**Ge 基板のラジカル酸化で形成した GeO₂膜質の熱処理による変化**

**Thermal annealing effect on the quality of GeO₂ film formed by radical oxidation of Ge**

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[Introduction] Low-temperature radical oxidation of Ge has been studied to achieve the superior Ge/GeO₂ interface due to higher reactivity of O radical [1,2]. In previous study, we have investigated the GeO₂ growth mechanism in O radical atmosphere, under the assumption that the O radicals are diminished exponentially in the GeO₂ film [3]. However, questions still remained on bulk properties of thin GeO₂ film grown at low temperature despite of its importance. In this study, bulk properties of GeO₂ film grown by radical oxidation are investigated in terms of the chemical shift between Ge⁰⁺ and Ge⁴⁺ in thin GeO₂ region, and the effects of additional annealing on Ge chemical shifts are discussed.

[Experimental] The HF-last Ge(100) is oxidized with O radicals which is filtered with quartz orifice and generated by microwave O₂ plasma at 350 °C. The GeO₂ thickness and Ge 3d chemical shift are determined by x-ray photoemission spectroscopy. Diluted H₂O (5%) solution was used to measure the etching rate of GeO₂ film. In order to investigate the effect of additional annealing on radical oxidized GeO₂ film, the GeO₂/Ge samples were annealed at low temperature (350 °C) for 30 s in vacuum (~2×10⁻⁸Pa).

[Results and Discussion] Fig. 1 shows the measured Ge 3d chemical shifts as a function of GeO₂ film thickness. The peak shifts of GeO₂ grown by radical oxidation indicate that the concentration of suboxide (GeO₃) becomes higher as GeO₂ thickness decreases (thinner than 3 nm). It is interesting to see that chemical shift of GeO₂ has changed to Ge⁴⁺ by additional annealing. It suggests that internal structure of Ge-O bonding is varied by additional annealing. As shown in Fig. 2, the etching rate of annealed GeO₂ film becomes faster compared to as-oxidized one. Since there is no significant change in the thickness of GeO₂ film, the enhanced etching rate of annealed GeO₂ film is possibly due to the dominant Ge⁴⁺ states, which is more soluble in water than Ge²⁺ or Ge³⁺. Two results are quite consistent with each other. The gradual peak shifts in thinner region (tₐox<1 nm) in Fig. 1 suggest the existence of the transition layer on Ge. As reported by Zhang et al.[4], it suggests that the GeO₂ is dominant in this thickness region. In tₐox>1.5nm region, however, the peak shifts becomes closer to Ge⁴⁺ state by annealing. Since it is clear that the radicals are diminished during oxidation, oxygen molecules may be created from recombination of O radicals inside the film. It is thought that these residual oxygen molecules may react with suboxide during annealing even in vacuum.