Surface Analysis of Thermally Growth Ge Oxide on Ge (100)

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***Abstract*—The understanding of Ge oxidation is utmost importance in order to form the good quality dielectric/Ge interface in fabricating Ge Metal Oxide Semiconductor Field Effect Transistor (MOSFETs). In addition, the mechanism of Ge oxidation is still under intensive studies. For Silicon oxidation, Deal and Grove Model have been accepted to explain the Si Oxidation mechanism. The purpose of this paper is to report the mechanism of Ge oxidation at two different temperatures, 375 and 490°C and the detail of Ge oxide composition at Ge oxide/Ge interface. After wet chemical cleaning with HCl, the thermal oxidation was performed at temperature 375 and 490°C at atmospheric pressure. The thickness and composition of Ge oxide were measured with spectroscopic ellipsometry and x-ray photoelectron spectroscopy, respectively. It was observed that the *n* value extracted from a log-log plot of oxidation time versus oxide thickness was dependent on the oxidation temperature. The oxygen-deficient region was formed during thermal oxidation of Ge and the electronic states of suboxide component were observed in the region within 2.3eV above the top valence band. The novelty of this work is to investigate the kinetics oxidation of Ge and evaluate the composition of oxide layer after thermal oxidation that becomes useful information for the development of Ge MOSFETs.**

***Index Terms*—Germanium; Oxidation; X-Ray Photoelectron Spectroscopy**

I. Introduction

GE has been regarded as a promising channel material for metal-oxide-semiconductor (MOS) field effect transistors (FETs) because it has higher carrier mobility than Si [1]-[2]. One of the most critical issues for developing Ge MOS FETs includes controlling the MOS interface and minimizing the defect state densities in the gate dielectric and at the dielectric/Ge interface [3]-[5]. Therefore, a better understanding of the Ge surface oxidation mechanism is quite important for fabricating a high-quality dielectric/Ge interface. As for the thermal stability of the GeO_2/Ge interface, there has been a report on the change in oxide network to generate Ge mono-oxide (Ge^{2+}) near the substrate interface by using vacuum annealing at 300ºC (~10^{-8} Torr) and thermal desorption of Ge oxide by further increasing the annealing temperature [6]. In addition, a thermal desorption spectroscopy (TDS) analysis of GeO_2/SiO_2 and GeO_2/Ge structures also has shown that GeO desorption was not derived from the decomposition of GeO_2 itself but from its reaction with a Ge substrate [4]. It is also confirmed that the desorption of GeO leads to the deterioration of the surface and interface of GeO_2/Ge systems and degrades the electrical characteristics, which places a large hysteresis on the C-V characteristics of MIS capacitors [7]- [8].

For Ge oxidation, the desorption process must be taken into account during the oxidation process. In fact, it was reported that the parabolic constant is not proportional to the partial pressure of oxygen for the oxidation of Ge for the thermal oxidation of Ge at 550°C with different oxygen pressures [9], which is contradictory to the thermal oxidation model for the Si oxidation proposed by Deal and Grove [10].

In contrast to Ge oxidation, there is no oxidation model that has been accepted. Therefore, the detailed mechanism of Ge surface oxidation is a great importance to develop oxidation model in detail. In this paper, the kinetics oxidation between high temperature and low-temperature oxidation is investigated in detail by using spectroscopic ellipsometry (SE) and high-resolution x-ray photoelectron spectroscopy (XPS).

II. Experimental Procedures

P-type Ge (100) with a resistivity of 10Ω·cm was used in this work. Before thermal oxidation, the wet chemical cleaning was performed as similar in our previous research work [11]-[12]. In this cleaning, the wafer was dipped in 15% H_2O_2 after dipping in deionized water. Then the wafer was dipped in the 30 % HCl. After the wet chemical cleaning, a GeO_2 layer was grown at 375 or 490°C in a dry oxygen ambience (O_2 gas flow rate: 4.0L/min) at atmospheric pressure. The oxide thicknesses were determined by using spectroscopic ellipsometry (SE) at wavelengths ranging between 192 and 1000 nm. The XPS measurement was used to characterized the chemical bonding features of the thermally grown Ge oxide with photoelectron take-off angles of 30° and 90° using monochromatized AlKα (1486.6 eV) radiation. From the Ge 3d core-line spectra, the oxidation states in thermally grown Ge oxide and in the region near the Ge oxide/Ge interface were evaluated. The valence band offset in Ge oxide/Ge (100) system was determined by the onset of the valence band.

III. Results and Discussion

Ge oxide growth on Ge (100) at 375°C and 490°C with the oxidation time were evaluated from spectroscopic ellipsometry (SE) as shown in Figure 1. Both oxidations were performed under atmospheric pressure in dry oxygen ambience. In this graph, the n value is the slope which is extracted in the log-log plot that indicates the oxidation rate. The slope of oxidation at the temperature of 490°C increases about three times of the oxidation slope for oxidation temperature of 375°C. The increases of slope indicate that the oxidation and the desorption rate may be enhanced during Ge

oxidation at higher temperature. In addition, the slope of 375°C is nearly to the slope of oxidation of silicon oxidation at 700°C which indicates that the oxidation is controlled by surface reaction [8]. To investigate the increasing of n value in detail, the XPS measurement was conducted to investigate the detail surface reaction between Ge and Ge oxide at these two different temperatures.

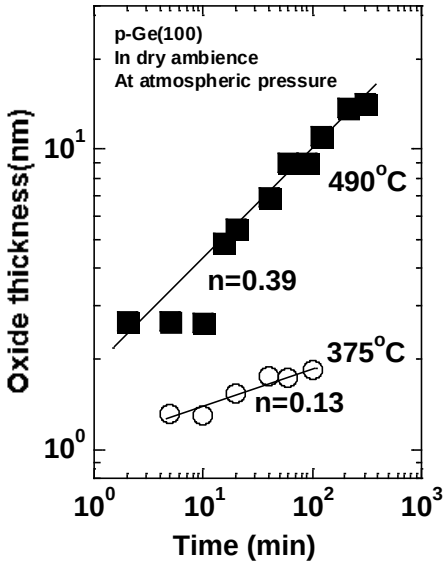

Figure 1: Thermal oxidation at temperature of 375 and 490 °C

Figure 2 shows the Ge $3d_{5/2}$ spectra of the thermally grown GeO_2 on Ge (100) at 375 and 490°C oxidations. The Ge oxide thicknesses for both samples were 2.0 nm and 2.6 nm, respectively. Each Ge $3d_{5/2}$ spectrum was obtained by the spectral deconvolution of the measured Ge 3d signals into two components in consideration with the spin-orbit splitting of Ge 3d core line, in which an energy splitting of 0.58 eV for Ge 3d and intensity ratios of Ge $3d_{5/2}$: $3d_{3/2}$ = 3: 2 were used in [13]. For both samples, the signals due to the sub-oxide components (around 31.5 eV in binding energy) were clearly observed. The detailed chemical bonding features were investigated from the Ge 3d spectral deconvolution into six components (Ge^{0+}: Ge-substrate, $Ge^{1\sim3+}$: Ge sub-oxides, Ge^{4+}: GeO_2, and $Ge^{\alpha+}$) using the same method as described in [14].

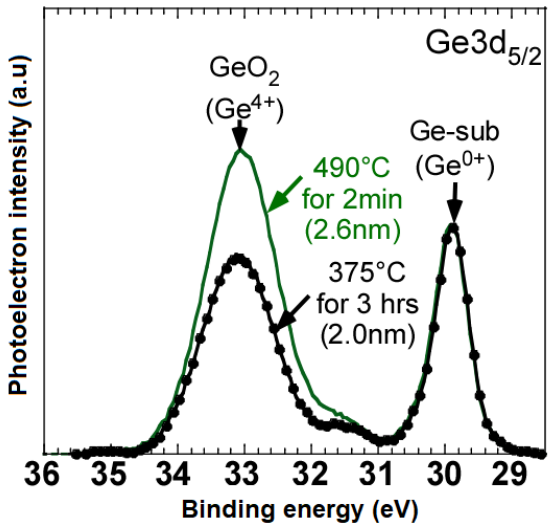

Figure 2: Ge 3d $_{5/2}$ spectra of thermally grown Ge oxide on Ge(100) surface at 375 and 490°C

The intensities of the sub-oxide component are summarized in Figure. 3. The Ge^{2+} and Ge^{3+} signals were slightly increased with the oxidation temperature, which implies that the formation of sub-oxides is likely to be expanded into GeO_2 bulk during the thermal oxidation at 490°C. In contrast to Ge^{4+}, the intensity was increased about one third with increasing temperature which indicates that Ge oxidation was enhanced with increasing temperature. In addition, the GeO diffusion may be enhanced with the increasing temperature and recombined with the oxygen and form the GeO_2 layer.

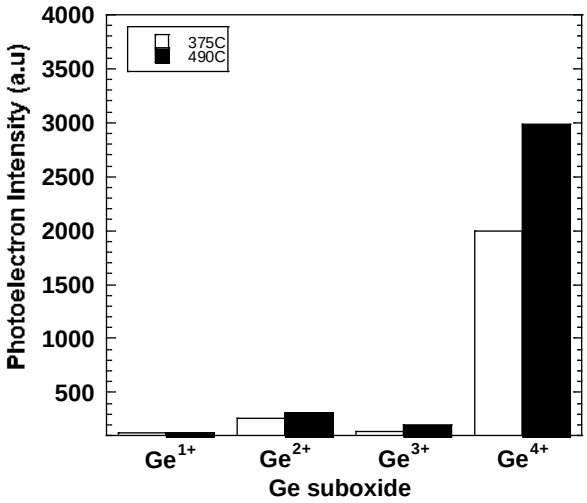

Figure 3: Signal intensity of deconvoluted Ge oxide components ($Ge^{1+\sim4+}$) for thermally grown Ge oxide/Ge(100) at 375 and 490 °C measured at take-off angle of 30°

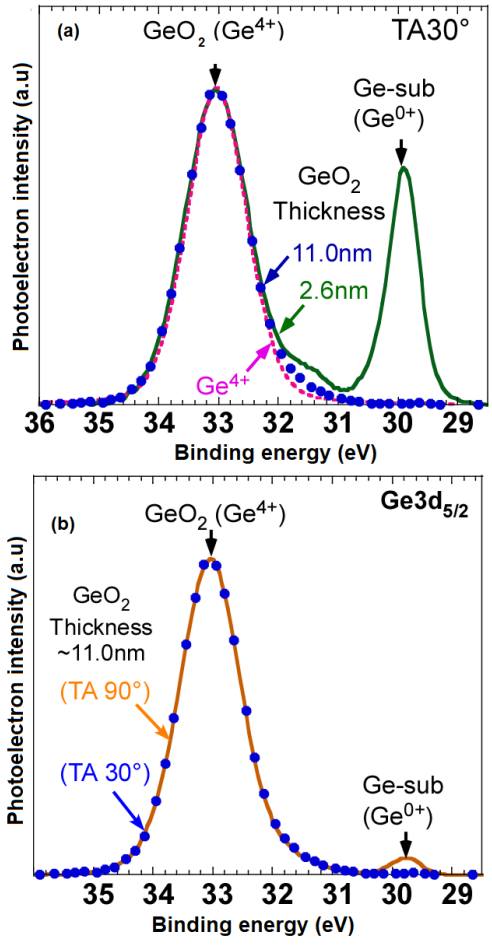

Figure 4: The thickness and takeoff angle dependence of GeO_2

To get a clearer insight into the sub-oxide like states in the GeO_2 bulk film, the chemical bonding feature of the thicker Ge oxide grown at 490°C was evaluated. Figure 4 shows the thickness dependence and take off angle dependence of GeO. From 4(a), an asymmetry Ge 3d spectra were observed for the 11.0 nm GeO_2-thick. Furthermore, no change in the signal intensity of sub-oxide components with increasing take-off angle from 30 to 90 as shown in Figure 4(b). The small signals were also observed in the valence band spectrum around 3 eV for 11.0 nm-thick GeO_2 (as shown in Figure. 5). These results suggest that the presence of oxygen-deficient sites were also generated in the Ge oxide during thermal. To investigate the oxygen-deficient sites in GeO_2 further, the valence band offset between Ge and GeO_2 was roughly estimated from the measured and deconvoluted valence band signals as shown in Figure 5. In the spectral deconvolution, the reference valence band spectrum taken for Ge(100) surface just after wet-cleaning was used. From the onset of each valence band signal, the valence band offset at the GeO_2/Ge interfaces was estimated to be ~4.0 eV, which is consistent with the reported values for GeO_2/Ge formed by the UV-O_3 oxidation [15]-[16], and the electronic states of the sub-oxides were observed within 2.3 eV above the top of the valence band of GeO_2 as summarized in the Figure 6.

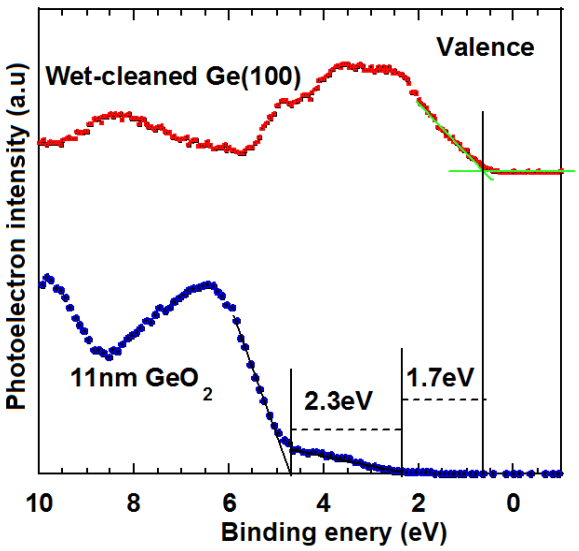

Figure 5: Valence band of 11.0 nm -thick Ge oxide

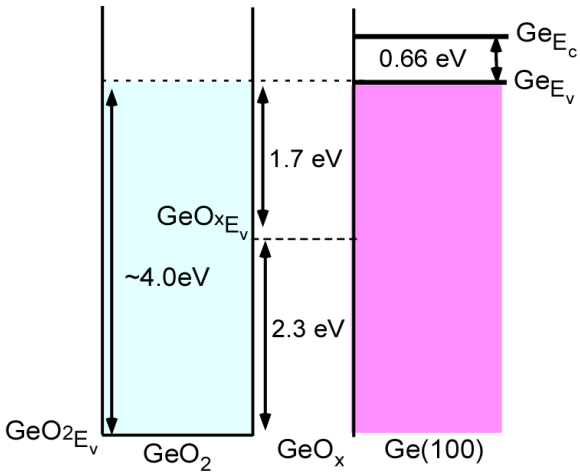

Figure 6: Energy band diagram of 11.0 nm-thick GeO_2

To reduce the Ge sub-oxide, the Ge/GeO_2 stack was annealed in oxygen ambience at lower temperature of 375 °C again. The XPS analysis was performed to evaluate the changes of sub-oxides component with the take-off angle dependence as shows in Figure 7. The relative intensity of sub-oxides component was plotted with the take-off angle dependence. The spectral deconvolution of the $Ge3d_{5/2}$ was obtained as similar as the analysis that performed in Figure 3. From the figure, it is clearly seen that Ge sub-oxides components (Ge^{1+}-Ge^{3+}) were increased with decreasing photoelectron take-off angle from 90° to 30° and no changes was observed on the Ge^{4+} which implies that Ge sub-oxides in the GeO_2 layer were decreased by oxygen anneal.

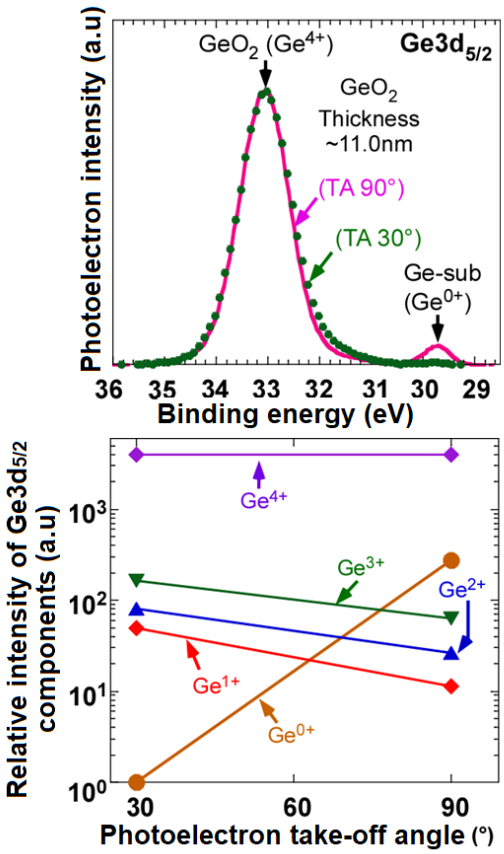

Figure 7 Take-off angle dependence of Ge/GeO_2 stack after anneal at temperature of 375°C

IV. Conclusion

The kinetics of the thermal oxidation of Ge and the chemical bonding features of thermally-grown Ge oxide on Ge (100) surfaces were investigated by using SE and XPS. The oxidation and desorption process were enhanced during Ge oxidation and increased with oxidation temperature. The XPS analysis shows an oxygen-deficient region in the GeO_2 grown by thermal oxidation at 490ºC. The valence band offset of a GeO_2/Ge (100) system prepared by thermal oxidation at 490°C was determined to be 4.0 eV and the electronic states of the sub-oxides were observed in the region within 2.3 eV above the top of the valence band. The lower temperature anneal can minimize the sub-oxides component in the GeO_2 layer.

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