Extended Abstracts of the 2014 International Conference on Solid State Devices and Materials, Tsukuba, 2014, pp12-13

High-k/Ge interface passivation using cycling ozone oxidation

Xu Yang[1,2], Sheng-Kai Wang[1], Le Han[1,2], Xiong Zhang[2], Bing Sun[1], Hu-Dong Chang[1], Wei Zhao[1], Zhen-Hua Zeng[1,2], Hong-Gang Liu[1*] and Yi-Ping Cui[2]

[1]Microwave Device and IC Department, Institute of Microelectronics of Chinese Academy of Sciences,
No.3 Bei-tu-cheng West Road, Chaoyang, Beijing 100029, China
Phone: +86-10-8299-5765 Fax: +86-10-6202-1601 E-mail: liuhonggang@ime.ac.cn
[2]Advanced Photonics Center, School of Electronic Science and Engineering, Southeast University,
Nanjing 210096, China

Abstract

An *in situ* cycling ozone oxidation (COO) method has been introduced into the atomic layer deposition (ALD) process to form an ultrathin GeO_x interfacial passivation layer with better interface quality. Also the quality of high-k film has been further improved with cyclic ozone treatment. MOS capacitors and MOSFETs fabricated with the engineered $Al_2O_3/GeO_x/Ge$ gate stacks exhibit good electrical characteristics.

1. Introduction

In order to build high quality high-*k* gate stack on Ge substrate, reducing D_{it} and improving high-*k* film quality are the critical challenges for high-performance Ge-MOS devices. Many efforts for reducing the interface states have been made, such as plasma oxidation,[1] sulfur passivation,[2] fluorine passivation,[3] etc. Among them, forming a thin GeO_2 interfacial layer (IL) between high-k and Ge is considered as one of the best solutions to improve the interface quality.[4-5] Ozone shows a high oxidation activity similar with oxygen plasma, making it a possible way to form superior GeO_2/Ge interface and to effectively repair the defects in high-*k* film generated during deposition at a low processing temperature. Therefore, starting from this point, in this study, we employed an *in situ* cycling ozone oxidation (COO) method in the ALD deposition process to form a high-quality $Al_2O_3/GeO_2/Ge$ stack with an ultrathin GeO_2 interfacial layer and to further eliminate the defects in high-*k* film. MOS capacitors and MOSFETs were fabricated to study properties of the $Al_2O_3/GeO_x/Ge$ gate stacks.

2. Experimental

N-type Ge (100) substrates (~$2\times10^{17}cm^{-3}$) were used in this study. After an HCl-last cleaning process, the wafers were transferred into ALD chamber for Al_2O_3 deposition. For comparison, four samples (denoted by A, B, C, D) were prepared. The details about the samples preparation are shown in Fig. 1. For samples A, B, C, 0.3nm-Al_2O_3 was firstly deposited followed by 10min ozone treatment at 300°C for interfacial GeO_x formation. Then, 4.8nm Al_2O_3 was deposited by 6 cycles (0.8nm for one cycle). After each cycle deposition, 10min (sample A) or 2min (sample B) or 0min (sample C) ozone treatment was employed. For 10min case, we denote it as "10min-COO", and similarly "2min-COO" for 2min case, and "0min-COO" for 0min case. For sample D, 5.1nm Al_2O_3 was deposited without any ozone treatment. All samples were subjected to PDA at 400℃ in pure oxygen ambient for 30 min.

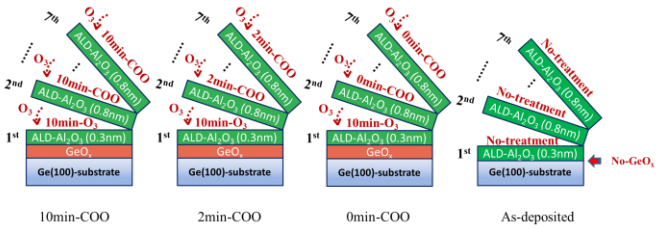

Fig. 1 Schematic illustration of fabrication procedure of $Al_2O_3/GeO_x/Ge$ gate stacks for four samples A, B, C and D.

For MOSCAPs fabrication, Ti/Au gate metal was formed by electron beam evaporation, followed by post metallization annealing at 350°C in N_2. The Ge pMOSFETs were fabricated using the above-mentioned stack. XPS, C-V, and I-V, characterization were performed.

3. Result and Discussion

Figure 2 shows the XPS spectra of Ge 3d for all samples. The peak at ~32.6 eV is attributed to GeO_x. There is no GeO_x growth detected at the interface for the sample without any ozone treatment, whereas the peak is apparent for the COO samples. Moreover, 2min-COO shows similar GeO_x thickness (~0.6nm) with the 0min-COO sample, while the thickness slightly increased for 10min-COO due to the diffusion of oxygen during the long time treatment.

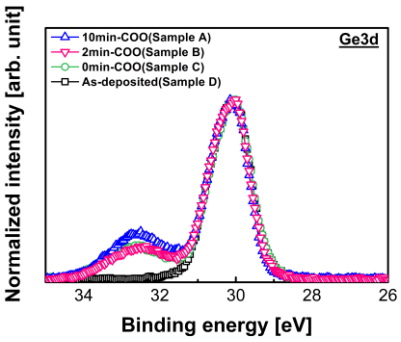

Fig. 2 XPS spectra of Ge3d for the four samples

Figures 3(a)-(d) show the C-V characteristics of sample A-D, respectively. For the sample D without any ozone treatment [Fig. 3(d)], large frequency dispersion is observed, indicating a poor interface with large D_{it}. For samples A, B, C, after introducing the GeO_x IL, the frequency dispersion has been greatly suppressed. By further comparison of the frequency dispersion between sample A, B, and C, it is observed that samples A and B show less frequency dispersion than sample C, indicating COO treatment is beneficial in reducing D_{it}, which is attributed to the enhancement of GeO_x IL quality during the COO treatment. For sample A, the D_{it} value near the midgap (~3×10^{11} cm^{-2} eV^{-1}) has been extracted by low temperature conductance method.[6]

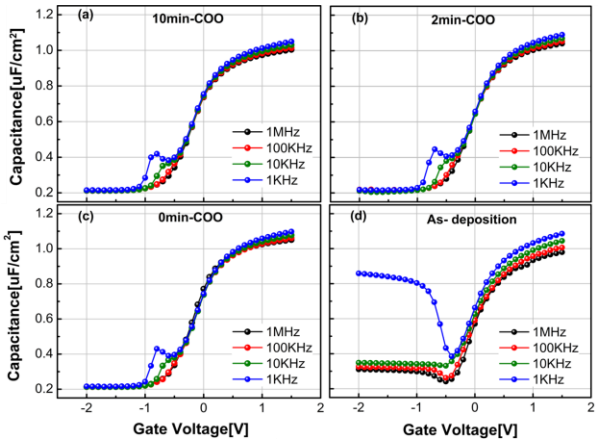

Fig. 3 C-V characteristics for samples A-D formed under various fabrication conditions, respectively.(10min-COO, 2min-COO, 0min-COO and as-deposited)

The gate leakage property of Ge MOS capacitors are shown in Fig. 4. It is obvious that the gate leakage current decreased by enhancing the COO treatment. By comparing the samples 2min-COO and 0min-COO, although both samples have the same thickness, the leakage current density (J_g) of sample 2min-COO is lower, indicating COO treatment is effective to improve the high-*k* quality. Moreover, sample 10min-COO (sample A) exhibits the least J_g at the high gate voltage, which is possibly owing to thicker GeO_x than sample B; This is consistent with the XPS results.

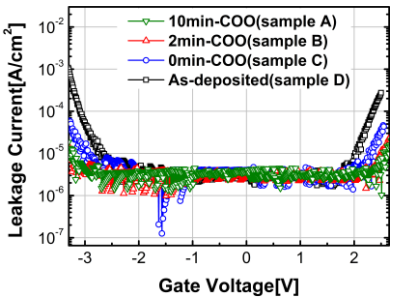

Fig. 4 Leakage current for samples A-D, respectively (10min-COO, 2min-COO, 0min-COO and as-deposited).

Figures 5(a) and 5(b) show the typical output (I_D-V_D) and transfer (I_D-V_G) characteristics of Ge (100) pMOSFETs with the Al_2O_3/GeO_x/Ge gate stack using the 2min-COO treatment（sample B）and 0min-COO treatment (sample C). The I_{on}/I_{off} ratio for 2min-COO sample and 0min-COO sample are about 2.4 × 10^4 and 1.6 × 10^4 at V_D=-50mV, respectively. Fig. 5(a) shows the well-behaved output characteristics of the 400-μm × 6-μm pMOSFETs devices, with flat drain current in the saturation region. The Ge pMOSFETs with 2min-COO treatment show a ~70% drive current improvement over the ones with 0min-COO treatment under the same overdrive of gate bias in the saturation region. A drive current of 24.3 mA/mm at V_G = −3.5 V is obtained for devices with COO method.

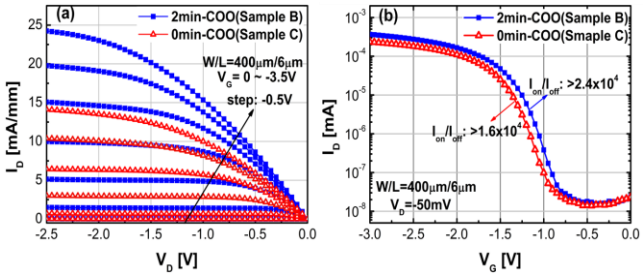

Fig. 5 I_D-V_D and I_D-V_G characteristics for the Ge (100) pMOSFETs (channel width=400μm / channel length =6μm). Devices with 0min-COO treatment show I_{on}/I_{off} ratio about 1.6 × 10^4, while devices for 2min-COO treatment exhibits I_{on}/I_{off} ratio about 2.4 × 10^4.

4. Conclusions

In conclusion, the cycling ozone oxidation process during high-*k* dielectric deposition has been found to be effective in improving quality of the GeO_2/Ge interface and scaling down the GeO_x interfacial layer thickness as Al_2O_3 servers as a barrier, as well as enhancing the high-*k* dielectric quality at low oxidation temperature. Moreover, *in situ* deposition and ozone treatment in ALD system could avoid the pollution of additional processes and simplify the utilization of equipment.

Acknowledgements

This work is supported by the National Basic Research Program of China under Grant No. 2011CBA00605, the National Natural Science Foundation of China under Grant No. 61204103, and the national Science &Technology Major Project of China under Grant No. 2011ZX02708-003.

References

[1] R. Zhang *et al.*, *Appl. Phys. Lett.* **98** (2011) 112902.
[2] R. Xie *et al.*, *IEEE Electron Device Lett.* **28** (2007) 976.
[3] R. Xie *et al.*, *Appl. Phys. Lett.* **92** (2008) 163505
[4] A. Delabie *et al.*, *Appl. Phys. Lett.* **91** (2007) 082904
[5] H. Matsubara *et al.*, *Appl. Phys. Lett.* **93**(2008) 032104
[6] E. H. Nicollian and A. Goetzberger: *Bell Syst. Tech. J.* **46** (1967) 1055.