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Effects of silicon nitride diffusion barrier on germanium MOS capacitors with HfON gate dielectrics*

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Abstract: MOS capacitors with hafnium oxynitride (HfON) gate dielectrics were fabricated on Ge and Si substrates using the RF reactive magnetron sputtering method. A large amount of fixed charges and interface traps exist at the Ge/HfON interface. HRTEM and XPS analyses show that Ge oxides were grown and diffused into HfON after post metal annealing. A Si nitride interfacial layer was inserted between Ge and HfON as diffusion barrier. Using this method, well behaved capacitance–voltage and current–voltage characteristics were obtained. Finally hystereses are compared under different process conditions and possible causes are discussed.

Key words: Ge MOS capacitor; HfON; Ge oxides; silicon nitride

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1. Introduction

Historically, the first transistor was made on Ge[1], but the low thermal stability and water solubility of Ge oxide made people choose Si because of the superior physical and electrical properties of silicon dioxide. When the feature dimensions of MOSFETs scale down to sub-50 nm, Si dioxide or Si oxynitride gate dielectric becomes very thin, which results in high gate leakage current[2]. To solve this problem, high dielectric constant (high-*k*) materials have been widely studied to replace Si dioxide[3]. Using high-*k* material as a gate dielectric, Ge has received much attention again, as Ge has a large intrinsic carrier mobility (about 2X the electron mobility and 4X the hole mobility of Si). Several groups have reported the deposition of HfO_2 or ZrO_2 films on Ge with various techniques such as chemical vapor deposition[4] and atomic layer deposition (ALD)[5].

In this paper, Ge MOS capacitors with hafnium oxynitride (HfON) dielectrics were fabricated and investigated. It is revealed that Ge oxides (GeO, GeO_2 or their mixture) were grown and diffused into HfON film during the high temperature annealing step. Si nitride (SiN) was deposited as a diffusion barrier before hafnium nitride (HfN) deposition and its effects are discussed.

2. Experiment

Ge or Si MOS capacitors with HfON dielectrics have been fabricated. N-type Ge substrates with resistivity about 0.1–0.3 Ω·cm and N-type Si substrates with resistivity about 1.5–4 Ω·cm were used. The Ge wafers were first cleaned in acetone and ethanol to remove organic contaminants, then it were cyclically oxidized in H_2O_2 solution and etched in HCl solution for three times to strip native oxide. Our recipe is based on Okumura's method[6]. After blowing dry with N_2, thin HfN was deposited using reactive sputtering of the Hf target in Ar and N_2 ambient. The base pressure of the vacuum chamber was 8×10^{-7} Torr. Post deposition annealing (PDA) was done in N_2 ambient by RTA at 500 °C for 1 min. HfN was oxidized by a trace amount of O_2 left in the RTA chamber (the O_2 concentration is about 5–10 ppm) during the PDA step. Subsequently about 2000 Å TaN was deposited and patterned using the lift-off technique. The diameter of the TaN electrode was 200 μm. Al was deposited on the backside to reduce series resistance. Finally post metal annealing (PMA) was performed at 300 or 400 °C for 40 min in N_2 ambient for thermal stability studies. Capacitance–voltage (C–V) and current–voltage (I–V) characteristics were measured using MDC 590 and HP 4200, respectively. The capacitance equivalent thickness (CET) was extracted from the accumulation capacitance at 1.5 V which was measured at 1 MHz.

3. Results and discussion

In order to study the oxidization behavior of HfN film, XPS spectra of Hf4f, O1s and N1s after 500 °C 1 min PDA are shown in Fig. 1. The binding energy is calibrated with C1s = 284.5 eV. The main peaks of Hf4f with binding energies of 20.1 eV and 18.8 eV are the Hf–O bonds corresponding to $Hf4f_{5/2}$ and $Hf4f_{7/2}$, respectively[7]. Hf–N peaks are not detected, as shown in Fig. 1. A large O1s signal is detected after PDA, which may be incorporated into the film during the transportation step or the PDA step. The N1s peak with a binding energy of 398.4 eV can be attributed to Si–N bonds[8]. The nitrogen atoms left after PDA seem to pile up at the dielectric/Si interface and bond to Si atoms[9]. The atom concentration of Hf, O and N are 31%, 65% and 4%, respectively. It is believed that most of the Hf–N bonds are oxidized by a trace

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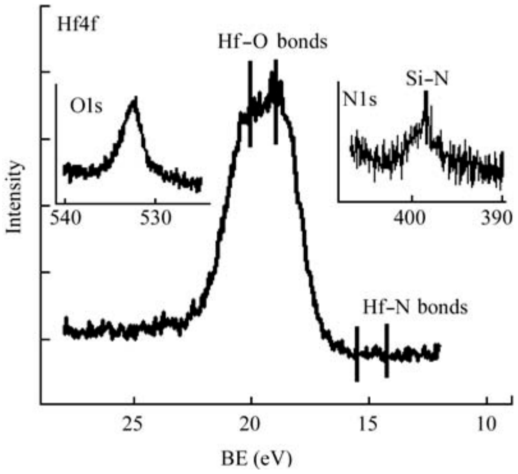

Fig. 1. XPS spectrum of Hf4f. O1s and N1s spectra are also shown in the inset. About 75 Å HfN was deposited on Si substrate and PDA was done at 500 °C for 1 min.

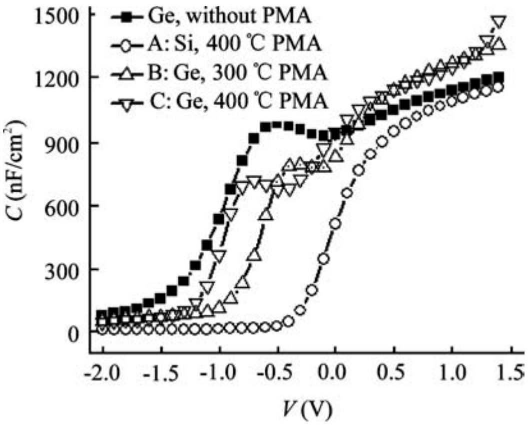

Fig. 2. *C–V* characteristics of HfON dielectric on Si and Ge substrates. PMA was done at 300 °C (B) or 400 °C (A and C) for 40 min.

amount of O_2 after the PDA step.

The *C–V* characteristics of the HfON dielectric on Si and Ge substrates are shown in Fig. 2. The thickness of HfON is about 80 Å. The CET of the Si capacitor is larger than that of Ge, because we have grown thin SiO_2 as an interfacial layer. For Ge capacitors, the accumulation capacitance is increased after 300 or 400 °C PMA compared with that without PMA. As the physical thickness of the HfON dielectric is almost unchanged, it is believed that dielectric constant increase caused by HfON full oxidization or densification during the PMA step may be the reason. Compared to the *C–V* curve of Si (condition A), a large negative flat band voltage shift for the Ge *C–V* curves (conditions B and C) was observed, indicating that many positive fixed charges exist at the Ge/HfON interface after PMA. There is a bump in the depletion region of the Ge *C–V* curves, suggesting that a large amount of acceptor interface traps are located in the upper part of the Ge bandgap[10]. Different authors have observed the bump in Ge *C–V* curves measured at different frequencies[11, 12].

Figure 3 shows HRTEM images of HfON on Si and Ge substrates after 400 °C, 40 min PMA. In Fig. 3(a), we can see that the HfON film on the Si substrate is amorphous, which is consistent with previous results[9]. It is interesting that HfON film is polycrystalline on the Ge substrate, as shown in Fig. 3(b). About 12% Ge was detected by EELS at the middle of the HfON film in Fig. 3(b). It is believed that Ge oxide incorporation in HfON may lower the crystallization temperature of HfON. Epitaxy growth of ZrO_2 on Ge directly using ALD has been found[5], but an interfacial layer was not observed between ZrO_2 and Ge. Our result is different and about 20 Å Ge oxide was grown after PMA. It is not good news for us to see crystallization of the HfON film. O_2 has a large solid solubility and can diffuse in HfON at high temperatures; in particular, it can diffuse fast in polycrystalline HfON through the grain boundary[13, 14]. Once O_2 diffuses to the HfON/Ge interface, it reacts with Ge to form oxides.

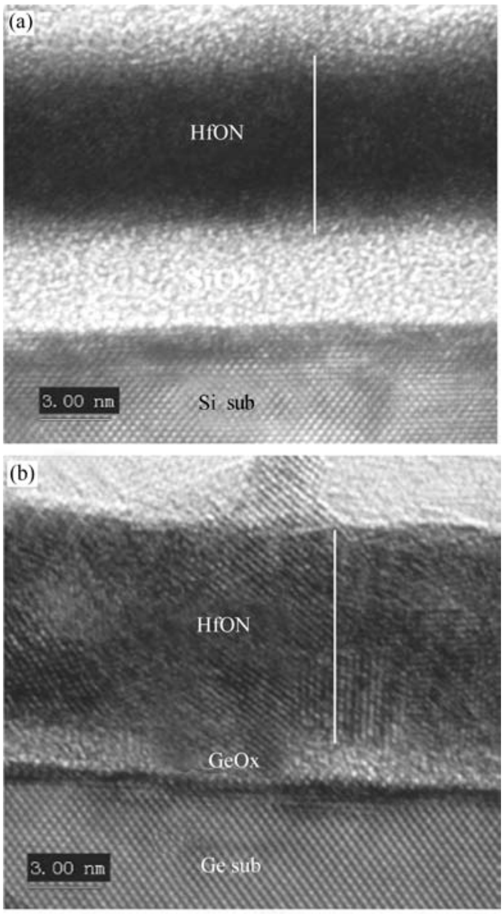

Fig. 3. HRTEM image of HfON on (a) Si and (b) Ge substrates after 400 °C 40 min PMA.

XPS analysis is used to study the chemical states of Ge in the HfON dielectric and at the Ge/HfON interface; about 15 Å thin HfN was deposited on Ge and annealed. Ge3d XPS spectra of HfN deposited and after 400 °C, 40 min PMA are shown in Figs. 4(a) and 4(b), respectively. In Fig. 4(a), the main peak with a binding energy of 28.9 eV is bulk Ge bond[7]. Using the peak decomposition method, two oxide components, GeO and GeO_2, with chemical shifts of 1.5 eV and 3.3 eV with respect to bulk Ge3d are clearly seen. Our result is consistent with Prabhakaran's result, where the chemical shifts of Ge3d in GeO and GeO_2 are 1.4 eV and 3.2 eV, respectively[15]. GeO is the main oxide form as shown in Fig. 4(a). After PMA, the

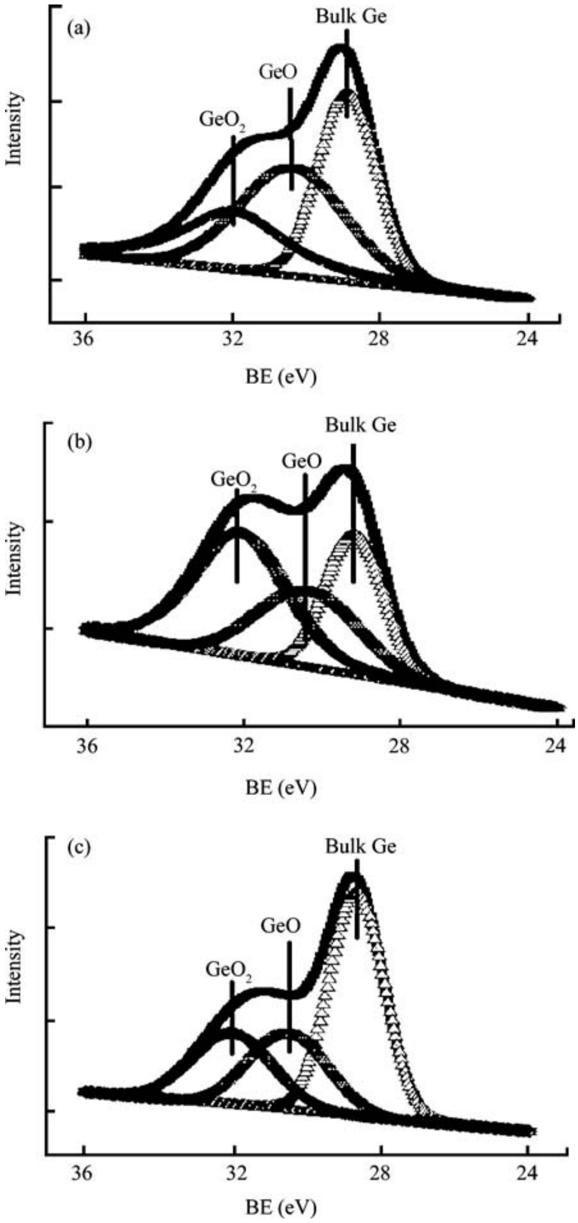

Fig. 4. XPS spectra of Ge3d. (a) 15 Å HfN deposited; (b) 15 Å HfN deposited and after 400 °C, 40 min PMA; (c) 9 Å SiN and 6 Å HfN deposited and after 400 °C, 40 min PMA. Peak decomposition is also shown in the figure.

peak of GeO_2 is significantly increased compared to that of GeO and bulk Ge, as shown in Fig. 4(b). Ge can be oxidized by a trace amount of O_2 in the annealing chamber. The possible reactions are as follows:

$$Ge + O_2 \rightarrow GeO_2; \quad 2Ge + O_2 \rightarrow 2GeO. \tag{1}$$

The first reaction in Eq. (1) dominates as a large amount of GeO_2 was detected after PMA. Ge oxides (GeO, GeO_2 or a mixture of them) can diffuse into the HfON dielectric and mix with each other to form HfGeON during the annealing step[4]. The Ge detected by EELS in Fig. 3(b) may be in oxide form. Unlike SiO_2 and hafnium silicate, Ge oxides[16] or HfGeON[17] have large defects, which may be the cause of the flat band voltage shift and depletion bump in the C–V curve of Ge MOS capacitors.

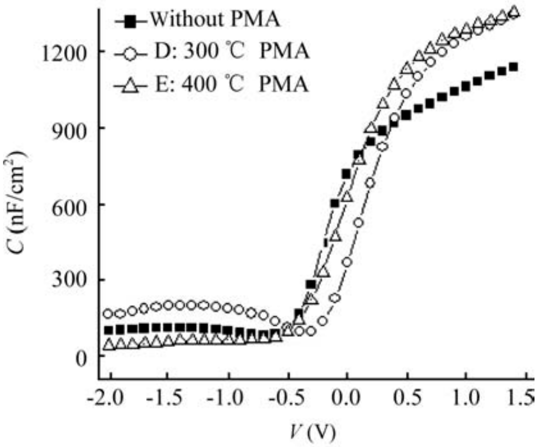

Fig. 5. C–V characteristics of Ge MOS capacitors. About 9 Å SiN and 39 Å HfN was deposited. PMA was done at 300 °C (D) or 400 °C (E) for 40 min.

In order to avoid the problem mentioned above, a diffusion barrier layer against O_2 and Ge oxide diffusion was “inserted” between the Ge substrate and the HfON high-k dielectric. The diffusion barrier layer should be amorphous and has a dense structure. SiN is a common diffusion barrier[18]. Figure 4(c) shows the Ge3d XPS spectrum with the SiN diffusion barrier. About 9 Å SiN and 6 Å HfN was deposited and PMA was done at 400 °C for 40 min. Compared to Fig. 4(b), much less GeO_2 was grown as shown in Fig. 4(c), indicating that SiN acts as an effective diffusion barrier. In our capacitor experiment, about 9 Å SiN was deposited using the reactive sputtering method, subsequently about 39 Å HfN was deposited in situ. The C–V characteristics of Ge MOS capacitors are shown in Fig. 5. After 300 or 400 °C PMA, the accumulation capacitance is increased compared with that without PMA, which was also observed in the HfON dielectric only. There is no bump in the depletion region. The flat band voltages of conditions D and E are –0.31 and –0.48 V, while those of conditions B and C are –0.73 and –1 V, respectively. The work function of TaN in our experiment is about 4.3–4.5 eV, and the work function of Ge we used is 4.29 eV. If we take the work function of TaN as 4.5 eV[19], then the ideal flat band voltage is 0.21 V. Much smaller flat band voltage shifts are obtained using SiN as a diffusion barrier.

I–V characteristics of Ge MOS capacitors with different conditions (C and E) are compared in Fig. 6. The CET of conditions C and E are 26 and 25 Å, respectively. Condition E has a lower gate leakage current than that of condition B, although it has a smaller physical thickness than that of condition B. When gate bias is set as 1 V, the leakage currents of conditions C and E are 1.6×10^{-2} and 9×10^{-4} A/cm^2, respectively. Compared to condition C, the gate leakage current of condition E is reduced about 18 times.

C–V hysteresis of high-k dielectrics has been identified as a potential problem because hysteresis leads to instability of the threshold voltage of MOSFETs[20]. In Fig. 7, hystereses of HfON on Si and Ge with different process conditions are compared. Hysteresis is defined as the flat band voltage

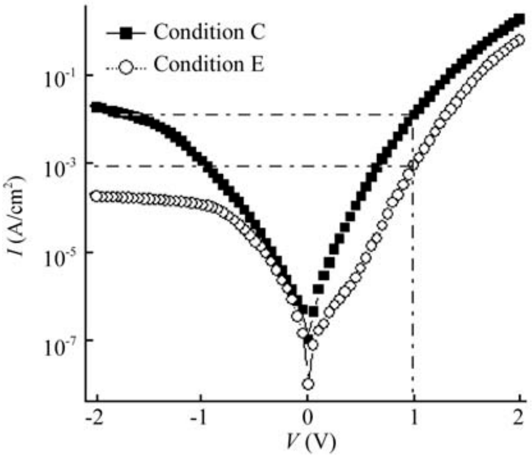

Fig. 6. *I*–*V* characteristics of Ge MOS capacitors after 400 °C, 40 min PMA. The conditions are: C: 75 Å HfN deposited; E: 9 Å SiN and 39 Å HfN deposited.

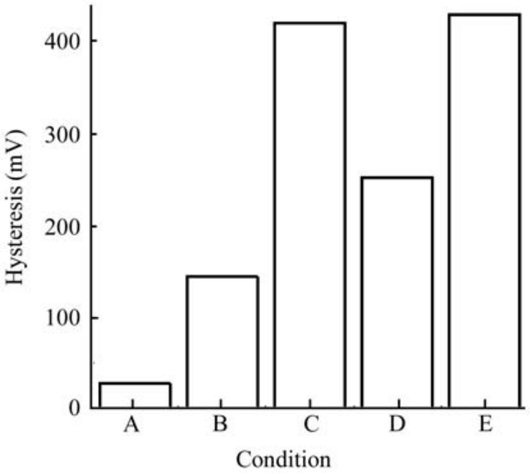

Fig. 7. Comparison of *C*–*V* hystereses with different conditions. Conditions A to E are the same as Fig. 2 and Fig. 5.

difference between the *C*–*V* curves swept from –2 to 1.5 V and vice versa. As shown in Fig. 7, the hystereses of Ge MOS capacitors in all conditions are larger than those of Si MOS capacitors, suggesting that the Ge/HfON interface is much poorer than the Si/HfON interface. Compared to condition B, the hysteresis of condition C is increased, which indicates that Ge oxides are the source of charge trapping centers as more oxides were grown after higher temperature PMA. Condition D has a larger hysteresis than condition B, which suggests that charge trapping centers exist in bulk SiN or at the interface between SiN and Ge oxides. The hysteresis of condition E is comparable to that of condition C, indicating that high temperature PMA can effectively passivate the trapping centers related to SiN.

4. Summary

Ge MOS capacitors with HfON high-*k* dielectrics have been fabricated. A large amount of fixed charges and interface traps exist at the Ge/HfON interface. HRTEM and XPS analyses show that Ge oxides were grown and diffused into the HfON dielectric after post metal annealing. In order to suppress the growth and diffusion of Ge oxides, a SiN diffusion barrier was deposited before HfN deposition. *C*–*V* and *I*–*V* characteristics are better than those of the HfON dielectric only. Finally *C*–*V* hystereses in different conditions are compared and possible causes are discussed.

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