Investigation on the dominant key to achieve superior Ge surface passivation by GeO\textsubscript{x} based on the ozone oxidation

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Abstract—The dominant key to achieve superior Ge surface passivation by GeO\textsubscript{x} interfacial layer is investigated based on ozone oxidation. The interface state density (D\textsubscript{i}) measured from low temperature conduction method is found to decrease with increasing the GeO\textsubscript{x} thickness (0.26-1.06 nm). The X-ray photoelectron spectroscopy (XPS) is employed to demonstrate the interfacial structure of GeO\textsubscript{x}/Ge with different GeO\textsubscript{x} thicknesses. And the XPS results show that Ge\textsuperscript{3+} oxide component is responsible to the decrease of the D\textsubscript{i} due to the effective passivation of Ge dangling bonds. Therefore, the formation of Ge\textsuperscript{3+} oxide component is the dominant key to achieve low D\textsubscript{i} for Ge gate stacks. Our work confirms that the same physical mechanism determines the Ge surface passivation by the GeO\textsubscript{x}, regardless of the oxidation methods to grow the GeO\textsubscript{x} interfacial layer. As a result, to explore a growth process that can realize sufficient Ge\textsuperscript{3+} component in the GeO\textsubscript{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\textsubscript{i}) 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\textsubscript{x}) can provide excellent electrical properties with the D\textsubscript{i} in the range of 10\textsuperscript{10}-10\textsuperscript{11} cm\textsuperscript{-2} eV\textsuperscript{-1} [6-17]. And the GeO\textsubscript{x} can be grown by thermal oxidation in atmospheric pressure O\textsubscript{2} [6; 7], high pressure O\textsubscript{2} (~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 HfO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3}/GeO\textsubscript{x}/Ge gate stacks can be scaled down to 0.7-0.8 nm with maintaining the D\textsubscript{i} in the level of 10\textsuperscript{11} cm\textsuperscript{-2} eV\textsuperscript{-1}. Simultaneously, the peak mobilities are 546 and 689 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1} for the holes and electrons, respectively. Lee et al. [19] reported the postoxidation of Y\textsubscript{2}O\textsubscript{3}/Ge structure in high pressure O\textsubscript{2} of ~70 atm at 500 °C. The EOT of 0.94 nm and D\textsubscript{i} in the level of 10\textsuperscript{11} cm\textsuperscript{-2} eV\textsuperscript{-1} are obtained with the peak electron mobility of 787 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1}. 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\textsubscript{i} [20]. Decreasing the GeO\textsubscript{x} thickness is an effective method due to its relatively low permittivity. However, it is found that the D\textsubscript{i} increases with decreasing the GeO\textsubscript{x} thickness [8; 17; 18; 20; 21]. Zhang et al. [18; 20; 21] observed that the D\textsubscript{i} at 0.2 eV below the intrinsic level in Ge increases from 1.7 to 8×10\textsuperscript{11} cm\textsuperscript{-2} eV\textsuperscript{-1} with decreasing the GeO\textsubscript{x} thickness from 1.2 to 0.23 nm [21]. Furthermore, Shibayama et al. [2] found that this dependence of the D\textsubscript{i} on the GeO\textsubscript{x} thickness can be attributed to the amount of the Ge\textsuperscript{3+} oxide component at the interface. It should be noted that this GeO\textsubscript{x} thickness dependence of the D\textsubscript{i} is experimentally obtained based on the plasma oxidation [17; 18; 20; 21], or post thermal oxidation in the O\textsubscript{2} [2]. In addition, Kuzum et al. [8] reported that increasing GeO\textsubscript{x} thickness was beneficial to the D\textsubscript{i} decrease based on the ozone oxidation, and they considered that the Ge\textsuperscript{4+} oxide component played a dominant role in the D\textsubscript{i} passivation. Therefore, the similar experimental results of the D\textsubscript{i} dependence on the GeO\textsubscript{x} thickness are observed for the plasma oxidation, thermal oxidation in O\textsubscript{2} 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\textsubscript{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 O\textsubscript{2} oxidation. The ozone oxidation method is fascinating because it can grow the GeO\textsubscript{x} at low temperature (~300 °C) to avoid the GeO\textsubscript{x} desorption above ~420 °C [22-24]. In addition, in order to further improve interface properties of GeO\textsubscript{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_n 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 \textmu m thick p-doped (100) epitaxial Ge on 8 inch p-doped (100) Si. After the cleaning of Ge surface by 100:1 H_2O:HF for 60 s, the wafers were immediately capped with low temperature oxide SiO_x. Then active areas were partially opened by lithography-defined wet chemical etching, and the exposed Ge surface was again dipped in 100:1 H_2O:HF for 60 s. After that the Ge surface was immediately subjected to O_3 surface passivation at 300 °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 °C. Then post deposition annealing (PDA) was performed at 400 °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 °C in 5% 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 Kα 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_n at GeO_x/Ge interface. The energy distributions of the D_n with different GeO_x thickness are shown in the inset of Fig. 2. It is clearly observed that the D_n decreases with increasing the GeO_x thickness. The lowest D_n detected in the experiments decreases from 6.25×10^{11} to 2.06×10^{10} cm^{-2} eV^{-1} when the GeO_x thickness increases from 0.26 to 1.06 nm. The D_n 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_n varies very slowly as a function of the GeO_x thickness and reaches a saturation value of ~3×10^{11} cm^{-2} 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.](image1)

![FIG. 2. The D_n values at 0.3 eV above the E_v and the energy distributions of the D_n (inset figure) of the](image2)
W/TiN/Al$_2$O$_3$/GeO$_x$/Ge MOS capacitors with different GeO$_x$ thicknesses.

![Figure 3](image_url)

**FIG. 3.** The XPS spectra of Ge 3d for 1 nm Al$_2$O$_3$/GeO$_x$/Ge structure with different GeO$_x$ thicknesses. The thickness of the GeO$_x$ is shown in the figures. The takeoff angel 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$_{3/2-3/2}$ doublets are not distinguished in the spectrum deconvolution. The Ge$^{2+}$, Ge$^{3+}$, Ge$^{4+}$ and Ge$^{5+}$ shown in the figure mean the binding energies of the Ge 3d$_{3/2}$ core level for each chemical state.

In order to physically understand this GeO$_x$ thickness dependence of the D$_2$ 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 Al$_2$O$_3$/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 Ge, the Ge 3d spectra are divided by 5 peaks related to Ge substrate (Ge$^0$), Ge suboxide (Ge$^{1+}$, Ge$^{2+}$, Ge$^{3+}$) and GeO$_x$ (Ge$^{4+}$) components as shown in the Fig. 3. It should be noted that the Ge 3d line shape but not the Ge 3d$_{3/2}$ and Ge 3d$_{5/2}$ doublets for each Ge chemical state is shown in the Fig. 3. And the chemical shifts of Ge$^{1+}$, Ge$^{2+}$, Ge$^{3+}$ and Ge$^{4+}$ relative to the Ge$^0$ are taken as 0.8, 1.8, 2.75 and 3.4 eV, respectively [27-30]. In addition, the chemical shift of Ge$^{4+}$ relative to the Ge$^0$ is also confirmed to be 3.4 eV by thicker GeO$_x$ of ~8.2 nm (not shown here), which is prepared by thermal oxidation in 1 atm O$_2$ at 550 °C. It should be noted that the thicker GeO$_x$ is grown by thermal oxidation in O$_2$ at 550 °C but not in O$_3$ at 300 °C. This is because the GeO$_x$ thicker than 1.06 nm is experimentally found not to be obtained by using O$_3$ oxidation at 300 °C. The full with at half maximum (FWHM) of the Ge oxide component (0.84 eV for Ge$^{2+}$, 0.89 eV for Ge$^{3+}$ and Ge$^{4+}$) increases compared with that of Ge$^0$ 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 Al$_2$O$_3$ layer is discussed as follows. We consider that the Ge atom diffusion into the Al$_2$O$_3$ 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 Al$_2$O$_3$/Ge structure in O$_2$ at 550 °C, the Ge atoms diffused into the Al$_2$O$_3$ 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 Al$_2$O$_3$ 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 Al$_2$O$_3$ (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 with 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 of 0.32 nm of one monolayer Ge-O-Ge [29]. In addition, there is rather negligible signals from Ge$^{2+}$, Ge$^{3+}$ chemical state in Fig. 3(a). Thus it can be concluded that the Al$_2$O$_3$/Ge interface is nearly abrupt and there is no diffusion of Ge atoms into the Al$_2$O$_3$. 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 Al$^{2+}$ without AlGeO$_x$. As a result, based on the above analysis, we are inclined to consider that the Ge atom diffusion into the Al$_2$O$_3$ layer is negligible and consequently not considered.

![Figure 4](image_url)

**FIG. 4.** Area intensity ratios of Ge oxide components (Ge$^{1+}$, Ge$^{2+}$, Ge$^{3+}$ and Ge$^{4+}$) to Ge$^0$ component as a function of the GeO$_x$ thickness.

Figure 4 gives the peak area intensity ratios of Ge$^{1+}$, Ge$^{2+}$, Ge$^{3+}$ and Ge$^{4+}$ components to the Ge$^0$ component as a...
function of the GeOx thickness. It can be seen that the area intensity ratio of the Ge³⁺ component is nearly unchanged for different GeOx thicknesses, indicating that the Ge³⁺ component is not responsible for the dependence of the D₈ on GeOx thickness. The Ge⁴⁺ component is not detected by the XPS for the GeOx thickness of less than 0.52 nm. However, there is a significant dependence of the D₈ on GeOx thickness in this region. Therefore the Ge⁴⁺ component can be ruled out. Similarly the Ge²⁺ component changes very slowly for the GeOₓ thickness of larger than 0.41 nm, thus it is reasonable to conclude that the Ge³⁺ component plays a negligible role in passivating the D₈. From the Fig. 4 it can be clearly observed that the Ge³⁺ component increases significantly with increasing the GeOₓ thickness. In other words, the D₈ decreases with the increment of Ge³⁺ component, suggesting that the Ge³⁺ formation is responsible to the D₈ passivation. This conclusion based on the ozone oxidation is consistent with some reports based on the thermal O₂ oxidation or plasma oxidation [2; 18; 20; 21]. As a result, the passivation mechanism by GeOₓ interlayer is the same regardless of the growth method of GeOₓ. Based on the above results, the passivation mechanism by Ge³⁺ component can be understood as follows. Due to the mismatch between the Ge substrate and GeO₂ structure, a transition layer composed of Ge¹⁺, Ge²⁺ and Ge³⁺ components is necessary. Considering that the dangling bonds are the physical origin of the D₈ in the Ge gate stacks [34-37], the occurrence of the Ge³⁺ 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 GeOₓ is investigated based on the ozone oxidation. It is experimentally found that the GeOₓ thicker than 0.6 nm is necessary to achieve fine Ge passivation. And for the GeOₓ thickness thinner than 0.6 nm, the interfacial property degrades dramatically with decreasing the interfacial GeOₓ 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 plasms, thermal O₂ or ozone oxidation. Therefore it can be concluded that the passivation mechanism of Ge surface by GeOₓ interlayer is the same for different GeOₓ growth method. Furthermore, the D₈ at GeOₓ/Ge interface is clarified to decrease with increasing the amount of Ge³⁺ state, due to the effective passivation of the Ge dangling bond by Ge³⁺ component. This indicates that the Ge³⁺ component is the dominant key to achieve superior Ge surface passivation. As a result, to explore a growth process that can realize sufficient Ge³⁺ component in the GeOₓ 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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