Effect of Interfacial Reactions in Radical Process on Electrical Properties of Al₂O₃/Ge Gate Stack Structure

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Abstract. We have investigated the interfacial reactions of Al₂O₃/Ge structure with nitrogen (N) radical process, and the effect of the chemical bonding states on electrical properties. The angle resolved hard X-ray photoelectron spectroscopy measurement revealed that oxygen is supplied from the Al₂O₃ film to the interface with Ge substrate during N radical process and Ge atoms diffuse into the Al₂O₃ film. As a result, AlGeON/Ge suboxide/Ge stacked structure is formed by N radical process. From capacitance-voltage characteristics of Al/AlGeON/Ge suboxide/Ge MOS capacitors, both the interface state density at the interface and the carrier trap density in the Al₂O₃ film are effectively decreased by the formation of AlGeON/Ge suboxide/Ge structure. The interface state density decreases with increasing in the thickness of Ge suboxide at the interface.

1. Introduction

Germanium (Ge) has much attention for the further increase in the operation speed of the metal-oxide-semiconductor field effect transistor (MOSFET), because of high mobilities for both electron and hole. Also, gate dielectrics with high dielectric constant (high-k) film become essential materials to reduce the equivalent oxide thickness (EOT) with suppressing the increase in the leakage current. To control the high-k/Ge interfacial structure is an important key technique for realizing of high-performance Ge based MOSFETs. For example, the interface state density at a high-k/Ge interface should be decreased to less than $10^{11}$ eV$^{-1}$cm$^{-2}$, and a high thermal stability of interfacial structure is also required. Focusing on the interface state density, there are many reports about realizing the low interface state density as low as $5	imes 10^{10}$ eV$^{-1}$cm$^{-2}$ with the GeO$_2$/Ge structure formed by the thermal or plasma oxidation [1-4]. However, it is difficult to realize the GeO$_2$/Ge structure with keeping the thin EOT and the high thermal stability. In particular, the poor thermal stability is reported in which the GeO desorption from the GeO$_2$/Ge interface easily occurs [5,6]. On the other hand, Al$_2$O$_3$/Ge structure has a superior thermal stability. The interfacial mixing between Al$_2$O$_3$ and Ge does not occur even after annealing in N$_2$ ambient at as high as 550°C [7-9]. We recently reported that AlGeO/Ge structure can be formed by Ge diffusion from a Ge substrate into an Al$_2$O$_3$ film with annealing to the 1 nm-thick-Al$_2$O$_3$/Ge structure in O$_2$ ambient at from 400 to 550°C [9]. The interface state density of this AlGeO/Ge interfacial structure can be decreased by O$_2$ annealing with keeping thin EOT. Therefore, the AlGeO film is a new attractive candidate as an interfacial control layer with the thin EOT and the high thermal stability.

The most important issue for the formation of the AlGeO/Ge structure is control of the oxygen (O) supply and reaction at the the Al$_2$O$_3$/Ge interface. Excess O supply to the interface causes the segregation of GeO$_2$ on the surface of the Al$_2$O$_3$ film, although O supply is essential to cause the Ge
Nitrogen radicals were formed by the inductively coupled plasma (ICP) source with an RF power of 500 W and a N\textsubscript{2} flow rate of 10 standard cubic centimeters per minute (sccm) (a) N and (b) O radical processes. The intensity of these peaks is normalized by the Al\textsubscript{2}p peak intensity in the Al2p spectra. The binding energy is corrected by that of the Ge substrate peak in ambient at an atmospheric pressure (H\textsubscript{2}O with (a) N and (b) O radical processes. The intensity of these peaks is normalized by the Al\textsubscript{2}p peak intensity in the Al2p spectra. The binding energy is corrected by that of the Ge substrate peak in the AR-HAXPES method. Also, we clarified the effect of the chemical bonding state on electrical properties of the Al\textsubscript{2}O\textsubscript{3}/Ge interface after N radical process in detail.

In this study, we investigated the reaction at the Al\textsubscript{2}O\textsubscript{3}/Ge interface with N radical process by using the angle resolved hard X-ray photoelectron spectroscopy (AR-HAXPES) method. Also, we clarified the effect of the chemical bonding state on electrical properties of the Al\textsubscript{2}O\textsubscript{3}/Ge interface after N radical process.

2. Experimental procedure
We used a Ga-doped p-type Ge(001) substrate with a resistivity of 1~5 Ω·cm. After the chemical cleaning of the substrate by using diluted-HF and deionized-H\textsubscript{2}O to remove native oxide, a 1 nm-thick Al\textsubscript{2}O\textsubscript{3} film (1st-Al\textsubscript{2}O\textsubscript{3} film) was formed by ALD method (Picosun SUNALE R-150B). We used precursors of trimethylaluminium (Al(\textsubscript{3}CH\textsubscript{3})\textsubscript{3}, TMA) and H\textsubscript{2}O with a pulse time are 0.1 and 1.0 s, respectively. The formation temperature of the Al\textsubscript{2}O\textsubscript{3} film was 300°C. We confirmed that the thickness of the Ge oxide interlayer between the Al\textsubscript{2}O\textsubscript{3} film and Ge substrate was as thin as 0.1 nm after the Al\textsubscript{2}O\textsubscript{3} film deposition at 300°C [11]. Then, we performed the N radical process to the 1st-Al\textsubscript{2}O\textsubscript{3}/Ge structure in an ultra high vacuum chamber with a base pressure of less than 7×10\textsuperscript{-7} Pa. Nitrogen radicals were formed by the inductively coupled plasma (ICP) source with an RF power of 500 W and a N\textsubscript{2} partial pressure of 4×10\textsuperscript{-3} Pa. The heater temperature for the 1st-Al\textsubscript{2}O\textsubscript{3}/Ge sample was set at 50°C during the N radical process. The process time was ranging from 1 to 20 min. The distance from the Al\textsubscript{2}O\textsubscript{3}/Ge sample and ICP source was 5 or 18 cm. Then, we additionally deposited a 3 nm-thick-Al\textsubscript{2}O\textsubscript{3} film (2nd-Al\textsubscript{2}O\textsubscript{3} film) on some samples at 300 °C to suppress the leakage current in the electrical property measurement. Gate electrodes with an area of 1.3~1.5×10\textsuperscript{-4} cm\textsuperscript{2} were fabricated with the vacuum deposition of Al. Finally, some samples were annealed at 300 °C for 30 min in H\textsubscript{2} ambient at an atmospheric pressure (H\textsubscript{2} annealing).

The chemical bonding states were investigated from the X-ray photoelectron spectroscopy (XPS) with AlK\textalpha{} line (h\nu{}=1486.6 eV). HAXPES was also performed at the beamline BL46XU in the super photon ring-8 GeV (SPring-8). The monochromated X-ray with the photon energy of 7939 eV was used in the HAXPES measurement. Photoelectron take-off angle was ranging from 8 to 90°. Capacitance-voltage (C-V) properties were measured at room temperature with a high-frequency of 1 MHz. Interface state density was evaluated from the peak value of conductance-voltage properties [13].

3. Results and discussion
Figure 1 shows the C-V characteristics of Al/2nd-Al\textsubscript{2}O\textsubscript{3}/1st-Al\textsubscript{2}O\textsubscript{3}/Ge MOS capacitors with N and O radical process. The increase in the capacitance from inversion to accumulation conditions in the C-V curve becomes steep after N radical processes, indicating the decrease in the interface state density. Also, the hysteresis voltage width decreases with the N radical process. The counterclockwise hysteresis in C-V characteristics is probably related to the carrier traps from the Ge substrate to the defects formed in the Al\textsubscript{2}O\textsubscript{3} film near the Al\textsubscript{2}O\textsubscript{3}/Ge interface. On the other hand, the hysteresis voltage width increases with the O radical process and it is much larger than that of the sample with the N radical process. Although, the interface state density decreases in the sample with the O radical process.

Figure 2 shows the Ge3d photoelectron core spectra measured with XPS of 1st-Al\textsubscript{2}O\textsubscript{3}/Ge samples with (a) N and (b) O radical processes. The intensity of these peaks is normalized by the Al\textsubscript{2}O\textsubscript{3} peak intensity in the Al2p spectra. The binding energy is corrected by that of the Ge substrate peak in
AlN process, since XPS with a small TOA enables surface sensitive measurement. On the other hand, we binding energy is corrected by that of the Ge substrate peak of 1217.0 eV. We can find the peak 8 samples with the N radical process for from 1 to 10 min. The TOA of the HAXPES measurement was 3/2 bonding state in detail and the interfacial reaction at Al 2 TOA. This result indicates that a Ge oxide layer formed at the Al 3/2 O radical process without H 2 annealing. Distance from Al 2 O 3/2 /Ge and ICP source is 5 cm.

Figure 1  C-V characteristics of Al/2nd-Al 2 O 3 /1st-Al 2 O 3 /Ge MOS capacitor after N and O radical process without H 2 annealing. Distance from Al 2 O 3 /Ge and ICP source is 5 cm.

Figure 2  Ge 3d photoelectron core spectra of 1st-Al 2 O 3 /Ge structures after (a) N and (b) O radical process measured by XPS with TOA of 90, 30, and 15°. Distance from Al 2 O 3 /Ge and ICP source is 5 cm. Binding energy is corrected by that of the Ge substrate peak and intensity is normalized by area intensity of the Ge substrate peak.

Ge 3d 5/2 spectra (29.2 eV). The take-off angles are 90, 30, and 15°. The area intensity of the Ge oxide peak at a binding energy of about 32 eV in the sample with the N radical process is much smaller than that of the sample with the O radical process. The area densities of Ge atoms bonding with O atoms are evaluated by the area intensity ratio of the Ge oxide peak to the Ge substrate peak. Those for the sample with N radical and O radical process are 9.8×10 10 and 3.0×10 15 cm -2, respectively. We can also observe the TOA dependence of the normalized area intensity of the Ge oxide peak for the sample after the O radical process. The normalized area intensity of the Ge oxide peak decreases with the TOA. This result indicates that a Ge oxide layer formed at the Al 2 O 3 /Ge interface with O radical process, since XPS with a small TOA enables surface sensitive measurement. On the other hand, we can find almost no TOA dependence of the normalized intensity of the Ge oxide peak in the sample with the N radical process. It is found that N radical process forms an AlGeON film on a Ge substrate due to the uniform diffusion of Ge atoms into the 1st-Al 2 O 3 film from the Ge substrate.

Next, we performed the AR-HAXPES measurement in order to investigate the interfacial chemical bonding state in detail and the interfacial reaction at Al 2 O 3 /Ge structure with N radical process.

Figure 3 shows (a) Ge 2p 3/2, (b) Al 1s, and (c) N 1s photoelectron core spectra of the 1st-Al 2 O 3 /Ge samples with the N radical process for from 1 to 10 min. The TOA of the HAXPES measurement was 8°. The intensity of Ge 2p 3/2 spectra is normalized by the area intensity of the Ge substrate peak and that of Al 1s and N 1s spectra is normalized by the area intensity of the Al 2 O 3 peak in Al 1s spectra. The binding energy is corrected by that of the Ge substrate peak of 1217.0 eV. We can find the peak related to AlGeON in Ge 2p 3/2 spectra at a binding energy of 1219.5 eV [14,15]. We can also find
peaks related to Ge suboxides of Ge$^{1+}$ and Ge$^{2+}$ in Ge2p$_{3/2}$ spectra at a binding energy of 1217.8 and 1218.6 eV, respectively, as shown in Figure 3. The radical process time dependence of the area intensity ratio of the Ge oxide peak to the Ge substrate peak is shown in Figure 4. In this figure, we represent the sum of Ge$^{1+}$ and Ge$^{2+}$ as Ge suboxide since both these components exist at the AlGeON/Ge interface as discussed later. The intensity ratio of the AlGeON peak increases with the radical process time, indicating the increase in the composition ratio of Ge in the AlGeON film. The intensity ratio of Ge suboxide increases with the N radical process time of shorter than 2 min, and it hardly changes with the N radical process for longer than 2 min.

Figure 5 shows the area intensity ratio of the Ge oxide peak in the Ge2p$_{3/2}$ spectra to the Al$_3$O$_3$ peak in Al1s spectra as shown in Figure 3 for the sample with the N radical process as a function of TOA. The N radical process time was 10 min. We can find almost no TOA dependence of the area intensity ratio of the AlGeON peak to the Al$_3$O$_3$ peak, indicating that Ge atoms are uniformly distributed in the 1st-Al$_3$O$_3$ film. This result supports the formation of the AlGeON film after the N radical process to the 1st-Al$_3$O$_3$/Ge structure. The atomic density ratio of Ge atoms to Al atoms in the AlGeON film is evaluated to be 16% by the photoelectron intensity ratio of the AlGeON peak in Ge2p$_{3/2}$ spectra to Al1s spectra. On the other hand, the area intensity ratios of the Ge suboxide peaks to the Al$_3$O$_3$ peak decreases with TOA. This result indicates that Ge suboxide exists at the AlGeON/Ge interface. The area intensity ratio of the Ge suboxide peaks to the Ge substrate peak corresponds to a thickness of 0.22 nm, which is less than a thickness of 1 monolayer of a quartz-GeO$_2$ (0.32 nm [16,17]). Here, we assumed the formation of the ideal GeO$_2$ film as a Ge oxide interlayer. The atomic densities used to evaluate the thickness of Ge suboxide are 2.53×10$^{22}$ and 4.42×10$^{22}$ cm$^{-3}$ for GeO$_2$ and bulk Ge, respectively [17, 18].

Next, we will discuss the chemical reaction in the film and at the interface with N radical process to the Al$_3$O$_3$/Ge structure using Al1s and N1s photoelectron core spectra as shown Figure 3(b) and 3(c). We can find the peak related to the 1st-Al$_3$O$_3$ film at a binding energy of 1561.5 eV in the Al1s spectra before the N radical process [7,19]. In the sample after the N radical process, the binding energy of the peak in the Al1s spectra decreases compared with that of the sample before the N radical process. The decrease in the binding energy of the peak indicates the formation of Al-N bonds in the 1st-Al$_3$O$_3$ film [20-22]. In the N1s spectra, we can find three peaks at binding energies of 398, 400, and 403 eV for the sample after the N radical process. These peaks relates to the AlON (~400 eV [21]), GeON (at a higher binding energy of AlN (~398 eV [21,22]), or Ge$_3$N$_4$ (~397.5 eV [23,24])). Also, the peak at a binding energy of 403 eV is probably attributed to the N-O bond.

Figure 6 shows the TOA dependence of the area intensity ratios of three peaks in N1s spectra to AlGeON peak in Al1s spectra for the sample after the N radical process for 10 min. The area intensity ratio for all peaks in N1s spectra increases with TOA. This result indicates that the N atoms exist

![Figure 4](image1.png)  
**Figure 4** Area intensity ratio of Ge oxide peak to Ge substrate peak in Ge2p$_{3/2}$ photoelectron core spectra of 1st-Al$_3$O$_3$/Ge structures as a function of N radical process time measured by HAXPES. TOA is 8°.

![Figure 5](image2.png)  
**Figure 5** TOA dependence of area intensity ratio of Ge oxide peak in Ge2p$_{3/2}$ photoelectron core spectra to Al$_3$O$_3$ peak in Al1s spectra of 1st-Al$_3$O$_3$/Ge structures measured by HAXPES. N radical process time is 10 min.

![Figure 6](image3.png)  
**Figure 6** TOA dependence of area intensity ratio of peaks in N1s photoelectron core spectra to Al$_3$O$_3$ peak in Al1s spectra of 1st-Al$_3$O$_3$/Ge structures measured by HAXPES. N radical process time is 10 min.
mainly near the AlGeON/Ge interface. Here, considering the TOA dependence of the area intensity ratio of Ge oxide peak to Al oxide peak as discussed with Figure 5, Ge atoms in the AlGeON film bind with O or N atoms and uniformly distribute in the AlGeON film. In addition, the composition ratio of Ge in the AlGeON film is not so large compared to that of N. Therefore, it is difficult to explain the depth distribution and composition ratio of N by the formation of Ge nitride and oxynitride in the Al2O3 film, and N atoms mainly bonds with Al atoms. At the same time, the N1s spectra shown in Figure 3(c) support the result of the formation of Al-N bonds, and it is considered that AlON is formed in the 1st-Al2O3 film. Here, in Figure 3(c), the intensity of the peak at a binding energy of 400 eV decreases with the N radical process time. At the same time, the intensity of the peak at a binding energy of 398 eV increases with the N radical process time. These results indicate that the composition ratio of N in the AlGeON film increases with the N radical process time.

From the above discussion, the interfacial reactions and interfacial structure for the sample after the N radical process are considered as follows. At first, Al-O bonds in the Al2O3 film are broken with the N radical irradiation to the Al2O3/Ge structure. At the same time, Al-N bonds are formed in the Al2O3 films with the N radical process to the Al2O3/Ge structure. Following that, O atoms diffuse from the Al2O3 film to the Al2O3/Ge interface, and the Ge of the substrate at the interface is oxidized. The oxidation of the Ge becomes a trigger for the diffusion of Ge atoms from the Ge substrate to the Al2O3 film. As a result, the AlGeON film is formed on the Ge substrate. The Ge suboxide with the thickness of 0.22 nm corresponds to the Ge atoms bonding with O atoms at the AlGeON/Ge interface.

Finally, we investigated the N radical process time dependence on the electrical properties of the Al2O3/Ge sample with the N radical process. Figure 7 shows the C-V characteristics of MOS capacitors after H2 annealing. The N radical process is performed for from 1 to 20 min to the 1st-Al2O3/Ge structure. Results of the C-V measurement indicate the decrease in the interface state density with increasing in the N radical process time as well as result shown in Figure 1. The interface state density for Al/Al2O3/Ge MOS capacitors decreases with increasing in the N radical process time. Here, we will show the relationship between the interface state density and the thickness of Ge suboxide at the AlGeON/Ge interface in Figure 8. The interface state density also tends to decrease with increasing in the thickness of the Ge suboxide. This trend implies that we can realize the low interface state density less than 1011 eV-1 cm-2 with the formation of very thin Ge suboxide film less than 1 monolayer. At the same time, we can find the decrease in the hysteresis voltage width in C-V characteristics with increasing in the N radical process time as shown in Figure 7. The hysteresis in C-V curve suggests that existence of defects near the Al2O3/Ge interface and in the Al2O3 film. This result indicates that the decrease in the oxide trap density with increasing in the N radical process time, and that is probably due to the incorporation of N or Ge atoms in the Al2O3 film.

![Figure 7](image-url)  
Figure 7  C-V characteristics of Al/2nd-Al2O3/1st-Al2O3/Ge MOS capacitor after N radical process and H2 annealing.

![Figure 8](image-url)  
Figure 8  Relationship between interface state density and thickness of Ge suboxide for samples Al/2nd-Al2O3/1st-Al2O3/Ge MOS capacitor after N radical process and H2 annealing.
4. Conclusions
We have investigated the interfacial reactions of the Al₂O₃/Ge gate stack structure with N radical process, and the effect of the chemical bonding states on electrical properties. In the AR-HAXPES results, we found that the uniform distribution of Ge atoms in the Al₂O₃ film and the formation of the AlGeON films. Also, the intensity ratio of the Ge suboxide peak to the Ge substrate peak hardly changes after the N radical process for more than 2 min, and it corresponds to the Ge suboxide thickness of 0.22 nm for the sample after the N radical process for 10 min. We can observe the steep increase in the capacitance from inversion to accumulation conditions and the decrease in the hysteresis voltage width in the C-V characteristics of the Al/Al₂O₃/Ge MOS capacitors. The interface state density decreases with increasing in the N radical process time. Also, that tends to decrease with increasing in the thickness of Ge suboxide. The interface state density of the sample after the N radical process for more than 10 min is as low as 4×10¹¹ eV⁻¹cm⁻². The relationship between the interface state density and the thickness of Ge suboxide implies that we can realize the interface state density less than 10¹³ eV⁻¹cm⁻² with the very thin Ge suboxide less than 1 monolayer. The oxide trap density in the oxide film also decreases with N radical process to Al₂O₃/Ge structure. Therefore, it is found that N radical process is an attractive process to control of the amount of O atoms from an Al₂O₃ film to the Al₂O₃/Ge interface. We can achieve the decrease in both the interface state density and oxide trap density with the formation of AlGeON/Ge suboxide/Ge structure.

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