How Ge atoms behave in thermal oxidation of SiGe?

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1. Introduction:

A slight and selective Si oxidation of SiGe, achieved by depositing and annealing a $YSiO_x$ film on it, has been proposed to improve dielectric/SiGe interface quality [1]. How Ge behaves in this process remains unclarified, which is a key to further improvement of SiGe gate stacks. This work discusses this issue by paying attention to Ge movement at SiGe interface based on TEM, SIMS, Raman and TDS measurements.

2. Results and discussion

Since SiGe oxidation through $YSiO_x$ is too slight, we have paid attention to the thermal oxidation in 1atm O_2 in which similar selective oxidation of Si was also observed after the initial stage [2]. **Fig. 1** shows TEM and SIMS results of SiGe oxidized at 750C for 1h. A Ge-rich interfacial SiGe layer (GRIL) is detected on SiGe surface while no obvious GeO_x is observed near there. The SiGe surface in this process has been studied by Raman [3], results are re-analyzed in **Fig. 2**. A new Ge peak with a positive shift higher than that of bulk Ge suggests that Ge is epitaxially precipitated with a compressive stress in GRIL. In addition, we also paid attention to the reaction between GeO_2 and SiGe by observing GeO desorption, as we recently found that Ge was oxidized more easily by GeO_2 than by O_2 [4]. No GeO desorption is observed from GeO_2/SiGe at low temperature as that in GeO_2/Ge. Instead, a peak appears at higher temperature, similar to that in GeO_2/Si (**Fig. 3**). With GeO desorption, GeO_2 is reduced, SiO_2 is newly formed and SiGe surface becomes Ge-rich (XPS, not shown). Thus, the reaction is $2GeO_2+SiGe=2GeO\uparrow+SiO_2+Ge$, indicating that Ge in SiGe is even not oxidized by GeO_2.

We next discusses Ge kinetics in SiGe oxidation energetically. SiGe is quite different from Si or Ge. As Si-Ge bond is stronger than Ge-Ge but weaker than Si-Si, the activation energy of Ge oxidation in SiGe should be enhanced while that of Si one should be lowered comparing with that in Ge and Si. Meanwhile, SiO_2 is thermodynamically more stable than GeO_2. Thus, SiO_2 should be preferentially generated. If O_2 is excess, Ge is also oxidized as that in initial stage. But if O_2 supply is limited and not enough, Ge is not oxidized, such as the cases with thick oxide, with a $YSiO_x$ film and with low P_{O2}[5]. In a word, no matter how to achieve selective oxidation of SiGe, the Ge kinetics is the same, that is epitaxial precipitation.

3. Conclusions

We conclude that Ge-rich SiGe layer is epitaxially grown at the interface associated with the selective oxidation of Si in SiGe. The remaining issue is whether this will induce interface states in SiGe gate stack formation or not. This will be clarified in future work.

References: [1] C-T. Chang et al, Tech. Dig. IEDM(2015). [2] Y. Zhang et al, JAP,**106**, 063508 (2009). [3]Y. Noma et al, Tech. Dig. EDTM(2018). [4]X. Wang *et al*, APL **111**, 052101 (2017). [5] W. Song et al, JAP **122**, 185301 (2017).

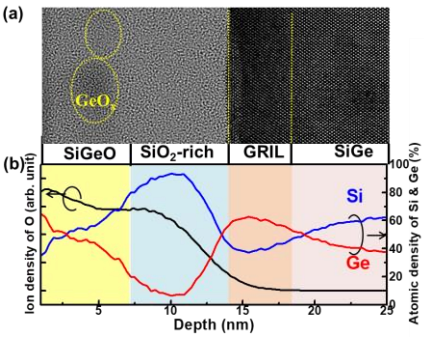

Fig.1 (a) TEM image and **(b)** SIMS profile of SiGe oxidized at 750C for 1h. A Ge-rich interlayer is detected on SiGe substrate and no obvious GeOx is observed near there.

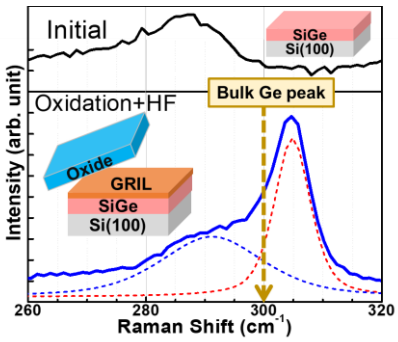

Table.I Raman spectrum of SiGe before and after oxidation at 750 C for 1h. A new peak with a positive shift appears after oxidation.

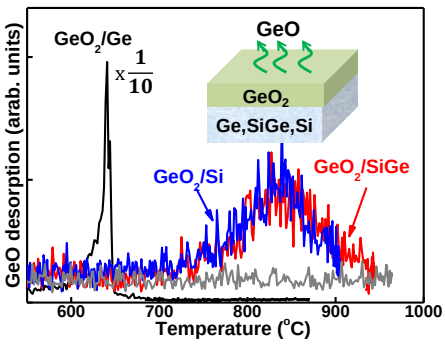

Fig.3 GeO desorption from GeO_2/Ge, GeO_2/Si and GeO_2/SiGe stacks. The same peak is observed from both GeO_2/SiGe and GeO_2/Si at about 850°C, which is different from that from GeO_2/Ge at about 650°C.