Effects of annealing gas species on the electrical properties and reliability of Ge MOS capacitors with high-k Y_2O_3 gate dielectric

C.X. Li[1], H.X. Xu[2], J.P. Xu[2], P.T. Lai[1,*]

***Abstract* – In this work, Ge MOS capacitors with Y_2O_3 gate dielectric were fabricated. The effects of annealing in N_2, NH_3 O_2 or NO ambient were investigated. Experimental results demonstrated that the NO annealing could improve both electrical properties and reliability of Ge MOS devices with Y_2O_3 dielectric. On the other hand, the NH_3 annealing resulted in H-related traps while the O_2 annealing suffered from extra GeO_x growth, thus both degrading the performance of the devices.**

I. INTRODUCTION

In order to improve the speed of MOS devices while scaling down the size of MOS devices, Ge MOS devices are researched due to high electron and hole mobilities of Ge. Also high-k materials such as HfO_2 [1-2], ZrO_2 [3] and HfTiON [4] have been investigated as the gate dielectric for Ge devices. However, the interface quality of high-k/Ge structure is not as good as that of the SiO_2/Si interface. One of the main reasons is that unstable GeO_x is grown during high-k gate-dielectric deposition and post-deposition annealing. Recently rare-earth oxides such as La_2O_3 [5] and CeO_2 [6] were studied as the gate oxide for Ge MOS devices. But CeO_2 has a small bandgap of 3.3 eV, which can cause large gate leakage current [6]; La_2O_3 [7] absorbs moisture, which can cause reliability problems. Y_2O_3 is a promising candidate for gate dielectric due to its relatively high dielectric constant (~14-18), high crystallization temperature (~2325 ^{0}C) and wide bandgap (~5.5 eV) [8~10]. So far, Y_2O_3 is an interesting candidate for Si MOS devices, but there is little work on Ge MOS devices [9]. In this paper, Y_2O_3 is researched as the gate dielectric for Ge MOS devices, and the effects of annealing in N_2, NH_3, O_2 or NO on the electrical properties of Ge MOS devices are investigated.

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978-1-4244-4298-0/09/$25.00 ©2009 IEEE

II. EXPERIMENT

Germanium MOS capacitors were fabricated on (100) n-type substrate with a resistivity of 0.040 ~ 0.047 Ωcm. The wafers were cleaned in organic solvent followed by a rinse in 2% HF and de-ionized water for several times[11]. After drying with N_2 gas, the wafers were immediately transferred into a sputtering system (Denton discovery series). Y_2O_3 film was subsequently deposited by sputtering Y_2O_3 target (99.9% purity) in an Ar ambient. Y_2O_3 target received a RF power of 40 W, and operating pressure was 4.4 mTorr. Post-deposition anneal (PDA) was performed in N_2, NH_3 O_2 or NO ambient at 500 ^oC for 300 s, producing the control, NH3, O2 and NO samples respectively. Subsequently, Al was evaporated and patterned as gate electrode with an area of 7.85×10^{-5} cm^{-2}. Finally, forming-gas anneal (5% H_2 + 95% N_2) was implemented at 280 ^oC for 20min.

High-frequency (1-MHz) capacitance-voltage (C-V) characteristics were measured at room temperature using HP4284A precision LCR meter. Gate-leakage current was measured by HP4156A precision semiconductor parameter analyzer. The cross section of the samples was measured by TEM. Surface morphology was measured by AFM. High-field stress (at 10 MV/cm) with the capacitors biased in accumulation by HP 4156A precision semiconductor parameter analyzer was used to examine device reliability in term of gate-leakage increase after the stress. All electrical measurements were carried out under a light-tight and electrically-shielded condition.

III. RESULTS AND DISCUSSION

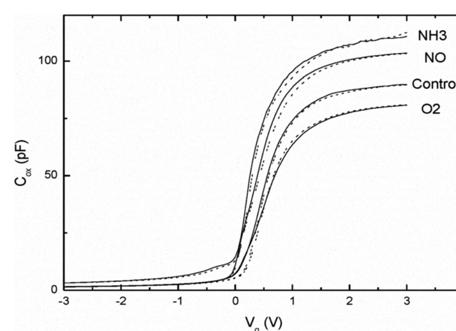


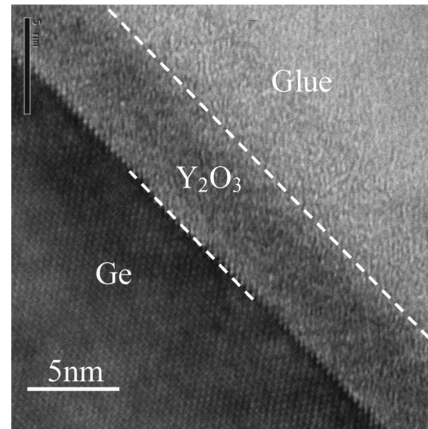
Fig.1 High-frequency (1-MHz) C-V curve of the Ge MOS capacitors.

Fig. 1 shows the C-V curves of the samples. Compared with the control sample, the capacitance of the O2 sample is smaller due to extra GeO_x interlayer growth during the O_2 annealing. However, the capacitances of the NO and NH3 samples are larger than that of the control sample, due to nitrogen incorporation. The incorporated nitrogen can increase the dielectric constant by passivating the oxygen vacancies which acts as vacuum or by replacing the oxygen atoms[12]. Among the samples, the NH3 sample has the largest capacitance, which is ascribed to the well-known best nitridation effect of the NH_3 gas.

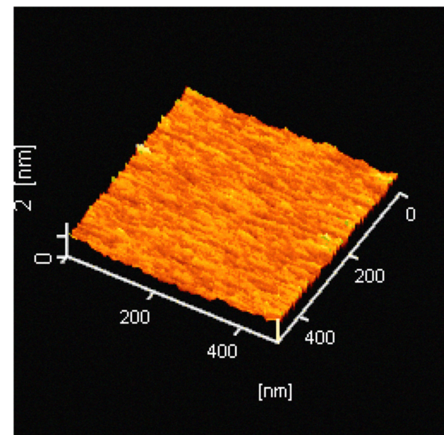
Table 1 lists the device parameters extracted from the high-frequency C-V curves. Interface-state density at midgap is extracted by using the Terman's method for comparison purpose only.[13] Compared with the control sample, the gate-oxide capacitance C_{ox} of the O_2 sample is decreased, due to extra growth of GeO_x during the annealing. On the other hand, the C_{ox} of the NO sample is increased due to increased dielectric constant, as mentioned above. The V_{fb} is positive for four samples, indicating negative charges which may be related to trapped charges in the dielectric bulk or at the Y_2O_3/Ge interface. Comparing with the control sample, the NO and NH3 samples have negative V_{fb} shift, implying positive charges formed during the PDA. This should be due to the nitrogen incorporation. In particular, the NH3 sample has more nitrogen incorporation, thus larger V_{fb} shift. The midgap interface-state density (D_{it}) of the NO sample is lower than that of the control sample, due to the nitrogen incorporation which could passivate the dangling bonds in the bulk or at the interface, thus improving the interface quality. The NH3 sample has larger D_{it} than that of the NO sample, which could be explained by H-related traps created during the NH_3 annealing. The O2 sample suffers from extra growth of GeO_x which would generate defects at the Y_2O_3/Ge interface, thus larger D_{it} than that of the control sample.

Fig.2 shows the TEM and AFM pictures of the control sample. It is shown that there is no obvious GeO_x interfacial layer grown at the Y_2O_3/Ge interface, which should be attributed to the stability of the Y_2O_3 gate dielectric in contact with the Ge substrate. The AFM picture for the gate dielectric of the control sample shows very good surface morphology, with a surface roughness of ~0.26 nm RMS. In a word, Y_2O_3 has good interfacial quality with germanium, with smooth interface and good surface morphology for the control sample.

From Fig. 3, it is observed that the NO sample has the smallest gate leakage current, indicating best interface quality (supported by its smallest D_{it} of 1.7×10^{11} $cm^{-2}eV^{-1}$), ascribed to the nitrogen incorporation which could passivate the dangling bonds of the gate dielectric or at the Y_2O_3/Ge interface. Compared with the control sample, the gate leakage currents of the O2 and NH3 samples are increased, which could be explained either by the extra GeO_x growth during the O_2 annealing or the H-related traps introduced during the NH_3 annealing.



(a)



(b)

Fig. 2 (a) TEM and (b) AFM pictures of the control sample

Table 1 Gate-oxide capacitance, equivalent oxide thickness, flatband voltage and midgap interface-state density extracted from the 1-MHz C-V curve, dielectric thickness measured by ellipsometer and dielectric constant for the samples.

Sample	C_{ox} (pF)	t_{eq} (A)	V_{fb} (V)	D_{it} at midgap ($cm^{-2}eV^{-1}$)	Q_{ox} (cm^{-2})	t_{die} (nm)	k
control	89.8	30	0.33	3.9×10^{11}	-1.87×10^{12}	5.5	7.2
NO	103.5	26	0.16	1.7×10^{11}	-1.55×10^{12}	6.1	9.3
NH3	110.7	25	0.13	2.1×10^{11}	-1.45×10^{12}	6.0	9.5
O2	80.9	34	0.36	4.3×10^{11}	-1.85×10^{12}	6.2	7.1

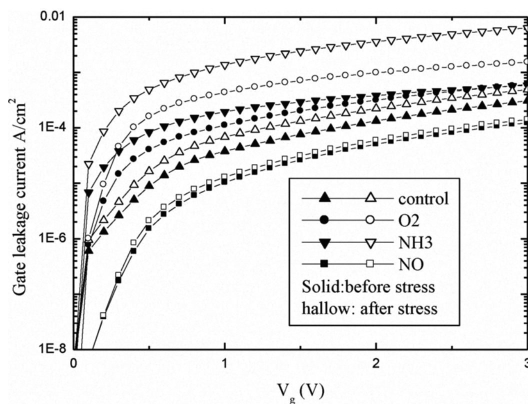


Fig. 4 Gate leakage current of the samples before and after stress

In order to evaluate the reliability of the samples, a high-field stress (at 10 MHz for 3600 s) is imposed on the samples. Fig. 4 shows the gate leakage currents before and after the stress. It is shown that the NO sample has the smallest increase of gate leakage current after the stress, while the NH3 sample has the largest increase of gate leakage current. The possible reason is that nitrogen incorporation can passivate the dangling bonds in the gate dielectric or at the interface, thus increasing the resistance against high-field stressing. On the other hand, the NH3 sample has a large number of weak H bonds which could be easily broken during the high-field stress, resulting in large increase of gate leakage current. The O2 sample has extra growth of unstable GeO_x, and thus large increase of gate leakage current after the stress and degraded reliability.

Rare-earth metal oxide Y_2O_3 is deposited as the gate dielectric of Ge MOS capacitors and then annealed in N_2, NH_3, NO and O_2 ambient respectively. Experimental results show that Y_2O_3 has good interface quality with Ge, with smooth interface and good surface morphology for the sample annealed in N_2 gas. Also, the NO sample has the smallest midgap interface-state density and gate leakage current before and after stress, due to nitrogen incorporation. The NH3 sample suffers from hydrogen-related electron traps, leading to the largest gate leakage current and largest stress-induced leakage increase. In conclusion, the Y_2O_3 should be a promising candidate as the gate dielectric of Ge MOS devices, and the NO annealing could introduce sufficient nitrogen into the dielectric to improve the interface properties and enhance the reliability of the Ge MOS devices.

ACKNOWLEDGEMENT

This work is financially supported by the Research Grants Council (RGC) of Hong Kong Special Administrative Region (HKSAR), China, under Project HKU 713308E, and the University Development Fund (Nanotechnology Research Institute, 00600009) of The University of Hong Kong.

REFERENCES

[1] W. P. Bai, N. Lu, J. Liu, A. Ramirez, D. L. Kwong, D. Wristers, A. Ritenour, L. Lee, and D. Antoniadis, "Ge MOS characteristics with CVD HfO_2 gate dielectrics and TaN gate electrode," in VLSI Symp. Tech. Dig., 2003, pp. 121-122.

[2] J. J. Chen, N. A. Bojarczuk, H. Shang, M. Copel, J. B. Hannon, et al., "Ultrathin Al_2O_3 and HfO_2 gate dielectrics on surface-nitrided Ge," IEEE Trans.

Electron Devices, vol. 51, no. 11, pp. 1441-1447, Nov. 2004.

[3] S. K. Mandal, S. Charkraborty, C. K. Maiti, “Ge-channel p-MOSFETs with ZrO_2 gate dielectric,” Microelectronic Engineering, vol.81, pp.206-211, 2005.

[4] C. X. Li, P. T. Lai, and J. P. Xu, “Improved reliability of Ge MOS capacitor with HfTiON high-k dielelctric by using Ge surface pretreatment in wet NO,” Microelectronic Engineering, vol. 84, no. 9-10, pp. 2340-2343, 2007.

[5] G. Mavrou, S. Galata, P. Tsipas, et. al., “Electrical properties of La_2O_3 and HfO_2/La_2O_3 gate dielectrics for germanium metal-oxide semiconductor devices,” J. Appl. Phys. 103 (2008) 014506

[6] D. P. Norton, J. D. Budai and M. F. Chisholm, “Hydrrogen-assisted pulsed-laser deposition of (001) CeO_2 on (001) Ge”, Appl. Phys. Lett. 76 (2003) 1677-1679

[7] Y. Zhao, K. Kita, K. Kyuno and A. Toriumi, “Band gap enhancement and electrical properties of La2O3 films doped with Y_2O_3 as high-k gate insulators”, Appl. Phys. Lett. 94 (2009) 042901

[8] K.H. Kwon, K.L. Chang, J.K. Yang, et.al., “Effective formation of interface controlled Y_2O_3 thin film on Si(100) in a metal-(ferroelectric)-insulator-semiconductor structure”, Micro. Engi. 85 (2008) 1781-1785

[9] L. K. Chu, W.C. Lee, M. L. Huang, et.al., “Metal-oxide-semiconductor devices with molecular beam epitaxy-grown Y_2O_3 on Ge,” Journal of Crystal Growth, vol. 311, pp. 2195-2198, 2009.

[10] C. O. Chui, H. Kim; D. Chi, P.C. McIntyre, and K.C. Saraswat, “Nanoscale germanium MOS Dielectrics-part II: high-k gate dielectrics,” IEEE Trans. Electron Device, vol. 53, no. 7, pp.1509-1516, 2006.

[11] K. Tse and J. Robertson, “Defect passivation in HfO_2 gate oxide by fluorine,” Appl. Phys. Lett., vol. 89, pp. 142914, 2006

[12]]L. M. Terman, “An investigation of surface states at a silicon/silicon oxide interface employing metal-oxide-silicon diodes,” Solid-State Electron., vol. 5, pp. 285–299, 1962

[13] Paskaleva, A. J. Bauer, M. Lemberger, et.al., “ Different current conduction mechanisms through thin high-k HfxTiySizO films due to the varying Hf to Ti ratio,” J. Appl. Phys. 95 (2004) 5583-5590