Fermi Level Depinning for Metal/Germanium Schottky Junction by CF₄ Plasma Treatment

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I. Introduction

Although high-mobility channel material such as germanium (Ge) has been regarded as one of the key elements to empower the next-generation nanoelectronics and many promising results have been reported, there are challenging issues for high-performance Ge MOSFET from the viewpoint of source/drain contact: (1) fast diffusion and low dopant activation for pentavalent impurities in Ge impede the formation of shallow and low resistance source/drain. (2) significant Fermi level pinning at metal/Ge interface makes it difficult to modulate a Schottky barrier height by metal work function and implement low resistance source/drain contact. To release Fermi level pinning, inserting a thin insulating layer such as Al_2O_3 [1], Ge_3N_4 [2], SiN [3] or MgO [4], between contact metal and Ge was proposed either to passivate the surface state or to block the tailing of the wave function. Much different from those using a thin insulating layer which may add tunneling resistance at the contact, prior to the contact metal deposition, Ge surface was treated by CF_4 plasma in this work to depin the Fermi level and the significant dependence of the Schottky barrier height on metal work function can be obtained.

II. Experiment

An epitaxial p- and n-type Ge layer of ~12 nm were respectively formed on p- and n-type Si substrate, and were used for the study of Fermi level depinning. To form an epitaxial Ge layer on Si, a thin single crystalline Si_{0.3}Ge_{0.7} was initially formed by depositing an amorphous Ge layer and a subsequent thermal annealing [5]. Then an epitaxial Ge layer was formed by wet oxidation of the $Si_{0,3}Ge_{0,7}$ layer and a subsequent SiGeO_x reduction process during a forming gas annealing performed at 700 °C [6]. Finally an oxide-free Ge surface was obtained by dipping in dilute hydrofluoric acid solution. Note that the Ge layer is a doped one where the dopants were incorporated from the starting Si wafer during the step of Si_{0.3}Ge_{0.7} formation and subsequent reduction. Thereafter, CF4 plasma treatment with radio-frequency (rf) power of 20 W and flow rate of 50 sccm without bias were performed on some p- and n-type Ge layers at 250 °C for 2, 6 and 10 minutes to investigate how fluorine treatment affects the surface states, bonding structure and consequent Fermi level pinning. Note that during the CF_4 plasma treatment, O_2 gas with flow rate of 5 sccm was also introduced into the chamber to avoid possible carbon byproduct. Then contact metals such as Al, Y, and Pt were deposited by e-beam evaporation and patterned to explore the correlation between various metal work functions and corresponding Schottky barrier heights. Besides the measurement of current density-voltage (J-V) characteristics for the metal/Ge Schottky diodes, the bonding structure of the Ge after CF₄ plasma treatment was examined by x-ray photoelectron spectroscopy (XPS).

III. Results and Discussion

Fig. 1 shows the impact of CF_4 plasma treatment on the J-V characteristics for Al/n-Ge diodes at room-temperature. Even with a low work function of 4.17 eV, because of the strong Fermi level pinning at the charge neutrality level close to the valence band edge [7], a rectifying behavior

can be observed for those without any CF₄ plasma treatment as reported by others. On the contrary, for samples with 2-min CF₄ plasma treatment, the reverse-biased current increases and becomes a nearly ohmic behavior with current density of 1.8 A/cm^2 at -1 V which suggests that Fermi level pinning is effectively released. As the plasma treatment time extends to 6 min, the current at reverse bias further increases and a complete ohmic behavior is observed. The phenomenon that the reverse-biased current is dependent on plasma treatment time implies that longer treatment time provides a more prominent fluorine passivation of Ge surface dangling bonds which decreases the number of surface states and therefore Fermi level depinning is achieved. As shown in Fig. 2, the formation of Ge-F binding is evidenced by the apparent F 1s peak in the XPS spectra for those with 6-min CF_4 plasma treatment. The effectiveness of alleviating Fermi level pinning by 6-min CF₄ plasma treatment for n-type Ge is further investigated by characterizing the J-V curves for contact metals with different work functions and the results are displayed in Fig. 3. For contact metal Ni, a rectifying behavior is observed because of its intrinsically high work function of 5.1 eV. However, for contact metal with a smaller work function such as Y (work function: 3.1 eV) and Al, ohmic contact characteristics are obtained. By plotting the graph of $\ln(J/T^2)$ against 1/T for various bias voltages where T denotes the absolute temperature, one can obtain the correlation between activation energy (Φ_B -V/n) and V as shown in Fig. 4 where $\Phi_{\rm B}$ is the effective Schottky barrier height, n is the ideality factor, V is the applied forward bias voltage. Therefore $\Phi_{\rm B}$ and n can be respectively extracted from the intercept and slope. The extracted $\Phi_{\rm B}$ as a function of metal work function for samples with and without 6-min CF₄ plasma treatment is shown in Fig. 5. The significant work function dependent Schottky barrier height implies that the pinning effect is greatly suppressed by CF₄ plasma treatment. Fig. 6 demonstrates the impact of surface treatment on relative contact resistance for various contact metals on n-type Ge. For low work function metals such as Al and Y, with 6-min CF₄ plasma treatment, contact resistance decreases apparently by a factor of 21-29 as compared to those without any treatment. This decrease in contact resistance is mainly attributed to the significant modulation of Schottky barrier height caused by the alleviation of Fermi level pinning through CF₄ plasma treatment. Since no resistance turning point [3] is present even for 10-min CF₄ plasma treatment, a larger process window can be expected. Fig. 7 shows how CF_4 plasma treatment affects the J-V curves of Al/p-Ge diodes at room-temperature. As expected, because of the depinning of Fermi level by CF₄ plasma treatment, transition from ohmic to rectifying behavior is observed and again verifies the effectiveness of CF₄ plasma treatment. Fig. 8 shows the atomic force microscopy (AFM) analysis for n-type Ge with 6-min CF₄ plasma treatment and a RMS roughness value of 0.81 nm is obtained. The relatively smooth surface is due to the low rf power and no bias during plasma treatment. Table I summarizes the correlation of barrier height and ideality factor for different metals on n-type Ge after 6-min CF₄ plasma treatment.

IV. Conclusion

Prior to the contact metal deposition, CF₄ plasma treatment on Ge surface is proposed to alleviate Fermi level pinning to valence band. Due to the effective fluorine passivation of dangling bonds at Ge surface which is beneficial to suppress surface states, Fermi level depinning can be observed which is evidenced by the transition in conduction behavior between Schottky and ohmic contact, and the modulated Schottky barrier height for contact metals with different work functions.



Fig. 1 J-V characteristics for Al/n-Ge diodes with different surface treatments.



Fig. 4 Plot of activation energy as a function of corresponding forward bias.



Fig. 7 J-V characteristic for Al/p-Ge diodes with and without CF₄ plasma treatment.



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Fig. 2 XPS F 1s spectra for Ge surface with and without CF4 plasma treatment.



Fig. 5 Extracted barrier height versus metal work function for samples with and without CF₄ plasma treatment.



Fig. 8 AFM image for n-Ge surface after 6-min CF₄ plasma treatment.



Fig. 3 J-V curves for different metal/n-Ge diodes with 6-min CF₄ plasma treatment.



resistance on surface treatments for n-Ge with various contact metals.

Contact	$\Phi_{\mathrm{B}}\left(\mathrm{eV} ight)$	Ideality factor
Y/n-Ge	0.14	1.15
Al/n-Ge	0.20	1.11
Ni/n-Ge	0.52	1.24

Table I Barrier height and ideality factor for samples with plasma treatment.