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Ge 基板のラジカル酸化で形成した GeO_2 膜質の熱処理による変化

Thermal annealing effect on the quality of GeO_2 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/GeO_2 interface due to higher reactivity of O radical [1,2]. In previous study, we have investigated the GeO_2 growth mechanism in O radical atmosphere, under the assumption that the O radicals are diminished exponentially in the GeO_2 film [3]. However, questions still remained on bulk properties of thin GeO_2 film grown at low temperature despite of its importance. In this study, bulk properties of GeO_2 film grown by radical oxidation are investigated in terms of the chemical shift between Ge^{0+} and Ge^{4+} in thin GeO_2 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 O_2 plasma at 350 °C. The GeO_2 thickness and Ge 3*d* chemical shift are determined by x-ray photoemission spectroscopy. Diluted H_2O (5%) solution was used to measure the etching rate of GeO_2 film. In order to investigate the effect of additional annealing on radical oxidized GeO_2 film, the GeO_2/Ge samples were annealed at low temperature (350 °C) for 30 s in vacuum (~2×10^{-3}Pa).

[Results and Discussion] **Fig. 1** shows the measured Ge 3*d* chemical shifts as a function of GeO_2 film thickness. The peak shifts of GeO_2 grown by radical oxidation indicate that the concentration of suboxide (GeO_x) becomes higher as GeO_2 thickness decreases (thinner than 3 nm). It is interesting to see that chemical shift of GeO_2 has changed to Ge^{4+} 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 GeO_2 film becomes faster compared to as-oxidized one. Since there is no significant change in the thickness of GeO_2 film, the enhanced etching rate of annealed GeO_2 film is possibly due to the dominant Ge^{4+} states, which is more soluble in water than Ge^{2+} or Ge^{3+}. Two results are quite consistent with each other. The gradual peak shifts in thinner region (t_{ox}<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 GeO_x is dominant in this thickness region. In t_{ox}>1.5nm region, however, the peak shifts becomes closer to Ge^{4+} 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.

[References] [1] M. Kobayashi *et al.*, J. Appl. Phys. 106 (2009) 104117; [2] A. Wada *et al.*, Jap. J. Appl. Phys. 51 (2012) 125603; [3] W. Song *et al.*, SSDM 2012, pp. 745; [4] R. Zhang *et al.*, IEDM 2012, pp. 371.

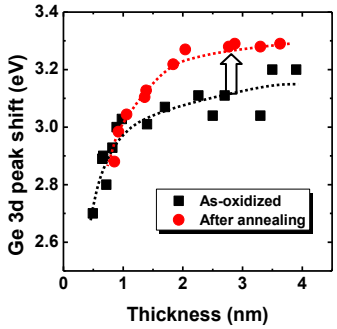

Fig. 1: Ge 3*d* chemical peak shift as a function of oxide thickness for thin region (annealed in vacuum).

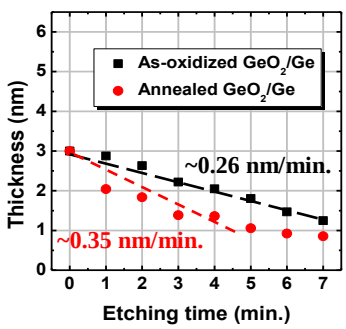

Fig. 2: Etching rate of GeO_2/Ge. In vacuum annealing, the etching rate becomes faster.