Impact of nitrogen plasma passivation on the Al/n-Ge contact

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Abstract

Severe Fermi level pinning at the interface of metal/n-Ge leads to the formation of a Schottky barrier. Therefore, a high contact resistance is introduced, debasing the performance of Ge devices. In this study, a Ge surface was treated by nitrogen plasma to form an ultra-thin Germanium oxynitride (GeO_xN_y) passivation layer. It was found that the Schottky barrier height (SBH) of metal/n-Ge contact was strongly modulated by the GeO_xN_y interlayer, indicating alleviation of Fermi-level pinning effect. By adjusting the principal parameters of N_2 plasma treatment and additional post anneal, a Quasi-ohmic Al/n-Ge contact was achieved. Furthermore, the introduced GeO_xN_y layer gave extremely lower leakage current density of the gate stack for HfO_2/Ge devices. These results demonstrate that GeO_xN_y formed by N_2 plasma would be greatly beneficial to the fabrication of the Ge-based devices.

1. Introduction

Germanium has received great interest as one of the possible candidates for next-generation high-performance metal-oxide-semiconductor field effect transistors (MOSFETs), due to the much higher electron and hole mobilities compared to Si as well as its compatibility with Si CMOS process [1]. Unfortunately, Ge devices with superior performance also suffer from several drawbacks, a key issue is the large Schottky barrier height of metal/n-Ge contact as a result of the strong Fermi level pinning (FLP) at the charge neutrality level (CNL) close to the Ge valence band. This will result in a high contact resistance at source/drain regions and the failure of devices [2]. Recently, inserting a thin passivation layer such as GeO_x [3,4], Ge_3N_4 [5,6], Al_2O_3 [7], and other metal oxide [8,9] has been demonstrated to be an effective way to release the FLP. Among them, GeO_2 and GeO_xN_y have achieved great success as a good passivation layer between high-k dielectrics and Ge with an equivalent oxide thickness of ~ 1 nm and a rather low interface state density [10-13]. While GeO_xN_y is more attractive, the incorporation of nitrogen can effectively suppress the interdiffusion of high-k dielectrics and Ge substrates [14,15]. If the same passivation layer can be simultaneously applied at source/drain and gate regions, the Ge-MOSFET fabrication process can be greatly simplified. In fact, the application of GeO_xN_y in metal/Ge contacts was rarely reported. The thin GeO_xN_y passivation layer has been reported to be formed by nitridation at 600 °C in NH_3 ambient [16,17]. However, as the electrodes passivation layer, the device structure has been fully prepared, a high nitridation temperature may deteriorate device performance. Hence, in our experiment, nitrogen (N_2) plasma treatment was taken, which can avoid a high temperature treatment. The GeO_xN_y formed by N_2 plasma treatment was certified by experiments [18-20], whereas, during N_2 plasma treatment, the effect of the principal parameters (Radio Frequency (RF) power and surface temperature) on the GeO_xN_y formation and the SBH of Al/n-Ge contact has never been reported.

In this study, with plasma enhanced chemical vapor deposition (PECVD) equipment, an ultra-thin GeO_xN_y layer was formed only by adjusting the RF power. X-ray photoelectron spectroscopy (XPS) was employed to reveal the composition and chemical bonds of the nitrided Ge surfaces. A low surface temperature was

added to enhance the GeO_xN_y formation, and a low post anneal temperature was applied to further reduce the SBH. These low temperature treatments were beneficial for device fabrication. Eventually, an Quasi-ohmic Al/n-Ge contact was achieved and the SBH can be modulated by altering the N_2 plasma parameters.

2. Experiment

The experiments were performed on (100) n-type Ge wafers with a resistivity of about $0.1 \Omega \cdot \text{cm}$. The wafers were first circularly degreased in an ultrasonic bath of acetone and ethanol, followed by successive washes in dilute hydrochloric acid solution ($\text{HCl}:\text{H}_2\text{O}=1:4$) and hydrofluoric acid solution ($\text{HF}:\text{H}_2\text{O}=1:50$) to remove the native oxide. After loading the wafers into the PECVD chamber, the PECVD chamber was evacuated to a base pressure of $\sim 10^{-3}$ Pa before the process gas was introduced. During process, the nitrogen gas flow rate and the total gas pressure were fixed at 40 sccm and 0.5 Pa, respectively. The RF power for plasma generation was varied between 50 W and 150 W to generate nitrogen plasma, and the Ge surface temperature was controlled between 100°C and 250°C . And the plasma exposure time was a minute for all samples. To further reduce the SBH, post anneal was performed at temperature from 200°C to 500°C by rapid thermal annealing (RTA) chamber in N_2 atmosphere. After that, the 300 nm aluminium (Al) electrodes were deposited using a shadow mask by sputtering. And Al (300 nm) was sputtered as the back electrode. Current-voltage (J-V) properties were acquired by a Keithley 4200 source/meter. The Schottky barrier heights (SBHs) were evaluated from the reverse current.

3. Results and discussion

3.1. The surface roughness of Ge

The influence of N_2 plasma on surface roughness was significant, as the ion bombardment appeared to physically modify the Ge surface. The plasma treatments with various RF power were carried out at room temperature. After plasma treatment, the root-mean-squares (RMS) of surface roughness were characterized by tapping mode atomic force microscope (AFM, Seiku Instruments, SPI4000/SPA-400) with each scanned area of $10 \times 10 \mu\text{m}^2$. As shown in Fig. 1, the RMS was 0.64 nm for bare Ge, and reduced to 0.47, 0.38, 0.42 and 0.28 nm as the RF powers were 50, 70, 100 and 150 W, respectively, indicating higher RF power is conducive to smooth the Ge surface. As the RF power up to 150 W, the physi-

cal etching was obviously; hence the Ge was etched by N ion and then became quite smooth. In short, N₂ plasma can remove contaminants as well as decrease the surface roughness.

Fig. 1. The effect of RF power on the Ge surface roughness (RMS). Measured by AFM with a scanned area of 10×10 μm².

3.2. The chemical states of Ge

To evaluate the chemical states of Ge surface after N₂ plasma treatment, XPS (Quantra/Quantum 2000Scanning ESCA Microprobe) measurements were carried out. The X-ray source of XPS measurement is Al K α X-ray with energy about 1486.6eV and the photoelectron emission angle is 45°. The profiles of the Ge 3d and N 1s core levels were calibrated by C 1s (284.8 eV). Figures 2(a), (b)–(d), and (e)–(g) correspond to the results of clean-bare Ge, sample with plasma treatments at room temperature (RT), and sample with plasma treatments at 100°C, respectively. For the bare Ge, the Ge 3d spectrum is detected at a binding energy of 29.86 eV (Ge-Ge bonds), and another small peak indicates a mixture of oxidation states, which was resulted from the exposure to air before the XPS measurement. The components of Ge after N₂ plasma treatment with RF power of 50 W, 100 W and 150 W were shown in Fig. 2(b)–(d) respectively. As shown in Fig. 2(b), the N 1s signal was not detected, which means the Ge-N bonds were not formed. That is, there are only Ge-O_x exists in Ge oxidation layer. A weak N 1s signal was shown in Fig. 2(c), indicating Ge-N bonds were formed. Besides, for the Ge 3d spectrum, the Ge-N and Ge-O bonding energies shift 2.5 and 3.4 eV from the bulk peak respectively also

confirmed the existence of GeO_xN_y [19,21,22]. Although, N 1s signal was also detected in Fig. 2(d), the peak at 398 eV was different from Fig. 2(c), and the GeO_xN_y peak shifted 0.26 eV, signifying the GeO_xN_y structure was different between Fig. 2(c) and (d). Comparing with Fig. 2(c), more obvious N 1s peak was observed in Fig. 2(e), meaning the additional surface temperature enhanced the GeO_xN_y formation. The relative concentrations of species can be obtained from integrated peak areas using known sensitivity of the XPS spectrometer. A nonstoichiometric Ge oxynitride film of $\text{GeO}_1\text{N}_{0.09}$ and $\text{GeO}_{0.85}\text{N}_{0.11}$ was formed for Fig. 2(d) and Fig. 2(e), respectively. It was found that, the nitrogen content increased with the surface temperature, while the oxygen content decreased, which means that the surface temperature can promote N atoms to take place of O atoms. Post anneals under temperature of 300°C and 500°C were performed in Fig. 2(f) and (g) respectively. As shown in Fig. 2(g), the anneal temperature of 500°C was too high to result in the shift of GeO_xN_y peak and N 1s peak, indicating the structure of GeO_xN_y had been changed.

All the samples were then measured by XPS depth profiling. After 2 nm sputtering processes, all the Ge 3d spectra were correspond to the Ge-Ge bonds, the XPS signals for N totally disappeared, indicating that the GeO_xN_y layer is no more than 2 nm in thickness (data not shown).

Fig. 2. XPS spectra of Ge 3d and N 1s core levels for (a) clean-bare Ge; (b)–(d) sample with plasma treatments at room temperature (RT) and various RF power was performed; (e)–(g) sample with plasma treatments at 100°C and various post anneal was taken.

To confirm the formation of GeO_xN_y layer, two samples after N_2 plasma treatment were measured by X-ray diffraction (Rigaku Ultima IV XRD). Powder diffractometer of $\text{Cu K}\alpha$ radiation ($\lambda_{\text{K}\alpha}=0.154 \text{ nm}$) and a graphite back-monochromator were used. The peaks were identified by comparison with PDF standards (Powder Diffraction Files) from ICDD. During plasma treatment, the RF power was 100 W for two samples, the surface temperature was RT for sample A, while 100°C for sample B. And not post anneal was performed. As show in Fig. 3, the XRD peaks of GeO_2 and GeO_xN_y were both presented in sample A and B. While a more obvious peak of GeO_xN_y was shown in sample B, signifying the surface temperature can promote the formation of GeO_xN_y , which was corresponded to the XPS results.

From the thermodynamic viewpoint, at constant temperature and pressure spontaneous chemical reactions proceed with a reduction of Gibbs free energy ($\Delta G < 0$), and

$$G = H - TS \quad (1)$$

Where H is enthalpy, S is entropy and T is temperature of system.

The formation of GeO_xN_y consists of the following two steps:

For the exchange reaction of (2), a recombination reaction between adsorbed species O_{ads} and species N coming from the gas phase was occurred, product N-O is supposed to leave the surface. Reaction $\text{O}_{\text{ads}} + \text{N} \rightarrow \text{N-O}$ will be thermodynamically favourable if

$$\Delta G = (H_{\text{NO}} - H_{\text{O}} - H_{\text{N}}) - T(S_{\text{NO}} - S_{\text{O}} - S_{\text{N}}) < 0 \quad (4)$$

From the equation (4), the higher temperature means the condition of $\Delta G < 0$ is more easily to be satisfied. This indicated the addition surface temperature could promote exchange reaction of (2), and then promote the formation of GeO_xN_y layer, which was consistent with our XPS and XRD results.

Fig. 3 XRD patterns for $\text{GeO}_x\text{N}_y/\text{Ge}$ samples.

3.3. J-V characteristics for Al/n-Ge contact

The influences of RF power and surface temperature on the JV characteristics of Al/n-Ge contact are shown in Fig. 4(a) and Fig. 4(b) respectively. From the J-V characteristics, SBHs of the contacts could be extracted based on a modified thermionic emission model (equation (5)), including both series resistances and parasitic leakages [23].

$$I = I_d + I_p = I_s (\exp((V - IR_s) / nkT) - 1) + G_p (V - IR_s)$$

(5)

In which:

$$I_s = AA^* T^2 \exp(-q\Phi_{bn} / kT)$$

(6)

Where I_d is the current flowing through the diode, I_p is the current flowing through the parallel resistance, Φ_{bn} is the SBH for the electrons, n is the ideal factor, R_s is the series resistance, and $G_p = 1/R_p$ is the parallel conductance. All these parameters are treated as adjustable parameters and estimated from the fits of the experimental data (Fig. 4). The symbol $A^* = 143 \text{ A} / (\text{cm}^2 \text{ K}^2)$ is the Richardson constant for n-Ge (100) [23].

The extracted SBHs are listed in Table 1. As shown in Fig. 4(a), a control sample of Al/n-Ge contact without plasma treatment was observed with a rectifying behavior and a SBH of 0.63 eV. N_2 plasma treatments with various RF power

(50 W, 70 W, 100 W, 150 W) all would release the Fermi level pinning. As shown in Table 1, the formation of GeO_xN_y (100 W) stimulated the release of the Fermi level pinning better than GeO_x (50 W). As the RF power higher than 100 W, the SBH increases instead. This may be due to the GeO_xN_y layer was formed and sputtered simultaneously, the GeO_xN_y structure was changed owing to the physical etching, which was certified in Fig. 2(d). As shown in Fig. 4(b). An additional surface temperature of 100°C can further reduce the SBH. However, a larger series resistance was introduced as the surface temperature higher than 200°C, which may result from the high-temperature process thickens the GeO_xN_y layer. The effect of post anneal on the Al/n-Ge contact was shown in Fig. 4(c), where the anneal temperatures of 200°C to 500°C were studied. The SBH was further reduced after 200°C and 300°C anneal, while a higher temperature anneal above 300°C would destroy the GeO_xN_y structure, as well as increase the SBH subsequently. Eventually, a Quasi-ohmic Al/n-Ge contact was achieved after 300°C anneal.

To further confirm the alleviation of the FLP effect in Ge, Al/p-Ge contacts with a GeO_xN_y interlayer were fabricated and the J-V characteristics are shown in Fig. 4(d). In general, metal/p-Ge contacts exhibit Ohmic properties regardless of the metal work function, owing to the CNL located close to the top of the valence band. By inserting a GeO_xN_y layer between metal and p-Ge, an obviously rectifying behaviour of the Al/ GeO_xN_y /p-Ge contact is observed, as plotted by the circular scatters in Fig. 4(d), confirming the alleviation of the FLP effect in Ge.

Fig. 4. J-V characteristics for Al/n-Ge contact with the N₂ plasma treatments, under the parameters of (a) different RF power; (b) different surface temperatures; (c) different post anneal temperatures. (d) J-V characteristic for Al/p-Ge contact with the N₂ plasma treatment.

Table 1 The effect of parameters variables on the SBHs.

Sample	RF power (W)	Surface temperature (°C)	Anneal temperature (°C)	SBH (eV)
(a)	0	RT	No	0.63
	50	RT	No	0.48
	70	RT	No	0.45
	100	RT	No	0.44
	150	RT	No	0.47
(b)	100	100	No	0.43
	100	150	No	0.45
(c)	100	100	200	0.41
	100	100	300	Quasi-ohmic
	100	100	400	0.44
	100	100	500	0.45

3.4. The model for the N₂ plasma passivation

When the Ge is exposed to the N₂ plasma, physical and chemical reactions happen simultaneously. As shown in Fig. 1, the physical reaction made the Ge surface more smooth, which was beneficial for the release of pinned Fermi level [24]. The chemical reactions were revealed in Fig. 2(b)-(d), the N ion energy adjusting by RF power allows to control the formation of GeO_xN_y layer. when the RF power is lower than 70 W, the kinetic energy of N ion is only enough to knock the contaminants out the wafer surface, as shown in Fig. 5(a), but fails to generate Ge-N bonds. The N atoms were only physisorbed to the Ge surface with a desorption energy of ~0.2 eV [25], and they would leave the surface during the pumping of the reactor after the treatment. While the surface after plasma treatment was more reactivity to adsorb the atmospheric oxygen atoms to form GeO_x. Interface states caused by the contaminants [26] and dangling bonds [27,28], were proposed to be responsible for the severe FLP effect in the metal/Ge contacts. The contaminants were removed and some dangling bonds was occupied by O atoms, hence, the SBH was lowered, as shown in Fig.

5(b). As shown in Fig. 2(c), when the RF power up to 100 W, Ge-N bonds were formed, signifying the N ion kinetic energy was mainly responsible for the Ge nitridation. As shown in Fig. 5(c) and (d), the N ions was chemisorbed with Ge surface, and GeO_xN_y layer was formed finally. However, once the RF power up to 150 W, the N ion energy was enough to break chemical bonds formed between the surface and chemisorbed species and even between atoms of the material. The sputtering effect destroyed the GeO_xN_y structure, and brought new dangling bonds. These suggests that an RF power of 100 W is more suitable for the GeO_xN_y formation, and gives a better passivation effect.

To enhance the formation of GeO_xN_y , an additional surface temperature was taken. As shown in Fig. 2(e), the formation of GeO_xN_y was enhanced, and the SBH was reduced by attaining a surface temperature of 100°C [Fig. 4(b)]. This results from the reduction of interface states. The N atoms can get thermal energy from the substrate, and diffuse to fill up the dangling bond formed by the sputtering effect, as shown in Fig. 5(e). However, the N atoms also can diffuse into the Ge substrate and thicken the GeO_xN_y layer, and the rate of diffusion was increased with the surface temperature increasment. Ultimately, the GeO_xN_y layer, as the surface temperature up to 200°C, a series resistance can not be neglected, which decreases the current density.

Post anneal was employed to further improve the quality of GeO_xN_y layer. However, An excessively high post anneal temperature (400°C and 500°C) was inadvisable, as shown in Fig. 4(c), a higher SBH was presented owing to the Ge oxide component decomposed at a lower temperature about 400 °C [29]. As shown in Fig. 5(f), the GeO formed at the interface of $\text{GeO}_x\text{N}_y/\text{Ge}$ diffuses out to the air, that changed the structure of GeO_xN_y passivation layer. Furthermore, a huge amount of interface defects and traps would be left after the GeO desorption [30]. These all result in the raise of SBH.

Fig. 5. The diagrammatic sketch of the interreaction between N plasma and germanium surface. (a)-(b) GeO_x layer was formed after a low RF power treatment; (c)-(d) GeO_xN_y layer was formed as the RF power higher than 100 W; (e) The effect of surface temperature on the N atoms diffusion; (f) the GeO formed at the interface of GeO_xN_y/Ge diffuses out to the air.

3.5. The application of N₂ plasma passivation on the Pt/HfO₂/Ge MOS capacitors

Formation of a GeO_xN_y interlayer by N₂ plasma has been demonstrated to effectively reduce the interface states between metal and n-Ge. GeO_xN_y was also formed on the interface between HfO₂ and Ge, to show its potential on the Pt/HfO₂/Ge MOS capacitors. Firstly, the n-Ge and p-Ge were cleaned, and then N plasma was treated at an RF power of 100 W and surface temperature of 100°C. The post anneal temperature of 300°C was performed after nitridation. Approximately 5 nm of HfO₂ was deposited as the gate dielectric by atomic layer deposition (ALD) for MOS capacitors. Finally, Platinum (Pt) was evaporated and patterned to form Pt/HfO₂/Ge MOS structures. The cross-section image of Pt/HfO₂/GeO_xN_y/Ge is characterized by transmission electron microscopy (JEM2100), as shown in Fig. 6(a). After N₂ plasma treatment, an ultrathin GeO_xN_y layer is formed and its thickness is about 1.2 nm. Moreover, the sharp and flat interface between the GeO_xN_y/HfO₂ stack and Ge substrate can be clearly observed in Fig. 6(a), while rugged and blurred interface exists in Ge/HfO₂ gate stack when where is not the GeO_xN_y layer, as shown in Fig. 6(b). For the Pt/HfO₂/GeO_xN_y/Ge sample, the corresponding SAD diffraction pattern was shown in Fig. 6(c). The electron diffraction

patterns observed could only have been caused by crystalline materials [31]. The crystalline materials of Ge, Pt and HfO_2 were signed in Fig. 6(c). However, the GeO_xN_y is not observed by the SAD diffraction pattern, this indicated the GeO_xN_y layer is amorphous, which is consistent with the report of Hao Yu[32].

Fig. 6 The Cross-section TEM images for (a) $\text{HfO}_2/\text{GeO}_x\text{N}_y/\text{Ge}$, (b) $\text{HfO}_2/\text{GeO}_x/\text{Ge}$ samples, and the corresponding TEM/SAD diffraction pattern for (c) $\text{Pt}/\text{HfO}_2/\text{GeO}_x\text{N}_y/\text{Ge}$ sample.

The J–V characteristics of the $\text{Pt}/\text{HfO}_2/\text{Ge}$ and $\text{Pt}/\text{HfO}_2/\text{GeO}_x\text{N}_y/\text{Ge}$ structures are shown in Fig. 7. By inserting the GeO_xN_y passivation layer, the gate leakage current density decreases about three orders of magnitude for n-Ge [Fig. 7(a)], and four orders of magnitude for p-Ge [Fig. 7(b)] in the voltage range of -2 to 2 V. We have noticed that the thickness of GeO_xN_y is only 1.2 nm and the formation of an ultra-thin GeO_xN_y layer between metal and Ge have no obvious effect on the forward current density of metal/n-Ge contacts, suggesting that the series resistance induced by forming the GeO_xN_y layer can be neglected. The improvement of the leakage is ascribed to the reduced interfacial state density as the Ge surface was nitridated to GeO_xN_y . The lower interfacial state density is beneficial for high performance Ge MOSFET devices.

Fig. 7 Gate leakage characteristics of Pt/HfO₂/Ge capacitor (blue symbols) and Pt/HfO₂/GeO_xN_y/Ge capacitor (red symbols) for (a) n-Ge; (b) p-Ge.

4. Conclusions

A thin GeO_xN_y layer was directly formed by N₂ plasma treatment on the Ge surface, which can release the Fermi level pinning effect in metal/Ge contact. The Schottky barrier height was reduced from 0.63 to Quasi-ohmic. For p-Ge, a thin GeO_xN_y layer invoked a rectifying behavior instead of Ohmic behavior. The ion energy controlled by RF power was enough to form Ge-N bond. To enhance the quality of GeO_xN_y layer, an additional surface temperature and post anneal was necessary. In the study of the gate stack for HfO₂/Ge devices, GeO_xN_y can be used for gate passivation to reduce the interfacial states and achieve extremely low leakage current density. Overall, Ge surface passivation by N₂ plasma is a useful method for the SBH reducing of Al/n-Ge contact, and is promising in Ge MOSFETs application.

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