

Passivation of HfO₂/Ge interface with YON fabricated by different approaches

Z. X. Cheng^{1,a}, Q. Xu¹, L. Liu¹ and J.P. Xu¹

¹School of Optical and Electronic Information, Huazhong University of Science and Technology, Wuhan 430074, China

Abstract. Nitrided Y₂O₃ (YON) interfacial passivation layer (IPL) is used to passivate the HfO₂/Ge interface for better interfacial and electrical properties of Ge metal-oxide-semiconductor (MOS) capacitor. Two different approaches were used to prepare the YON IPL, one is to deposit YON directly by sputtering Y₂O₃ target in Ar+N₂ ambient, and the other is to deposit YN first by sputtering Y target in Ar+N₂ ambient followed by the annealing in N₂+O₂ to convert YN to YON. Experimental results indicate that the MOS capacitor fabricated by the latter approach could achieve more excellent interfacial and electrical properties due to more effective suppression of the formation of Ge oxides.

1 Introduction

As the Si-based metal-oxide-semiconductor field-effect transistor (MOSFET) is approaching its physical limits, novel substrate materials and devices have been extensively studied [1, 2]. Among the novel substrates with high mobility, Ge is believed to be one of the most promising candidate to replace the traditional Si substrate, due to its much higher and more symmetrical mobilities [3]. However, direct deposition of high-*k* dielectric on Ge substrate usually results in a poor interface with high interface-state density (*D*_{it}). Specifically, when HfO₂, which is considered to be the most widely-used dielectric for Si MOSFET, is used for Ge MOSFET, the parasitically grown unstable GeO_x (*x*<2) between HfO₂ and Ge substrate severely degrades its interface quality [4]. Moreover, HfGeO_x formed by the intermixing between Ge substrate (or GeO_x) and HfO₂ dielectric will also result in the increased *D*_{it} because of the fivefold coordinated Hf in HfGeO_x [5]. Recently, Y₂O₃ has attracted much attention to solve this problem as an alternative passivation layer on Ge substrate [6-8], because it can react with Ge substrate to form stable YGeO_x interlayer and suppress the formation and diffusion of GeO_x. Moreover, the so-called “valency passivation” could effectively suppress the dangling bonds in the interface and consequently improve the interface quality by considering the trivalent nature of Y [8]. Therefore, Y₂O₃, which has high *k* value (12-17) [6, 9] and large bandgap (~5.5 eV) [6, 9] is considered to be one of the most promising IPLs for Ge MOS devices. However, the crystallization of Y₂O₃ is still an issue because of its low crystalline temperature (400°C) [10], which generates a large amount of defects in the film and causes the increase of leakage current [11]. N incorporation into Y₂O₃ has been suggested to increase the crystalline temperature [11]. Moreover, the barrier effect introduced by N could effectively suppress the diffusion of Ge and O to prevent the formation of GeO_x, and further improve the interface quality [12]. In this paper, we further investigate the effect of

^a Corresponding author : zxcheng@hust.edu.cn

YON, which is used as IPL in the Ge MOS with HfO_2 as dielectric. Two different methods were used to prepare YON, one is to deposit YON directly by sputtering Y_2O_3 target in $\text{Ar}+\text{N}_2$, and the other is to deposit YN first by sputtering Y target in $\text{Ar}+\text{N}_2$ followed by annealing in N_2+O_2 to convert YN to YON. The interfacial and electrical properties of samples were compared and discussed.

2 Experiment

Figure 1 (a) shows the fabrication process of Ge MOS capacitors. N-type (100) Ge wafers with a resistivity of $0.02 \sim 0.1 \Omega\cdot\text{cm}$ were used for fabricating the Ge MOS capacitors. The Ge wafers were cleaned in trichloroethylene, acetone and ethanol in sequence, and then the native oxide was removed by a cyclic rinsing in diluted HF (1:50) and deionized water. After drying by N_2 gas, the wafers were immediately transferred into a sputter chamber. The stacked gate dielectric of HfO_2/YON (denoted as YON sample) was formed by successively depositing 2-nm YON by sputtering Y_2O_3 target in $\text{Ar} + \text{N}_2$ and 6-nm HfO_2 by sputtering HfO_2 target in Ar ambient. And the stacked gate dielectric of HfO_2/YN (denoted as YN sample) was formed by successively depositing 2-nm YN by sputtering Y target in $\text{Ar} + \text{N}_2$ and 6-nm HfO_2 by sputtering HfO_2 target in Ar ambient. For comparison, 8-nm HfO_2 gate dielectric (denoted as control sample) was also deposited using the same sputtering conditions as above. Then a post-deposition annealing (PDA) was carried out in N_2 (500 sccm) + O_2 (50 sccm) ambient at 500°C for 5 min to improve the film property and convert YN to YON. Al was evaporated and patterned as gate electrode with an area of $7.85 \times 10^{-5} \text{ cm}^2$, followed by forming-gas (5% $\text{H}_2 + 95\% \text{ N}_2$) annealing at 300°C for 20 min to reduce contact resistance. The schematic of fabricated MOS capacitor is shown in figure 1 (b).

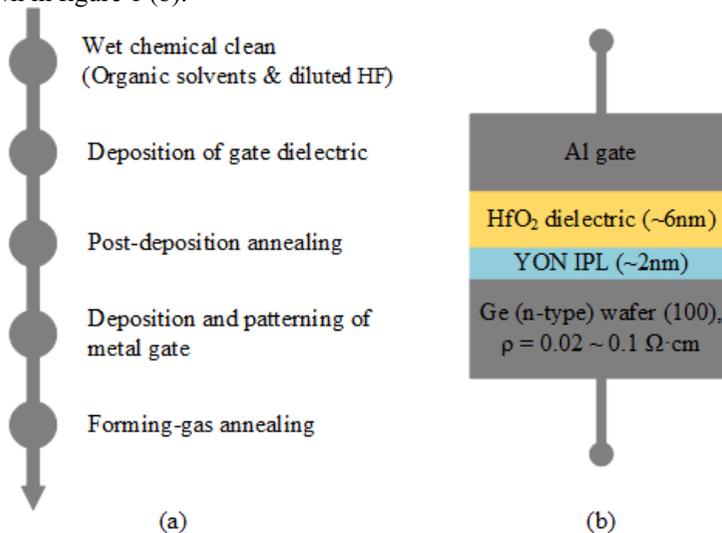


Figure 1. (a) Fabrication process flow, (b) Schematic of Al/ HfO_2 /IL/Ge capacitor

Capacitance-voltage ($C-V$) and gate leakage current density versus gate voltage (J_g-V_g) characteristics were measured under a light-tight and electrically-shielded condition by HP4284A precision LCR meter and HP4156A semiconductor parameter analyzer, respectively. X-ray photoelectron spectroscopy (XPS) was used to analyze the chemical states near/at the high- k/Ge interface, which was performed using a Thermo VG Multilab 2000 photoelectron spectrometer with a monochromatic Al $K\alpha$ radiation source ($h\nu = 1486.6 \text{ eV}$ and width = 0.47 eV) under a vacuum lower than $3 \times 10^{-7} \text{ Pa}$. In order to analyze the interface between gate dielectric and Ge substrate, the thickness of the gate dielectric layer was thinned to $\sim 5 \text{ nm}$ from the Ge surface with a slow etching rate of $\sim 1 \text{ nm/min}$ by using an in-situ Ar^+ ion beam. And meanwhile, Atomic force microscopy (AFM) was used to check the HfO_2 surface morphology, which was influenced by the out-diffused Ge from the interface into the HfO_2 dielectric.

3 Results and discussion

Figure 2 shows the typical high-frequency (1-MHz) C - V curves of the three samples. Obviously, the control sample without IPL exhibits poor C - V behavior with the largest stretch out along the horizontal axis and even a large distortion in the weak inversion region, indicating the poor interface quality between HfO_2 dielectric and Ge substrate due to the formation of GeO_x and defective HfGeO_x . The reduction of accumulation capacitance is understood by considering the formation of this low- k GeO_x (~ 5) [13, 14]. With YON IPL inserted for the YON sample, the stretch out and distortion of C - V curve is reduced significantly, indicating much improvement of the interface quality. This is attributed to the formation of stable YGeO_xN_y IPL in the interface, which could effectively suppress the formation of GeO_x and HfGeO_x , and introduce the so-called “valency passivation” [8]. Furthermore, the YN sample exhibits even better C - V behavior than the YON sample, which has smaller stretch out and eliminated distortion in the weak inversion region. As a result, the YON IPL of YN sample could improve the interface quality more effectively. Both of the three samples exhibit positive flat-band voltage (V_{fb}), due to the negative oxide-charge density (Q_{ox}) caused by the diffusion of Ge (or GeO_x) into the HfO_2 dielectric [15]. The YN sample exhibits the smallest V_{fb} , indicating the most effective suppression of the diffusion of Ge (or GeO_x).

The typical gate leakage properties of the samples are shown in the inset of figure 2. Due to the poor interface quality, large Q_{ox} and reduced conduction-band offset caused by the formation of Ge oxides [16], the control sample without IPL exhibits the largest gate leakage current. With YON IPL inserted, the gate leakage current is greatly reduced for the YON sample. Moreover, the YN sample achieves the smallest gate leakage current due to its best interface quality and smallest Q_{ox} .

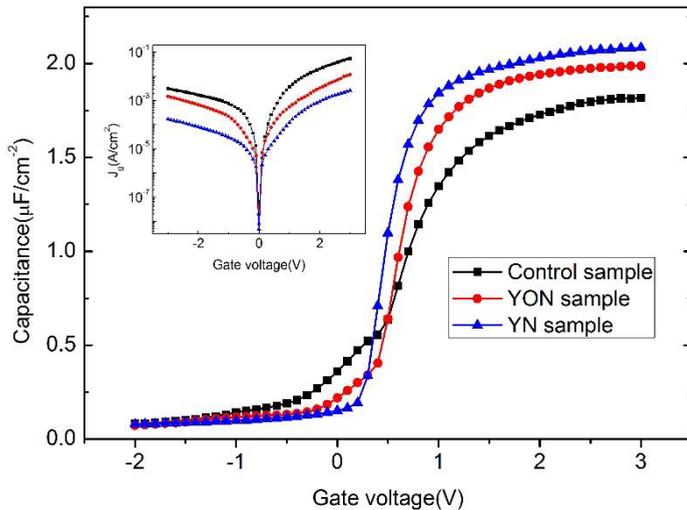


Figure 2. High-frequency (1-MHz) C - V curves of the three samples. The inset shows the J_g - V_g curves of the three samples.

The frequency dispersion of C - V curves for the three samples is measured and shown in figure 3 to further compare the interface quality of the samples. The dispersive behavior of C - V curves from depletion to accumulation region and from weak to strong inversion region is attributed to the interface traps near the Ge valance band and conduction band, respectively [17]. Obviously, the control sample without IPL exhibits the largest frequency dispersion in both regions, implying a poor interface quality. With IPL inserted, much smaller frequency dispersion has been obtained. Moreover, the YN sample exhibits the smallest frequency dispersion, indicating the best interface quality.

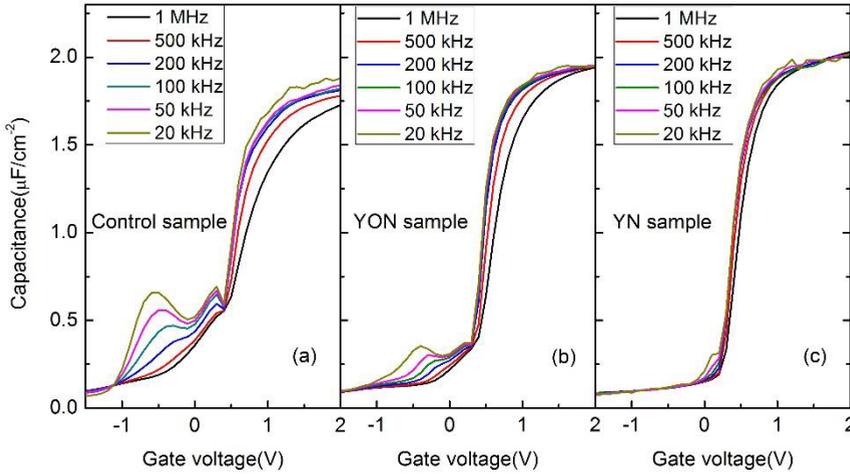


Figure 3. Frequency dispersion of C - V curves: (a) control sample, (b) YON sample and (c) YN sample

In order to analyse the reason for the different electrical and interfacial properties of the samples, XPS analysis is used to investigate the composition and chemical states of the interface. The energy scale is calibrated by fixing the Ge $3d$ peak of Ge substrate at a binding energy (BE) of 29.4 eV to eliminate the charging effect of samples [18]. Ge $2p_{3/2}$ core level spectra for the samples are shown in figure 4 (a) - (c). For the control sample, large GeO_x and HfGeO_x peaks in figure 4 (a) indicate the formation of Ge sub-oxide and HfGeO_x in the interface respectively, both of which will degrade the interface quality and cause poor electrical properties. With YON IPL inserted for the YON and YN samples, the defective HfGeO_x is replaced by stable YGeO_xN_y , which could significantly suppress the formation of Ge oxide and thus less GeO_x is observed in figure 4(b) and (c). Compared to the YN sample, there is still an amount of GeO_x in the interface for the YON sample, which is 11.33% described as the GeO_x/Ge -Sub peak-area ratio. This may be formed during the formation of YGeO_xN_y , due to the oxidation of Ge surface by the in-diffused O [4]. The YN sample exhibits much less GeO_x (1.5%) than the YON sample, due to the absorption of in-diffused O by YN IPL prior to Ge substrate, which could effectively suppress the diffusion of O to the Ge surface and thus the formation of Ge oxide. The defective GeO_x is known to be an obstacle to improve the interface quality of Ge substrate. Therefore, the YN sample with the least GeO_x leads to the best interface quality and consequently exhibits the best electrical properties.

To further verify the conclusion above, O $1s$ core level spectra for the samples are also shown in figure 4 (d) - (f). The peak with the BE of 529.5 eV is attributed to the O-Hf bond, which corresponds to the HfO_2 dielectric. The peak of Ge-O-Hf, Ge-O-Y and O-Ge indicates the formation of HfGeO_x , YGeO_xN_y and Ge oxide in the interface, respectively. The amount of Ge oxide for the control, YON and YN samples, described as the O-Ge/O $1s$ peak-area ratio, is 20.9%, 13.1% and 4.6% respectively. This indicates that the YON IPL could effectively suppress the formation of Ge oxide and the YN sample exhibits better efficiency than the YON sample, which is consistent with the result from Ge $2p_{3/2}$ XPS spectra.

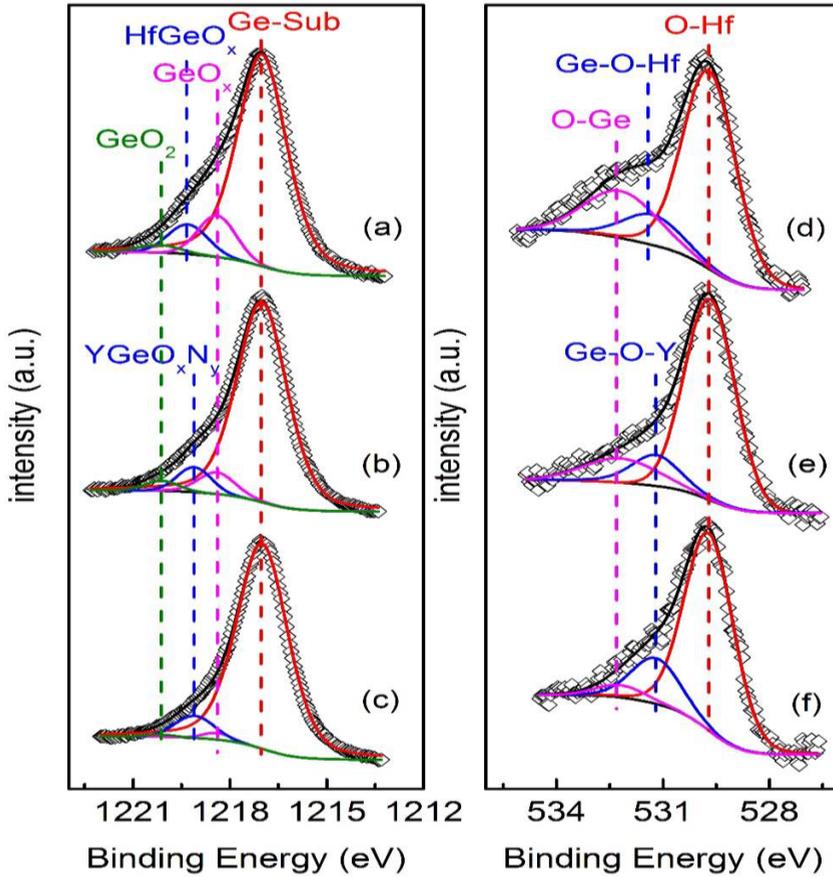


Figure 4. Ge $2p_{3/2}$ XPS spectrum: (a) control sample, (b) YON sample and (c) YN sample, and O $1s$ XPS spectrum: (d) control sample, (e) YON sample and (f) YN sample

The AFM is used to check the HfO_2 surface morphology of the samples, as shown in figure 5. The control sample exhibits rough surface with a large root mean square (rms) roughness of 0.467nm, due to the poor interface and formation of GeO_x , which could diffuse into the HfO_2 dielectric and worsen the film property. With YON IPL inserted, the improved interface quality and suppressed formation of GeO_x lead to a smoother surface for both the YON and YN samples. Moreover, the rms roughness of YN sample is 0.158 nm, which is smaller than that of the YON sample (0.233nm). This is attributed to the more effective suppression of the formation of GeO_x for the YN sample, as confirmed by the XPS analysis.

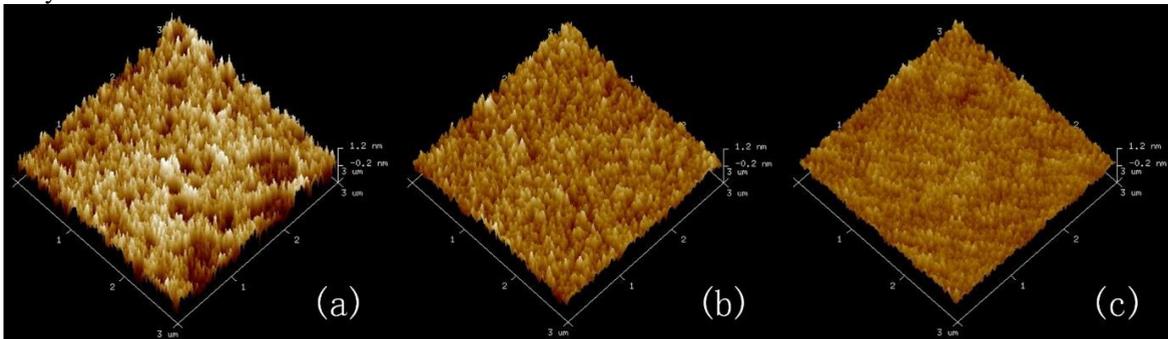


Figure 5. AFM image: (a) control sample, (b) YON sample and (c) YN sample

4 Conclusion

With YON IPL inserted between HfO_2 dielectric and Ge substrate, much improvement of the interface quality could be obtained. Compared to the YON IPL fabricated by sputtering Y_2O_3 target in $\text{Ar}+\text{N}_2$, the YON IPL, which is fabricated by sputtering Y target in $\text{Ar}+\text{N}_2$ to deposit YN first followed by annealing in N_2+O_2 to convert YN to YON, could suppress the formation of Ge oxide in the interface more efficiently to achieve more excellent interfacial and electrical properties.

Acknowledgments

This work is financially supported by the National Natural Science Foundation of China (Grant No. 61274112, 61176100, 61404055).

References

- [1] Iwai H 2015 *Solid State Electron.* **112** 56-67
- [2] Takagi S, Kim S H, Yokoyama M, Zhang R, Taoka N, Urabe Y, Yasuda T, Yamada H, Ichikawa O, Fukuhara N, Hata M, Takenaka M 2013 *Solid State Electron.* **88** 2-8
- [3] Kamata Y 2008 *Mater. Today* **11** 30-38
- [4] Jung H, Yu I, Kim H K, Lee S Y, Lee J, Choi Y, Chung Y J, Lee N, Park T J, Choi J, Hwang C S 2012 *IEEE T. Electron Dev.* **59** 2350-2356
- [5] Houssa M, Pourtois G, Caymax M, Meuris M, Heyns M M 2008 *Appl. Phys. Lett.* **92** 242101
- [6] Li C X, Lai P T 2009 *Appl. Phys. Lett.* **95** 22910
- [7] Chu L K, Lee W C, Huang M L, Chang Y H, Tung L T, Chang C C, Lee Y J, Kwo J, Hong M 2009 *J. Cryst. Growth* **311** 2195-2198
- [8] Wu M, Wu Y, Lyu R, Chao C, Wu C, Lin C, Chen L 2013 *Microelectron. Eng.* **109** 216-219
- [9] Rouffignac P D, Park J S, Gordon R G 2005 *Chem. Mater.* **17** 4808-4814
- [10] Rastogi A C, Sharma R N 1992 *J. Appl. Phys.* **71** 5041
- [11] Liu Z, Liang L, Yu Z, He S, Ye X 2011 *Journal of Physics D Applied Physics* **44** 155403
- [12] Bethge O, Zimmermann C, Lutzer B, Simsek S, Smoliner J, Stöger-Pollach M, Henkel C, Bertagnolli E 2014 *J. Appl. Phys.* **116** 214111
- [13] Murad S N A, Baine P T, Mcneill D W, Mitchell S J N, Armstrong B M, Modreanu M, Hughes G, Chellappan R K 2012 *Solid State Electron.* **78** 136-140
- [14] Zhang R, Iwasaki T, Taoka N, Takenaka M, Takagi S 2011 *Microelectron. Eng.* **88** 1533-1536
- [15] Sun Q Q, Shi Y, Dong L, Liu H, Ding S J, Zhang D W 2008 *Appl. Phys. Lett.* **92** 102908
- [16] Li X F, Liu X J, Cao Y Q, Li A D, Li H, Wu D 2013 *Appl. Surf. Sci.* **264** 783-786
- [17] Zhang L L, Li H L, Guo Y Z, Tang K C, Woicik J, Robertson J, McIntyre P C 2015 *ACS Appl. Mater. Inter.* **7** 1173044747
- [18] Dimoulas A, Tsoutsou D, Panayiotatos Y, Sotiropoulos A, Mavrou G, Galata S F, Golias E 2010 *Appl. Phys. Lett.* **96** 12902