Reduction of Interface States Density due to Post Oxidation with Formation of AlGeO Layer at Al₂O₃/Ge Interface

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Interface control of high-k/Ge structures is one of important issues for realizing high performance Ge channel MOSFETs. State-of-the-art Si devices achieve a low interface state density (D_{it}) and an equivalent oxide thickness thinner than 1 nm [1]. Therefore, the Ge MOSFETs could also require the similar interface properties. One of solutions to achieve the interface properties is Ge surface oxidation through thin insulator layer (post oxidation). Recently, Zhang et al. have reported that the post plasma oxidation of the Ge surface through a 1-nm-thick Al₂O₃ layer gives good interface properties [2]. They concluded that an ultra-thin GeO$_x$ layer formed at the Al₂O₃/Ge interface, which is detected as Ge^{3+} component for a GeO₂/Ge structure in Ge3d spectrum, is a key for improvement of the interface property. On the other hand, some reports also suggest that the Ge^{3+} component is owing to AlGeO layer due to Ge or GeO diffusion into the Al₂O₃ layer [3]. These conflicted results mean that the interface structures and reactions during the oxidation have not been comprehensively understood yet. Therefore, in order to further improve the interface properties, it is quite important to understand reaction mechanisms between Al₂O₃ and Ge surface and to clarify the relationship between the interface structures and the electrical interface properties. In this study, we systematically investigated the reaction mechanisms at the Al₂O₃/Ge interface by the detailed XPS analysis and the electrical interface properties using the conductance method.

A 1-nm-thick Al₂O₃ layer was formed by using atomic layer deposition (ALD) method at 300°C on p- and n-type Ge substrates treated with chemical cleaning using diluted HF and deionized water. Subsequently, the samples were oxidized at 200-600°C for 2-180 min. Then, to suppress gate leak current, a 3-nm-thick Al₂O₃ layer was deposited on the Al₂O₃ layer. Finally, Al electrodes were formed with vacuum evaporation. Angle resolved hard X-ray photoelectron spectroscopy (AR-HAXPES) and conventional X-ray photoelectron spectroscopy (XPS) method were performed to evaluate the interface structures for the 1-nm-thick Al₂O₃/Ge structure. Also, the electrical interface properties of the Al₂O₃/Ge structures were characterized by capacitance-voltage (C-V) measurement and conductance method including the surface potential fluctuation at 110-300 K.

Ge2p$_{3/2}$ and Ge3d spectra obtained from the HAXPES and XPS measurements were deconvoluted into 5 components related to Ge substrate (Ge^{0+}), Ge sub-oxide (Ge^{1+}-Ge^{3+}), and GeO₂ (Ge^{4+}) components. Ge2p$_{3/2}$ and Ge3d spectra mainly consist of Ge^{0+}, Ge^{3+}, and Ge^{4+} components. In addition, the peak intensities of Ge^{3+} and Ge^{4+} components increase with the oxidation temperature or the oxidation time. Figure 1 shows area density (D_{area}) of sum of Ge^{1+} and Ge^{2+} (Ge^{1+}+Ge^{2+}), Ge^{3+}, and Ge^{4+} components as a function of the oxidation temperature. Here, the oxidation time is 10 min. D_{area} of Ge^{x+} (x=1-4) components were evaluated from the area intensity ratios of the Ge^{x+} peaks to the Ge substrate peaks. D_{area} of the Ge^{3+} component at the oxidation temperature around 400°C is larger than that of the Ge^{4+} component, suggesting that the Ge^{3+} component is preferentially formed compared to the GeO₂ layer. This result is consistent with the reported XPS results as mentioned before. In addition, we found that a layer associated with the Ge^{3+} components is formed at near the Al₂O₃/Ge

interface from the take-off-angle dependencies of area intensity ratios between Al oxide and Ge^{x+} components. Also, we found that D_{area} of the Ge^{3+} component is saturated at around 3×10^{15} cm^{-2} more than 500°C. This value is in good agreement with the saturated value obtained from the samples oxidized at 400°C by changing the oxidation time. Also, the values correspond to the third of D_{area} of the Al oxide. This ratio well corresponds to that of a stable AlGeO phase, which is Al₆Ge₂O₁₃ [4]. Therefore, the increase in D_{area} of the Ge^{3+} component is attributed to the formation of AlGeO layer near the Al₂O₃/Ge interface.

D_{it} at an energy, $E_{SF}-E_i$ of −0.20 and 0.25 eV from the midgap of Ge for the p-type and n-type substrates, respectively, are shown in Fig. 2. The D_{it} values decrease with the oxidation temperature, and then, the D_{it} values are saturated more than 500°C. It seems that the D_{it} values strongly depend on D_{area} of the Ge^{3+} component as shown in Fig. 1. This implies that the reduction of D_{it} is attributed to the AlGeO formation at the Al₂O₃/Ge interface. Consequently, the AlGeO formation near the Al₂O₃/Ge interface is a possible key factor to improve the interface properties.

References

[1] S. Natarajan et al., IEDM, p. 941 (2008).
[2] R. Zhang et al., IEEE Trans. Electron Devices **59**, 335 (2012).
[3] S. Shibayama et al., Thin Solid Films **520**, 3397 (2012).
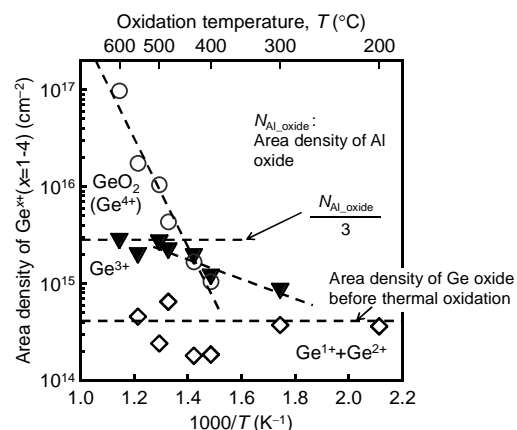[4] J. L. Miller et al., J. Am. Ceram. Soc. **50**, 268 (1967).

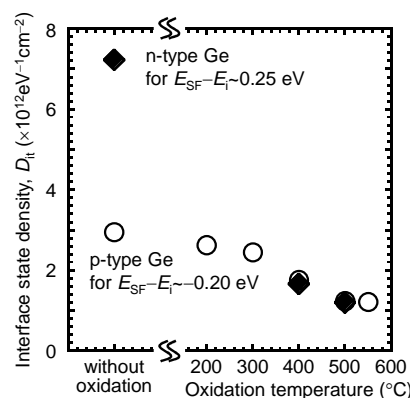Fig. 1 Oxidation temperature dependences of D_{area} of Ge^{x+} (x=1-4) components.

Fig. 2 Oxidation temperature dependences of D_{it}. D_{it} value is extracted around $E_{SF}-E_i$ ~ −0.20 and 0.25 eV. E_{SF} and E_i is the Fermi energy at Ge surface and the intrinsic Fermi energy of Ge.