

Investigation on the dominant key to achieve superior Ge surface passivation by GeO_x based on the ozone oxidation

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Abstract—The dominant key to achieve superior Ge surface passivation by GeO_x interfacial layer is investigated based on ozone oxidation. The interface state density (D_{it}) measured from low temperature conduction method is found to decrease with increasing the GeO_x thickness (0.26-1.06 nm). The X-ray photoelectron spectroscopy (XPS) is employed to demonstrate the interfacial structure of GeO_x/Ge with different GeO_x thicknesses. And the XPS results show that Ge³⁺ oxide component is responsible to the decrease of the D_{it} due to the effective passivation of Ge dangling bonds. Therefore, the formation of Ge³⁺ component is the dominant key to achieve low D_{it} for Ge gate stacks. Our work confirms that the same physical mechanism determines the Ge surface passivation by the GeO_x regardless of the oxidation methods to grow the GeO_x interfacial layer. As a result, to explore a growth process that can realize sufficient Ge³⁺ component in the GeO_x interlayer as thin as possible is important to achieve both equivalent oxide thickness scaling and superior interfacial property simultaneously. This conclusion is helpful to engineer the optimization of the Ge gate stacks.

Keywords—Ge; MOS; XPS; interface trap density; passivation

I. INTRODUCTION

Ge channel is a rather potential booster for the future high performance metal-oxide-semiconductor field-effect-transistor (MOSFET) owing to its high carrier mobility [1]. A high quality Ge MOS gate stacks with low interface state density (D_{it}) is imperative for the successful industrial application [2]. After about 15 years' intensive studies [3-5], it has been demonstrated that Ge dioxide or sub-oxide (GeO_x) can provide excellent electrical properties with the D_{it} in the range of 10^{10} - 10^{11} cm⁻²·eV⁻¹ [6-17]. And the GeO_x can be grown by thermal oxidation in atmospheric pressure O₂ [6; 7], high pressure O₂ (~70 atm) [13; 14], oxygen plasma [9-12; 17], or ozone oxidation [8; 15; 16]. Zhang *et al.* [18] demonstrated that by using the electron cyclotron resonance oxygen plasma post oxidation method, the equivalent oxide thickness (EOT) of the HfO₂/Al₂O₃/GeO_x/Ge gate stacks can be scaled down to 0.7-0.8 nm with maintaining the D_{it} in the

level of 10^{11} cm⁻²·eV⁻¹. Simultaneously, the peak mobilities are 546 and 689 cm²/V·s for the holes and electrons, respectively. Lee *et al.* [19] reported the postoxidation of Y₂O₃/Ge structure in high pressure O₂ of ~70 atm at 500 °C. The EOT of 0.94 nm and D_{it} in the level of 10^{11} cm⁻²·eV⁻¹ are obtained with the peak electron mobility of 787 cm²/V·s. In order to further improve the performance of Ge MOSFET, the EOT should be continually scaling down to about 0.5 nm while maintaining the low D_{it} [20]. Decreasing the GeO_x thickness is an effective method due to its relatively low permittivity. However, it is found that the D_{it} increases with decreasing the GeO_x thickness [8; 17; 18; 20; 21]. Zhang *et al.* [18; 20; 21] observed that the D_{it} at 0.2 eV below the intrinsic level in Ge increases from 1.7 to 8×10^{11} cm⁻²·eV⁻¹ with decreasing the GeO_x thickness from 1.2 to 0.23 nm [21]. Furthermore, Shibayama *et al.* [2] found that this dependence of the D_{it} on the GeO_x thickness can be attributed to the amount of the Ge³⁺ oxide component at the interface. It should be noted that this GeO_x thickness dependence of the D_{it} is experimentally obtained based on the plasma oxidation [17; 18; 20; 21], or post thermal oxidation in the O₂ [2]. In addition, Kuzum *et al.* [8] reported that increasing GeO_x thickness was beneficial to the D_{it} decrease based on the ozone oxidation, and they considered that the Ge⁴⁺ oxide component played a dominant role in the D_{it} passivation. Therefore, the similar experimental results of the D_{it} dependence on the GeO_x thickness are observed for the plasma oxidation, thermal oxidation in O₂ and the ozone oxidation, but the passivation mechanisms of the three oxidation methods seem inconsistent, especially for the ozone oxidation. As a result, the passivation mechanism of GeO_x on the Ge surface needs further investigation. Especially the ozone oxidation needs further and systematic investigations to clarify whether its passivation mechanism is the same as the plasma or thermal O₂ oxidation. The ozone oxidation method is fascinating because it can grow the GeO_x at low temperature (~300 °C) to avoid the GeO_x desorption above ~420 °C [22-24]. In addition, in order to further improve interface properties of GeO_x/Ge interface, it is quite important to clarify the dominant factor determining

the interface properties. Therefore, the comprehensive understandings of the passivation mechanism by the GeO_x interfacial layer and the relationship between interface structure and electrical properties are necessary. In this paper, the passivation mechanism and dominant key of the Ge surface passivation by the GeO_x is systematically investigated by the ozone oxidation method. It is experimentally found that the D_{it} decreases with increasing the GeO_x thickness. The X-ray photoelectron spectroscopy (XPS) characterization shows that the Ge^{3+} is the dominant factor in determining the electrical properties at the GeO_x/Ge interface. Our work indicates that no matter of the oxidation methods to grow the GeO_x interfacial layer the same physical mechanism determines the Ge surface passivation by the GeO_x .

II. EXPERIMENTAL

The Ge based MOS capacitors were fabricated as follows. The starting substrate is 2 μm thick p-doped (100) epitaxial Ge on 8 inch p-doped (100) Si. After the cleaning of Ge surface by 100:1 $\text{H}_2\text{O}:\text{HF}$ for 60 s, the wafers were immediately capped with low temperature oxide SiO_2 . Then active areas were partially opened by lithography-defined wet chemical etching, and the exposed Ge surface was again dipped in 100:1 $\text{H}_2\text{O}:\text{HF}$ for 60 s. After that the Ge surface was immediately subjected to O_3 surface passivation at 300 $^\circ\text{C}$ to form GeO_x . The O_3 oxidation time was varied in order to modulate the thickness of the GeO_x interlayer. Subsequently, 10 nm Al_2O_3 was deposited by atomic layer deposition (ALD) using Trimethylaluminum (TMA) and H_2O as precursors at 300 $^\circ\text{C}$. Then post deposition annealing (PDA) was performed at 400 $^\circ\text{C}$ in N_2 for 5 min, followed by the deposition of the metal gate of 3 nm TiN and 75 nm W by the ALD. After that the metal gate was patterned by lithography-defined dry etching. Then Al electrode was sputtered as backside contact. Finally the wafers were subjected to the forming gas annealing at 400 $^\circ\text{C}$ in 5% $\text{H}_2/95\%$ N_2 for 30 min. The capacitance-voltage (C-V) characteristics were measured by Agilent semiconductor parameter analyzers. The angle resolved X-ray photoelectron spectroscopy (XPS) were recorded using Thermo Scientific ESCALAB 250xi equipped with a monochromatic Al $K\alpha$ radiation source. All the high resolution spectra were collected with pass energy of 15 eV.

III. RESULTS AND DISCUSSION

The electrical properties of the ozone oxidation W/TiN/ Al_2O_3 / GeO_x /Ge gate stacks are examined by using MOS capacitors. Figure 1 shows the C-V curves of W/TiN/ Al_2O_3 / GeO_x /Ge MOS capacitor at room temperature, which has a 1.06 nm thick GeO_x . The thickness of GeO_x is evaluated from the corresponding XPS spectrum. The superior C-V characteristics are observed. The kink at the depletion region is attributed to the minority carrier response associated with the small band gap and high intrinsic carrier density of Ge [25; 26]. The conduction method at low temperature was employed to quantitatively evaluate the D_{it} at GeO_x/Ge interface. The energy distributions of the D_{it} with different GeO_x thickness are shown in the inset of Fig. 2. It is

clearly observed that the D_{it} decreases with increasing the GeO_x thickness. The lowest D_{it} detected in the experiments decreases from 6.25×10^{11} to $2.06 \times 10^{11} \text{ cm}^{-2} \cdot \text{eV}^{-1}$ when the GeO_x thickness increases from 0.26 to 1.06 nm. The D_{it} at 0.3 eV above the valence band maximum (E_v) are compared as a function of the GeO_x thickness in the Fig. 2. It can be found that, with the GeO_x thicker than ~ 0.6 nm, the D_{it} varies very slowly as a function of the GeO_x thickness and reaches a saturation value of $\sim 3 \times 10^{11} \text{ cm}^{-2} \cdot \text{eV}^{-1}$. On the other hand, when the GeO_x is thinner than ~ 0.6 nm, the GeO_x/Ge interfacial property encounters a drastic degradation with decreasing the GeO_x thickness. These results indicate that the interfacial property at GeO_x/Ge interface is dependent on the GeO_x thickness, and the 0.6 nm thick GeO_x is necessary to realize fine passivation of the Ge surface. As a result, considering the similar results from plasma oxidation and thermal O_2 oxidation [2; 18; 20; 21], it is reasonable to conclude that the same passivation mechanism by the GeO_x appears regardless of the oxidation method such as plasma, thermal O_2 or O_3 oxidation.

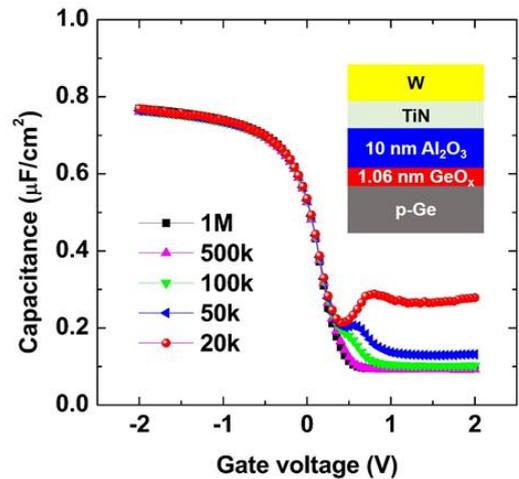


FIG. 1. C-V characteristic of the W/TiN/ Al_2O_3 / GeO_x /Ge MOS capacitor with 1.06 nm thick GeO_x . The inset figure is a schematic of the W/TiN/ Al_2O_3 / GeO_x /Ge MOS capacitor.

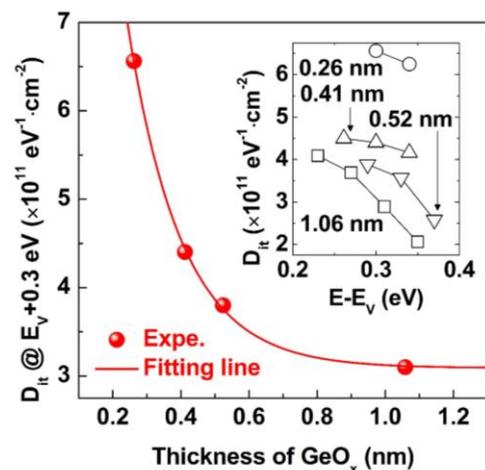


FIG. 2. The D_{it} values at 0.3 eV above the E_v and the energy distributions of the D_{it} (inset figure) of the

W/TiN/Al₂O₃/GeO_x/Ge MOS capacitors with different GeO_x thicknesses.

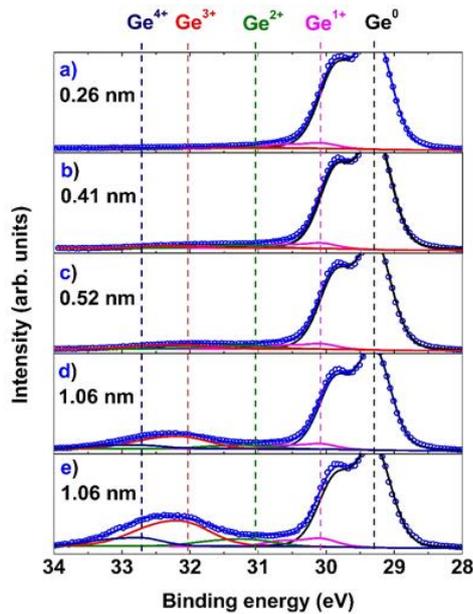


FIG. 3. The XPS spectra of Ge 3d for 1 nm Al₂O₃/GeO_x/Ge structure with different GeO_x thicknesses. The thickness of the GeO_x is shown in the figures. The takeoff angle in the Fig. 3(a)-(d) is 90° (normal to the sample surface) while that is 35° in the Fig. 3(e). The Ge 3d line shape is used for the peak fitting and the Ge3d_{5/2-3/2} doublets are not distinguished in the spectrum deconvolution. The Ge⁰, Ge¹⁺, Ge²⁺, Ge³⁺ and Ge⁴⁺ shown in the figure mean the binding energies of the Ge 3d_{5/2} core level for each chemical state.

In order to physically understand this GeO_x thickness dependence of the D_{it} passivation, the XPS technique is employed to characterize the chemical states and composition of each electronic state at the GeO_x/Ge interface. Fig. 3 shows the Ge 3d spectra of Al₂O₃/GeO_x/Ge structure with different GeO_x thicknesses. It is observed that the peak corresponding to the GeO_x increases with thicker GeO_x, and the GeO_x peak energy shifts toward higher binding energy, suggesting that the oxidation state of Ge and the GeO_x/Ge interfacial structure are dependent on the GeO_x thickness. In order to quantitatively evaluate each oxidation state of the Ge, the Ge 3d spectra are divided by 5 peaks related to Ge substrate (Ge⁰), Ge suboxide (Ge¹⁺, Ge²⁺, Ge³⁺) and GeO₂ (Ge⁴⁺) components as shown in the Fig. 3. It should be noted that the Ge 3d line shape but not the Ge 3d_{5/2} and Ge 3d_{3/2} doublets for each Ge chemical state is shown in the Fig. 3. And the chemical shifts of Ge¹⁺, Ge²⁺, Ge³⁺ and Ge⁴⁺ relative to the Ge⁰ are taken as 0.8, 1.8, 2.75 and 3.4 eV, respectively [27-30]. In addition, the chemical shift of Ge⁴⁺ relative to the Ge⁰ is also confirmed to be 3.4 eV by thicker GeO₂ of ~8.2 nm (not shown here), which is prepared by thermal oxidation in 1 atm O₂ at 550 °C. It should be noted that the thicker GeO₂ is grown by thermal oxidation in O₂ at 550 °C but not in O₃ at 300 °C. This is because the GeO_x thicker than 1.06 nm is experimentally found not to be obtained by using O₃

oxidation at 300 °C. The full width at half maximum (FWHM) of the Ge oxide component (0.84 eV for Ge²⁺, 0.89 eV for Ge³⁺ and Ge⁴⁺) increases compared with that of Ge⁰ component (0.57 eV), which is due to the broadening of the Ge 3d photoemission peaks arising from static disorder in the amorphous GeO_x. In addition, the symmetric Gaussian-Lorentzian sum function was used in the peak fitting and the optimized %Gaussian-Lorentzian was found to be 18%.

The issue of Ge atom diffusion into the Al₂O₃ layer is discussed as follows. We consider that the Ge atom diffusion into the Al₂O₃ layer is little or negligible in our experiment. This is because the highest process temperature in our experiment is 400 °C. This temperature of 400 °C is below the GeO_x desorption temperature of ~420 °C. In addition, Shibayama *et al.* [31] found that after a thermal oxidation of Al₂O₃/Ge structure in O₂ at 550 °C, the Ge atoms diffused into the Al₂O₃ film. However, there was no Ge diffusion at 400 °C thermal annealing. As a result, it is reasonable to conclude that the Ge atom diffusion into the Al₂O₃ layer is negligible and consequently not considered. Furthermore, we analyze the Al 2p spectra of the four experimental examples to investigate the Ge diffusion into the Al₂O₃ (not shown here). Based on the peak fitting, it was found all the Al 2p spectra can be fitted with only one chemical state, and the full width at half maximums (FWHM) for the four examples are all 1.47 eV. On the other hand, from the Ge 3d spectrum in the Fig. 3(a), it can be obtained that the GeO_x thickness is only 0.26 nm, which is less than the thickness 0.32 nm of one monolayer Ge-O-Ge [29]. In addition, there is rather negligible signals from Ge³⁺ chemical state in Fig. 3(a). Thus it can be concluded that the Al₂O₃/Ge interface is nearly abrupt and there is no diffusion of Ge atoms into the Al₂O₃. Considering the same FWHM of the Al 2p spectra for the four examples, it can be obtained that the Al chemical states are same for the four examples, i.e., they are both Al₂O₃ without AlGeO_x. As a result, based on the above analysis, we are inclined to consider that the Ge atom diffusion into the Al₂O₃ layer is negligible and consequently not considered.

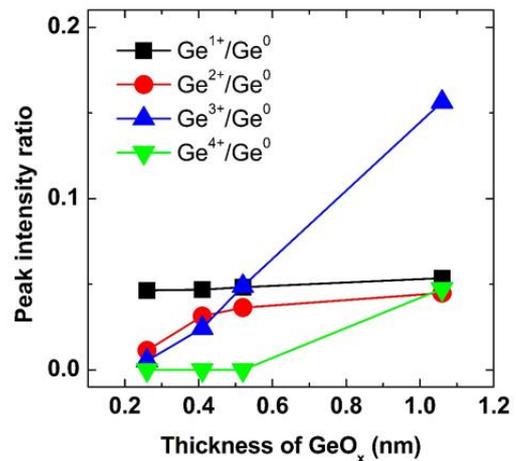


FIG. 4. Area intensity ratios of Ge oxide components (Ge¹⁺, Ge²⁺, Ge³⁺ and Ge⁴⁺) to Ge⁰ component as a function of the GeO_x thickness.

Figure 4 gives the peak area intensity ratios of Ge¹⁺, Ge²⁺, Ge³⁺ and Ge⁴⁺ components to the Ge⁰ component as a

function of the GeO_x thickness. It can be seen that the area intensity ratio of the Ge^{1+} component is nearly unchanged for different GeO_x thicknesses, indicating that the Ge^{1+} component is not responsible for the dependence of the D_{it} on GeO_x thickness. The Ge^{4+} component is not detected by the XPS for the GeO_x thickness of less than 0.52 nm. However there is a significant dependence of the D_{it} on GeO_x thickness in this region. Therefore the Ge^{4+} component can be ruled out. Similarly the Ge^{2+} component changes very slowly for the GeO_x thickness of larger than 0.41 nm, thus it is reasonable to conclude that the Ge^{2+} component plays a negligible role in passivating the D_{it} . From the Fig. 4 it can be clearly observed that the Ge^{3+} component increases significantly with increasing the GeO_x thickness. In other words, the D_{it} decreases with the increment of Ge^{3+} component, suggesting that the Ge^{3+} formation is responsible to the D_{it} passivation. This conclusion based on the ozone oxidation is consistent with some reports based on the thermal O_2 oxidation or plasma oxidation [2; 18; 20; 21]. As a result, the passivation mechanism by GeO_x interlayer is the same regardless of the growth method of GeO_x . Based on the above results, the passivation mechanism by Ge^{3+} component can be understood as follows. Due to the mismatch between the Ge substrate and GeO_2 structure, a transition layer composed of Ge^{1+} , Ge^{2+} and Ge^{3+} components is necessary. Considering that the dangling bonds are the physical origin of the D_{it} in the Ge gate stacks [34-37], the occurrence of the Ge^{3+} component is beneficial to decrease the Gibbs free energy of the transition layer and to passivate the dangling bonds of Ge.

IV. CONCLUSIONS

In summary, the passivation of Ge surface by GeO_x is investigated based on the ozone oxidation. It is experimentally found that the GeO_x thicker than 0.6 nm is necessary to achieve fine Ge passivation. And for the GeO_x thickness thinner than 0.6 nm, the interfacial property degrades dramatically with decreasing the interfacial GeO_x thickness. These results suggest the trade-off relationship between the EOT scaling and the interfacial quality. This conclusion is verified regardless of the grow method such as plasmas, thermal O_2 or ozone oxidation. Therefore it can be concluded that the passivation mechanism of Ge surface by GeO_x interlayer is the same for different GeO_x growth method. Furthermore, the D_{it} at GeO_x/Ge interface is clarified to decrease with increasing the amount of Ge^{3+} state, due to the effective passivation of the Ge dangling bond by Ge^{3+} component. This indicates that the Ge^{3+} component is the dominant key to achieve superior Ge surface passivation. As a result, to explore a growth process that can realize sufficient Ge^{3+} component in the GeO_x interlayer as thin as possible is important to achieve both EOT scaling and superior interfacial property simultaneously. This conclusion is helpful to the optimization of the Ge based gate stacks for future CMOSFET.

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