# Interfacial Reaction Mechanism in Al<sub>2</sub>O<sub>3</sub>/Ge Structure by Oxygen Radical

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# 1. Introduction

Oxidation and decomposition reactions of Ge or Ge oxides are key factors to control the interfacial structures of high-k/Ge stack structures in MOSFETs. The oxygen (O) plasma process to an Al<sub>2</sub>O<sub>3</sub>/Ge structure can effectively reduce the interface state density ( $D_{it}$ ) in spite of the quite low diffusivity of oxygen in an Al<sub>2</sub>O<sub>3</sub> layer [1,2]. On the other hand, Ge diffuses into an Al<sub>2</sub>O<sub>3</sub> layer with the O<sub>2</sub> thermal annealing, although the formation of a Ge oxide interlayer following to the oxygen supply to Al<sub>2</sub>O<sub>3</sub>/Ge structures does not occur [3]. These results mean that the oxidation at the Al<sub>2</sub>O<sub>3</sub>/Ge interface is not able to be understood by the oxidation mechanism at a SiO<sub>2</sub>/Si interface [4], and that mechanisms of interfacial reactions at a high-k/Ge interface have not yet clarified in detail.

In this study, we investigated mechanisms of interfacial reactions in the  $Al_2O_3/Ge$  structure during O radical process through analyses of chemical bonding states and the electrical interface properties of MOS capacitors. We clarified the oxidation reaction at the  $Al_2O_3/Ge$  interface. We demonstrate that the depth distribution of Ge can be controlled by the O radical process, hardly depending on the process temperature, and the O radical process at a low temperature can effectively reduce  $D_{it}$ .

## 2. Experimental

The fabrication process flow of the MOS capacitors using the O radical process and the resulting sample structure are shown in Fig. 1. After cleaning p-Ge(001) substrates, a 1-nm-thick-Al<sub>2</sub>O<sub>3</sub> layer (1st-Al<sub>2</sub>O<sub>3</sub> layer) was formed at 300°C using atomic layer deposition (ALD) method. Then, the N-O mixture radical process was performed at from 50 to 500°C for 5 min in an ultra high vacuum chamber. The O radical density was controlled by adjusting the mixture ratio of O2 and N2 gases. The ratio of the O<sub>2</sub> gas partial pressure  $(R_0 = P_{O2}/(P_{N2} + P_{O2}))$  was ranging from 1.8% to 100%, and the sum of  $N_2$  and  $O_2$  partial pressures was kept at  $4 \times 10^{-3}$  Pa. Finally, to suppress gate leakage current, a 3-nm-thick Al<sub>2</sub>O<sub>3</sub> layer (2nd-Al<sub>2</sub>O<sub>3</sub> layer) was deposited on the 1st-Al<sub>2</sub>O<sub>3</sub> layer, and then gate Al electrodes were formed by vacuum evaporation. Chemical bonding states and electrical properties of the MOS interfaces were evaluated by X-ray photoelectron spectroscopy (XPS), C-V and conductance-voltage (G-V) methods.

## 3. Results and discussion

Figure 2 shows *C-V* characteristics of the MOS capacitors after the O radical process at 50°C in various  $R_0$ . A hump is obviously observed in the *C-V* curves without the O radical process. On the other hand, after the O radical process, the hump is hardly observed in the *C-V* curves. *G-V* method clarified that  $D_{it}$  effectively decreases with increasing  $R_0$  by the O radical process at 50°C (Fig. 3).

In order to clarify the reduction mechanism of  $D_{it}$ , the chemical bonding states for the 1st-Al<sub>2</sub>O<sub>3</sub>/Ge sample after

the O radical process were investigated by hard X-ray photoelectron spectroscopy (HAXPES) method (Fig. 4). The intensity of the peaks associated with  $Ge^{3+}$  suboxide or  $GeO_x$ increases with  $R_0$  (Fig. 4 and 5). On the other hand, from the  $R_{\rm O}$  dependence of the area intensity ratio of Ge oxide peaks to Ge substrate peak shown in Fig. 5, the dependence of  $Ge^{1+}$  and  $Ge^{2+}$  hardly changes. This indicates that the chemical bonding states at the Al<sub>2</sub>O<sub>3</sub>/Ge interfaces hardly change. To obtain information concerning depth profiles of the sub-oxides, the area intensity ratios of the Ge oxide peaks to the Al<sub>2</sub>O<sub>3</sub> peak as a function of take-off angle (TOA) were evaluated (Fig. 6). The intensity ratio decreases with TOA in the case of  $R_0=100\%$ , indicating the segregation of the Ge atoms near the Al<sub>2</sub>O<sub>3</sub>/Ge interface. As mentioned before, after the  $O_2$  thermal annealing, Ge can easily diffuse to the surface of the Al<sub>2</sub>O<sub>3</sub> layer as shown in Fig. 7(a) [3]. However, as shown in Fig. 6, Ge is segregated near the Al<sub>2</sub>O<sub>3</sub>/Ge interface rather than the surface of the Al<sub>2</sub>O<sub>3</sub> layer. These results mean that the O radical process at 50°C leads to oxidation reaction of the Ge surface through the  $Al_2O_3$  layer (Fig. 7(b)). As a result, the formation of the  $Ge^{3+}$  suboxide or  $GeO_x$  near the Al<sub>2</sub>O<sub>3</sub>/Ge interface leads the low  $D_{it}$  interface.

In order to make a difference of the oxidation mechanisms between the O radical process and the O<sub>2</sub> thermal annealing more evident, temperature dependences of the interfacial reactions at the Al<sub>2</sub>O<sub>3</sub>/Ge interface were investigated. Figure 8(a) and (b) show  $Ge2p_{3/2}$  spectra for the 1st-Al<sub>2</sub>O<sub>3</sub>/Ge samples after the O<sub>2</sub> thermal annealing at various temperatures and the O radical process with the  $R_{\rm O}$ of 100% at 50°C, respectively. The normalized intensity of the Ge oxides for the sample after O radical process at 50°C is larger than that for the sample after O<sub>2</sub> annealing at 300°C. In addition, the process temperature dependence for areal density of Ge oxide formed by the O radical process is much smaller than that formed by O<sub>2</sub> thermal annealing (Fig. 9). In particular, there is almost no temperature dependence of areal density of Ge oxide at a process temperature ranging from 50 to 200°C, suggesting that the activation energy is quite small. The small activation energy for the formation of the Ge oxide indicates the formation of Ge oxide owing to the introduction of O atoms to the  $Al_2O_3/Ge$  interface. In the temperature above 400°C, the temperature dependence of the Ge oxidation by the O radical process approaches to that by the O<sub>2</sub> thermal annealing.

From the above discussion, we can control the oxidation reaction and depth distribution of Ge in the  $Al_2O_3$  layer by the O radical process at a low temperature. It is also found that the control of the density of  $GeO_x$  in the  $Al_2O_3$  film is effective to reduce  $D_{it}$ .

#### 4. Conclusions

We have systematically investigated the interfacial structures and the electrical properties of the  $Al_2O_3/Ge$  stacked structure, focusing on oxidation reactions by the O

radical process. We clarified that the oxidation by the O radical process at low temperature occurs near the  $Al_2O_3/Ge$  interface in contrast to that by the O<sub>2</sub> thermal annealing. Also, we found that the O radical process can control the oxidation reaction of Ge at the  $Al_2O_3/Ge$  interface and the depth distribution of Ge in the  $Al_2O_3$  film at a low temperature. We have also clarified that the possibility for decreasing in  $D_{it}$  with controlling the depth distribution of Ge in the  $Al_2O_3$  film.

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Fig. 1 Sample preparation flow and schematic diagrams of cross-sectional structures of the samples for HAXPES (XPS) and *C-V* measurement.



Fig. 4 Ge2p<sub>3/2</sub> photoelectron core spectra for the 1st-Al<sub>2</sub>O<sub>3</sub>/Ge stacked structure after the O radical process with several  $R_0$  measured by hard X-ray photoelectron spectroscopy method (hv = 7939 eV).



Fig. 5  $R_{\rm O}$  dependence of area intensity ratio of the Ge oxide peaks to the Ge substrate peak in Ge2p<sub>3/2</sub> photoelectron core spectra for 1st-Al<sub>2</sub>O<sub>3</sub>/Ge stacked the structure after the O radical process. Ge suboxides of Ge14 and  $Ge^{2+}$  exist at the Al<sub>2</sub>O<sub>3</sub>/Ge interface, while  $Ge^{3+}$  or  $GeO_x$ diffuses into the  $Al_2O_3$  film.



Fig. 8  $Ge2p_{3/2}$  photoelectron core spectra for the 1st-Al<sub>2</sub>O<sub>3</sub>/Ge stacked structure after (a) O<sub>2</sub> thermal annealing and (b) O radical process.

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Fig. 2 C-V characteristics for the MOS capacitors after the O radical process at 50°C with several  $R_0$ .



Fig. 6 TOA dependence of the area intensity ratio of the Ge oxide peaks to the  $Al_2O_3$ peak in Ge3d<sub>5/2</sub> and  $Al2p_{3/2}$ photoelectron core spectra for the 1st-Al<sub>2</sub>O<sub>3</sub>/Ge stacked structure after the O radical process measured by XPS.



Fig. 3  $R_0$  dependence of  $D_{it}$  for the MOS capacitors after the O radical process. The energy level of  $D_{it}$  is 0.18-0.20 eV from  $E_V$ .



Fig. 7 Schematic diagrams of the 1st-Al<sub>2</sub>O<sub>3</sub>/Ge samples after (a) O<sub>2</sub> thermal annealing and (b) O radical process. From the detailed HAXPES analysis, the thin layer concerning Ge<sup>1+</sup> and Ge<sup>2+</sup> locates at the Ge<sup>3+</sup> suboxide(or GeOx)/Ge interface (*not shown*).



Fig. 9 Arrhenius plot for the areal density of the Ge oxide in the  $1st-Al_2O_3/Ge$  stacked structure after the O radical process and the  $O_2$  thermal annealing.