{2} \sqrt{\frac{N_D}{m^* e_S}}, \quad (7)$$

$$E_0 = E_{00} \coth \left( \frac{E_{00}}{k_BT} \right), \quad (8)$$

where $\Delta E_F$ is the energy difference between the conduction band edge and the Fermi level in Ge, $h$ is the Dirac constant, and $m^*$ is the electron effective mass of Ge. In this model, $J_{\text{TFE}}$ at $V = 0$ corresponds to $J_S$. The values of SBH and $A^*$ were estimated by fitting the temperature dependence of $J_S$ using Eqs. (6) to (8), as shown in Figure 5(c). In this fitting, the impurity concentration values estimated from the $C−V$ characteristics were used. The estimated SBH and $A^*$ were 0.25 eV and 3.6 A cm$^{-2}$ K$^{-2}$ for the 20 µm sample, 0.31 eV and 3.9 A cm$^{-2}$ K$^{-2}$ for the 45 µm sample, and 0.31 eV and 4.5 A cm$^{-2}$ K$^{-2}$ for the 90 µm sample, respectively. The conduction area corresponding to these $A^*$ values is approximately 3% over the entire area. This is still too small to consider local conduction, inferring another mechanism should be coexisted. As the reason of low $A^*$ value, the tunneling current through the dipole interlayer model was proposed [34]. According to this model, the existence of the ultra-thin dipole layer at metal/semiconductor interface is considered. From the TEM images, the epitaxial-HfGe$_2$/Ge(001) interface is not perfectly uniform and there are transition region. This transition region might work as the dipole layer. The electrical conduction model that the both current components (tunneling current through a dipole layer and TFE currents) are flowed in series is rather likely than local conductance model.

Under this model, $A^*$ values estimated from the analysis based on the TFE model can be written as follows,

$$A^* = A^*_{\text{ideal}} \times T_1, \quad (9)$$

where $T_1$ is the transmission probability and $A^*_{\text{ideal}}$ is the ideal Richardson’s constant for n-Ge(001), which is 143 A cm$^{-2}$ K$^{-2}$ [31]. Since $A^*$ values for the all samples are similar, the $T_1$ values are also similar, which were estimated to an approximately 0.03. When the tunnel probability is same, the lower SBH for the 20 µm sample might be originated from the higher impurity concentration compared to the 45 and 90 µm samples. We believe that this is a possible reason underlying the SBH decrease observed in the temperature dependence of the $J−V$ characteristics.

The obtained results reveal that the epitaxial HfGe$_2$/n-Ge(001) contact may be utilized to realize a low SBH on average. Additionally, we found that the strain applied to the epitaxial HfGe$_2$ layer, which was controlled via microfabrication in this study, is an important factor for realizing a uniform HfGe$_2$/n-Ge contact. Furthermore, the strain control of HfGe$_2$ may be achieved by controlling the thicknesses of the Hf and TiN layers, suggesting that there is a room for further decreasing SBH on average, which will be considered in a future study.

**IV. CONCLUSION**

We examined microfabrication of epitaxial HfGe$_2$/n-Ge(001) contacts and investigated the interface structures and electrical conduction properties with different electrode sizes. We found that the interface uniformity can be significantly improved via microfabrication of the Hf/Ge structure. In addition, TEM analysis revealed that microfabrication at a micrometer order affects the strain relaxation of HfGe$_2$. Strain relaxation is then suppressed via the microfabrication process.

Next, according to the $C−V$ analysis, the SBHs of the HfGe$_2$/n-Ge(001) contacts were determined to be approximately 0.4 to 0.5 eV, which is lower than the SBH of the previously reported epitaxial germanide/Ge contact. In addition, the temperature dependence of the $J−V$ characteristics suggests that the electrical conduction model that the TFE current and the tunneling current through an ultra-thin dipole layer flow in series is most likely. The SBHs estimated via the temperature dependence of the $J−V$ characteristics were 0.25 eV for the 20 µm sample and 0.31 eV for the 45 and 90 µm samples. This SBH decrease achieved via microfabrication may be due to the increase of the impurity concentration for the 20 µm sample.

It can be concluded that the epitaxial HfGe$_2$/n-Ge(001) contact demonstrated in this study may be utilized to realize a low SBH on an average. Additionally, the strain control, which was varied via microfabrication in this study, is an important engineering factor in determining the potential of this system.

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