Fabricating GeO_2 passivation layer by N_2O plasma oxidation for Ge NMOSFETs application*

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(Received 6 October 2013; revised manuscript received 16 December 2013; published online 20 April 2014)

In this paper, oxidation of Ge surface by N_2O plasma is presented and experimentally demonstrated. Results show that 1.0-nm GeO_2 is achieved after 120-s N_2O plasma oxidation at 300 °C. The GeO_2/Ge interface is atomically smooth. The interface state density of Ge surface after N_2O plasma passivation is about $\sim 3\times10^{11}$ $cm^{-2}\cdot eV^{-1}$. With GeO_2 passivation, the hysteresis of metal–oxide–semiconductor (MOS) capacitor with Al_2O_3 serving as gate dielectric is reduced to ~ 50 mV, compared with ~ 130 mV of the untreated one. The Fermi-level at GeO_2/Ge interface is unpinned, and the surface potential is effectively modulated by the gate voltage.

Keywords: Ge, GeO_2 passivation, N_2O plasma oxidation, Ge NMOSFETs

PACS: 77.55.D–, 77.55.df, 77.55.E–, 73.40.Qv **DOI:** 10.1088/1674-1056/23/6/067701

1. Introduction

As the scaling of Si-based metal–oxide–semiconductor field-effect transistors (MOSFETs) approaches its fundamental limitation, the introduction of novel material such as high carrier mobility material is becoming essential to further increase the drive current. As for the channel material, Ge is considered as a competitive candidate due to its higher and more symmetric carrier mobility. For Ge MOSFETs, high dielectric constant material (high K) is utilized as gate dielectric, such as Al_2O_3, HfO2, and ZrO_2.[1–3] However, the performance of Ge MOSFETs is far from satisfactory, especially for the n-type metal–oxide–semiconductor field-effect transistor (NMOSFET). One of the critical issues is Fermi-level pinning at Ge surface. Fermi-level at Ge surface is proved to be pinned at charge-neutral level (CNL), which is just ~ 0.1 eV above the valence band, caused by a large number of the interface states.[4] The low position of CNL would result in negative fixed charge at the interface of metal–oxide–semiconductor (MOS) capacitor. Therefore, electrons were repelled from the interface, leading to poor performance of NMOSFETs.[5] Many pre-gate passivation methods have been proposed to solve this problem. It was reported that GeO_2 is an alternative passivation method due to its low interface trap density, and Fermi-level at GeO_2/Ge interface is unpinned,[6] exhibiting great potential for fabricating high performance Ge NMOSFET.[7,8] The Fermi-level pinning also results in Schottky-like behavior of metal/n-Ge contact, irrespective of the metal work function.[4] GeO_2 with an appropriate thickness can also be introduced as an inserting layer between the metal and Ge substrate to de-pin the Fermi-level.[9] GeO_2 has been reported to be grown by O_2 thermal treatment, ozone oxidation, and O_2 plasma oxidation.[10–17] However, GeO_2 grown by N_2O plasma oxidation was rarely investigated. It is known that the energy needed to break the nitrogen–oxygen bond in a N_2O molecule (242 kJ/mol) is smaller than that of the oxygen–oxygen bond in an O_2 molecule (494 kJ/mol).[18] In addition, plasma treatment is proposed due to its low temperature characteristics, which is compatible with Ge MOSFET fabrication process. So, N_2O plasma oxidation may provide an alternative method for growing a high quality GeO_2 passivation layer.

However, previous studies reported that the plasma process would induce damage to the substrate or thin gate oxide of MOSFETs.[19] It must be pointed out that the damage just occurs in the etching process or in the presence of metal or polysilicon electrodes. In the etching process, ions are accelerated by bias or self-bias voltage induced by reactive ion etching (RIE) power to the substrate, resulting in physical damage. As for the case in the presence of a metal or polysilicon electrode, ions and electrons accumulate on the electrode, leading to steady-state voltage on the electrode, which would degrade the underlying gate oxide. To avoid the physical damage resulting from ion bombardment, only inductive coupled plasma (ICP) power for generating plasma is applied during the process. The reactants for oxidation transfer to the substrate by diffusion. Also, for plasma oxidation treatment, plasma treat-

*Project supported by the National Basic Research Program of China (Grant No. 2011CBA00601) and the National Natural Science Foundation of China (Grant Nos. 60625403, 60806033, and 60925015).

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ment may be carried out without an electrode. In this work, oxidation of the Ge surface by N_2O plasma created in an ICP chamber is experimentally investigated. It is found that stoichiometric GeO_2 is achieved after oxidation. The interface state density at GeO_2/Ge is low, and the Fermi-level at GeO_2/Ge interface is unpinned. With GeO_2 passivation, the hysteresis of MOS capacitor with Al_2O_3 serving as gate dielectric is reduced to $\sim$ 50 mV.

2. Experiment

P-type (100) Ge substrates with a resistivity of 3 Ω·cm–3.6 Ω·cm were utilized to fabricate MOS capacitors. After being cleaned by diluted HCl solution, the samples were loaded into the ICP chamber to be treated with N_2O plasma oxidation. The power of the N_2O plasma was fixed at 1000 W at a pressure of 20 mTorr (1 Torr = 1.33322×10^2 Pa), and the exposure time was 120 s. N_2O plasma oxidation was performed at 300 °C. A sample without passivation was fabricated as a control sample. Then, 10-nm Al_2O_3 was deposited by atomic layer deposition (ALD) system at 200 °C, followed by TiN_x (80 nm) gate deposition and patterning. Ti($\sim$ 20 nm)/Al ($\sim$ 200 nm) back contact was deposited to reduce contact resistance. Finally, post metallization annealing was carried out in ambient N_2. The chemical composition of the interfacial layer after N_2O plasma oxidization was characterized by x-ray photoelectron spectroscopy (XPS) using Al Ka x-ray. Capacitance–voltage (C–V) measurement was performed using Agilent 4294A precision impedance analyzer to electrically characterize the nMOS capacitors.

3. Results and discussion

The chemical states of Ge surface before and after N_2O plasma oxidation are studied by XPS measurement, as shown in Fig. 1. For the sample without N_2O plasma oxidation, the Ge 3d peak centered at 30.231 eV corresponds to that of the bulk Ge, and a chemical shift of 2.674 eV toward the bulk Ge indicates the presence of Ge^{3+},[16] which may be the native oxide or originates from air oxidation after HCl cleaning. As for the sample oxidized by N_2O plasma, the Ge 3d spectra can be deconvoluted into two evident components of Ge^{4+} at 32.9914 eV and Ge° at 29.7917 eV, suggesting the formation of stoichiometric GeO_2.[20,21] Figure 2 shows the transmission electron microscope (TEM) images of the MOS capacitor without (a) and with (b) N_2O plasma oxidation. As shown in Fig. 2(a), the GeO_2/Ge interface is smooth compared with that in the control sample, indicating that N_2O plasma oxidation would not induce surface roughness degradation.

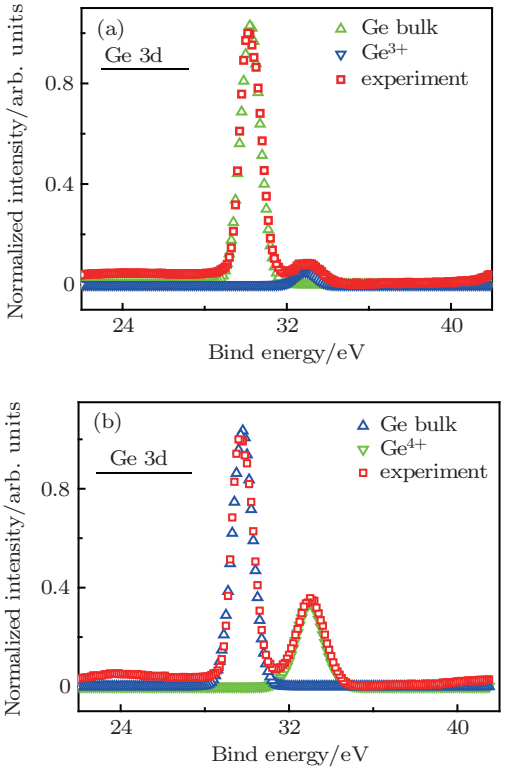


Fig. 1. (color online) Ge 3d spectra on Ge substrate before (a) and after (b) N_2O plasma oxidation.

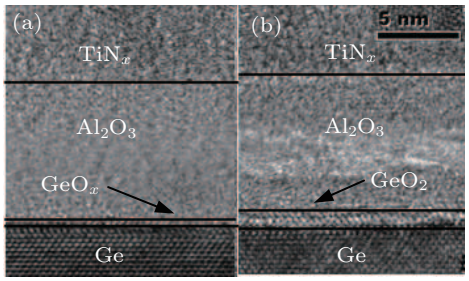


Fig. 2. Cross-sectional TEM images of samples without (a) and with (b) N_2O plasma treatment.

Figure 3 shows the typical C–V characteristics of nMOS capacitors without (a) and with (b) N_2O plasma oxidation treatment. The hump in the depletion region near the inversion of the C–V curve with a frequency of 100 kHz can be ascribed to a weak inversion response. However, previous studies suggest that impurities diffused from the gate dielectric act as minority generation/recombination centers in Ge,[22] which would enhance the minority generation. The hump is invisible for the sample passivated by N_2O plasma, indicating that the formed GeO_2 may block the impurities from diffusing from the gate dielectric into the Ge substrate. The hysteresis between forward and reverse sweeping results from a slow interface state, as illustrated in Fig. 3(b). The hysteresis is reduced from 130 mV to $\sim$ 50 mV by N_2O plasma treatment, which is much less than by thermal oxidation ($\sim$ 120 mV) and comparable to electron–cyclotron-resonance plasma oxidation ($\sim$ 50 mV).[17] The interface state density is extracted based

on high–low frequency method,[23] which can be expressed as follows:

$$D_{\rm it}=\frac{C_{\rm ox}}{q}\left(\frac{C_{\rm lf}/C_{\rm ox}}{1-C_{\rm lf}/C_{\rm ox}}-\frac{C_{\rm hf}/C_{\rm ox}}{1-C_{\rm hf}/C_{\rm ox}}\right), \quad (1)$$

where $D_{\rm it}$ is the interface state density, q is electronic charge, $C_{\rm ox}$ is the capacitance of gate oxide, $C_{\rm lf}$ and $C_{\rm hf}$ are the MOS measured capacitances with low and high frequencies, for example 1 kHz and 1MHz. The interface state densities of treated and untreated capacitors are shown in Fig. 4. It is shown that GeO_2 passivation by N_2O plasma oxidation can reduce the interface state density located at 0.11 eV below the midgap to $\sim 3\times10^{11}$ eV$\cdot^{-1}$cm^{-2} compared with $\sim 1.0\times10^{12}$ eV$^{-1}\cdot$cm^{-2} of the control sample. GeO_2 interlayer is a robust passivation for reducing interface state density and achieving high interface quality between substrate and high K dielectric.

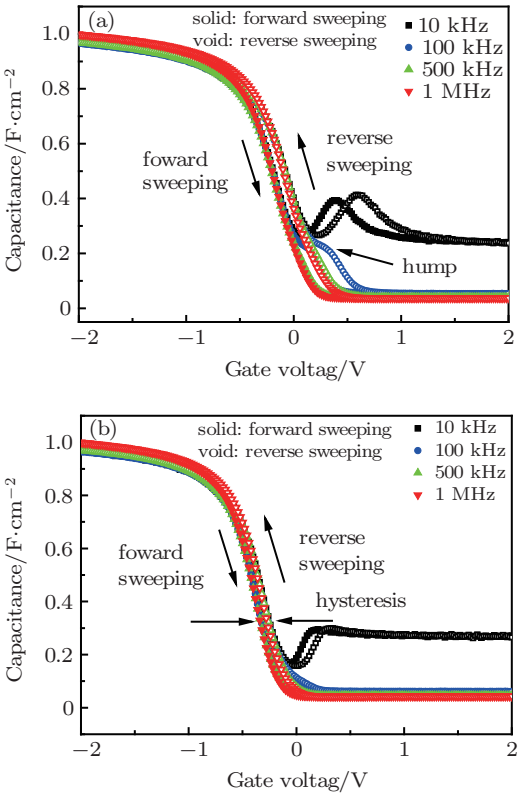


Fig. 3. (color online) C–V characteristics of nMOS capacitor sample without (a) and with (b) N_2O plasma oxidation treatment.

The surface potential as a function of gate bias of N_2O plasma oxidation-treated sample is extracted by Berglund method,[24] as presented in Fig. 5. As mentioned above, poor dielectric/Ge interface would induce Fermi-level pinning at CNL due to a large number of interface states. The modulation of surface potential is ~ 0.74 eV, which is larger than the bandgap of Ge (0.66 eV). Therefore, the Fermi-level can sweep entirely across the bandgap as gate voltage sweeps, which can be ascribed to high quality GeO_2/Ge interface with a low density of interface states. In addition, the gate voltage needed to modulate the surface potential from the flat band to the onset of strong inversion is 0.06 V larger than $2\psi_{\rm B}$ ($\psi_{\rm B}$ is the energy between the flat band and midgap), implying that $\sim 80\%$ of gate voltage is utilized for surface potential modulation and $\sim 20\%$ is employed for charging the interface traps in the bandgap of Ge, which is comparable to that of GeN_x passivation.[25] The Fermi-level at GeO_2/Ge interface is unpinned, which is promising for high performance NMOSFET fabrication.

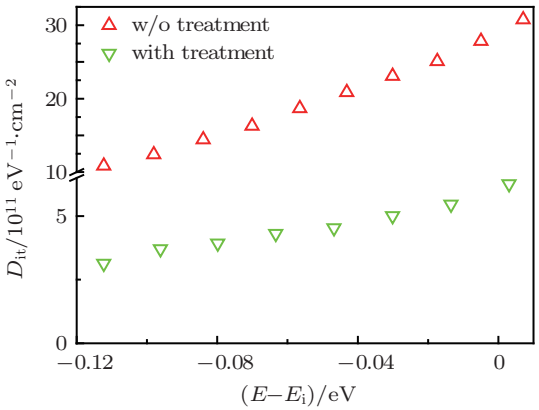


Fig. 4. (color online) Interface state density distributions in the lower half of the p-Ge band gap of MOS capacitor fabricated without and with N_2O plasma treatment.

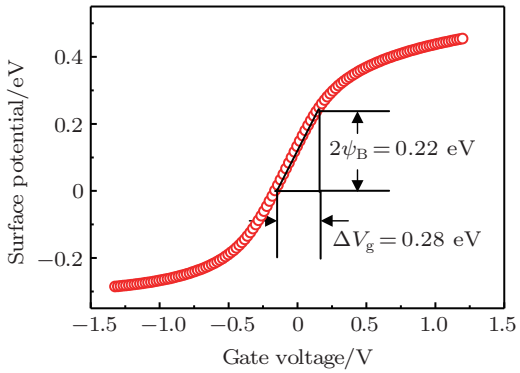


Fig. 5. (color online) Surface potential as a function of gate voltage.

4. Conclusions

In this paper, oxidation of Ge surface by N_2O plasma is investigated. Stoichiometric GeO_2 is formed after N_2O plasma oxidation. The interface between GeO_2 and Ge substrates is smooth with an interface state density of $\sim 3\times10^{11}$ cm$^{-2}\cdot$eV^{-1}. In addition, the Fermi-level at GeO_2/Ge interface is unpinned. N_2O plasma oxidation is proved to be an effective way to fabricate high quality GeO_2 passivation layer. Due to low temperature, the method is promising for Ge high performance NMOSFET fabrication.

Acknowledgment

The authors would like to thank the Key Laboratory of the Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Science for the equipment support.

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