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Evaluation of Thermally-Grown Ge Oxide on Ge(100) and Ge(111) Surfaces

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1. Introduction

Ge has been regarded as a promising channel material for metal-oxide-semiconductor (MOS) field effect transistors (FETs) because of its higher carrier mobilities than Si [1]. The most critical issues for the development of Ge MOS FETs include to control the MOS interface and to minimize the generation of defect state densities in the gate dielectric and at the dielectric/Ge interface. Presumably related to the fact that Ge oxide is chemically and thermally unstable in contrast to SiO_2 [2, 3], the detailed mechanism of Ge surface oxidation is still a matter of research. And the nature of the interfaces between GeO_2 and Ge with different orientations has not clarified yet.

In this work, we have studied the kinetic oxidation of Ge(100) and (111) surfaces by thermal oxidation at temperatures of 375 and 490°C in dry oxygen ambience. The chemical bonding features at GeO_2/Ge interfaces were characterized by photoemission measurement.

2. Experimental

P-type Ge(100) and (111) with a resistivity of 10-20 Ωcm were used in this work. The Ge wafers were first dipped in deionized ultrapure water to dissolve native oxide and followed by immersing in 15% H_2O_2 to re-oxidize the surface intentionally. Then the wafers were rinsed with deionized ultrapure water and subsequently dipping in 30% HCl solution to remove the surface oxide layer. Finally, deionized ultrapure water rinse was made shortly to minimize residual Cl atom. After the wet chemical cleaning, a GeO_2 layer was grown at 375 and 490°C in dry oxygen ambience at atmospheric pressure.

3. Results and Discussion

Ge oxide growth on Ge(100) and Ge(111) at 375°C and 490°C with oxidation time were evaluated from spectroscopic ellipsometry (SE) as shown in Figs. 1 and 2. With considering the measurement error of the oxide thickness about 0.2nm, the thermal oxidation rate on Ge surface at 375°C was almost similar between two different crystallographic orientations, which indicates no significant difference in Ge surface reaction rate with O_2 molecules between Ge(100) and (111) surfaces. On the other hand, the growth of Ge oxide on Ge(100) at 490ºC is faster than that of (111) case in the Ge oxide thickness region thicker than 5nm. The faster oxidation rate of Ge(100) than Ge(111) is presumably caused by the easily penetration of oxygen molecule with a size of 0.271 nm through to the (100) surface which has atom void sizes of ~0.3nm [4].

The chemical bonding features of thermally grown GeO_2 on Ge(100) were evaluated by X-ray photoelectron spectroscopy (XPS) under monocromatized AlKα radiation (hv=1486.6eV). Figures 3 and 4 show $Ge3d_{5/2}$ and valence band spectra for the samples after thermal oxidation at ~490°C for 2min (~2.6nm) and 120min (~11.0nm). From the Ge3d signals for the sample after 2nm oxidation, Ge sub-oxide components (~31.5eV in binding energy) were clearly observed. For the sample after 120min oxidation, asymmetric Ge3d signals due to the GeO_x were observed, which indicates the formation of low-oxidized Ge bonding units in the Ge oxide, while Ge signals due to the Ge substrate were significantly decreased. And, no change in the signal intensity of sub-oxide components with increasing photoelectron take angle from 30 to 90º was confirmed, which means the presence of sub-oxide bonding units in the ~490°C grown Ge-oxide. In addition, signals due to sub-oxide bonding units were observed in the valence band spectrum around 3eV for 11.0nm-thick GeO_2. These results suggest that oxygen deficient sites were also generated in the Ge oxide during thermal oxidation.

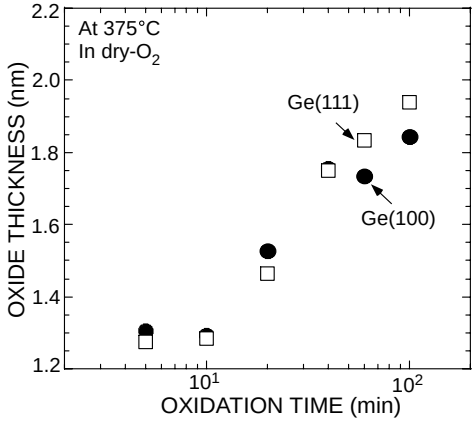

Fig. 1 Ge oxide growth on Ge(100) and on Ge(111) by thermal oxidation at 375°C in pure dry-O_2 ambience.

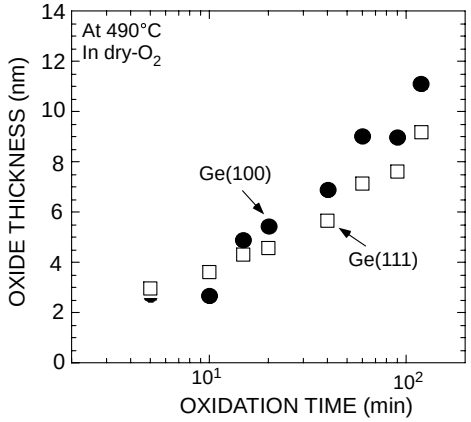

Fig. 2 Ge oxide growth on Ge(100) and on Ge(111) by thermal oxidation at 490°C in pure dry-O_2 ambience.

The valence band offset between Ge oxide and Ge(100) was roughly estimated from the deconvolution of valence band signals for GeO_2 on Ge(100) as shown in Fig. 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 signals, the valence band offset at the GeO_2/Ge interfaces was estimated to be ~4.0eV being in consistency with reported values of GeO_2/Ge form by UV-O_3 oxidation [5], and electronic states of sub-oxides are observed within 2.3eV above the top of the valence band of GeO_2.

To eliminate the oxygen deficiency, GeO_2 layer grown at ~490°C for 120min was annealed at 375°C for 30min in dry oxygen ambience at atmospheric pressure. After O_2 annealing, no change in the GeO_2 thickness was confirmed from SE. In Fig. 6, $Ge3d_{5/2}$ spectra show that the Ge sub-oxide signals especially Ge^{3+} components was clearly decreased. And, we also observed the reduction of valence band signals due to the Ge sub-oxide component after O_2 annealing. From these results, low temperature anneal in oxygen ambience can improve the quality of Ge-oxide network.

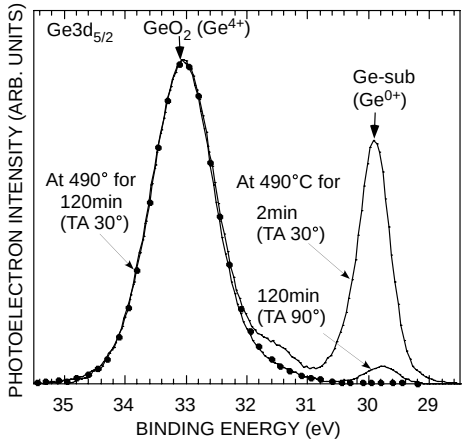

Fig. 3 $Ge3d_{5/2}$ spectra taken for thermally grown GeO_2 on Ge(100) surface at 490°C for 2 and 120min which were measured at two different photoelectron take-off angles at 90º and 30º. The intensity normalization was made by Ge3d signals due to the GeO_2 (Ge^{4+}) component.

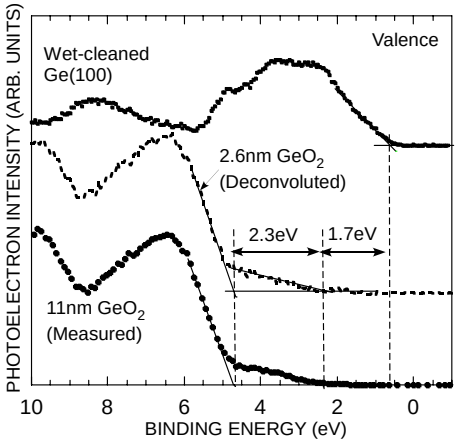

Fig. 5 Deconvoluted valence spectra for ~ 2.6nm-thick and measured valence band spectra for ~11nm-thick Ge oxide on Ge(100). The photoelectron take-off angle was set at 30º.

Conclusions

For Ge oxidation at 375°C, almost no crystallographic orientation dependence on the oxidation rate was observed. And, the growth of Ge oxide on Ge(100) at 490ºC is faster than that of (111) case in the Ge oxide thickness region over 5nm. From the XPS analysis, the oxygen deficient region in the GeO_2 grown by thermal oxidation at 490ºC was observed. And lower temperature anneal at around 375ºC after GeO_2 growth was effective to eliminate the oxygen deficiency.

Acknowledgements

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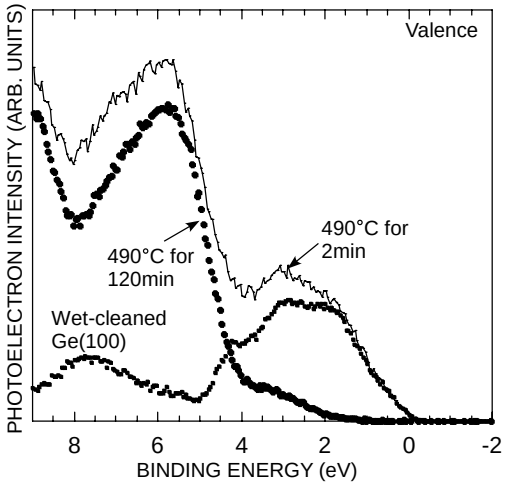

Fig. 4 Valence band spectra at ~ 490°C for 2 and 120min which were measured at a photoelectron take-off angle of 30º. The intensity was normalized by Ge3d signals due to the GeO_2 (Ge^{4+}) component.

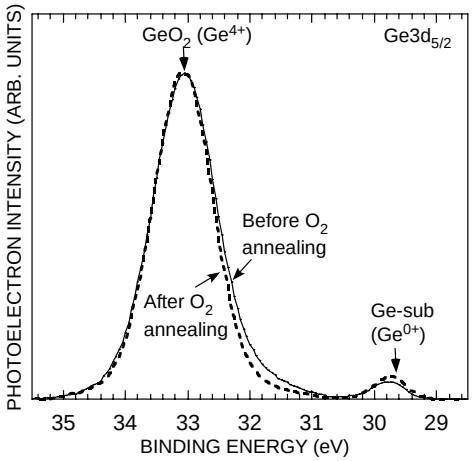

Fig. 6 $Ge3d_{5/2}$ spectra taken for thermally grown GeO_2 on Ge(100) surface at 490°C for 120min before and after O_2 annealing at temperature of 375°C for 30min. The photoelectron take-off angle was set at 90º.