

# Impact of “struggle for oxygen” at oxidized interface on SiGe gate stacks

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## Abstract

This work discusses the impact of oxidation kinetics of SiGe on the interface degradation by paying attention to the reaction between  $\text{GeO}_2$  and SiGe. Unlike in  $\text{GeO}_2/\text{Ge}$ , no reaction between  $\text{GeO}_2$  and Ge occurs in  $\text{GeO}_2/\text{SiGe}$  and at the oxidized SiGe interface. Insufficient oxygen passivation of Ge on Ge-rich SiGe surface, as a result of “struggle for oxygen” between Si and Ge in oxidation, may degrade the interface quality of SiGe gate stacks.

## 1. Introduction

High-Ge content SiGe pFETs are intensively under investigation for higher performance CMOS [1]. A most critical point is that the oxidation of SiGe is considerably different from that of Si or Ge:  $\text{GeO}_x$  is mixed in  $\text{SiO}_2$  and Ge-rich layer is precipitated on SiGe surface, leading to a poor interface quality [2]. In  $\text{GeO}_2/\text{Ge}$  stack, the oxygen vacancy ( $V_O$ ) generated by  $\text{GeO}_2/\text{Ge}$  reaction is responsible for the interface degradation [3]. This view has also been considered to explain the poor interface in SiGe gate stacks [4]. To shape well-behaved SiGe gate stacks, it is crucial to understand the interface reaction very correctly. Therefore, the objective of this work is to clarify what occurs at oxidized SiGe interface, and to discuss the intrinsic origin of the interface degradation in SiGe oxidation.

## 2. Experiments and results

The interface reactions between  $\text{GeO}_2$  and SiGe was

studied by the thermal desorption spectroscopy (TDS) measurement. Two sets of samples were prepared. i) 9-nm-thick  $\text{GeO}_2$  were deposited by sputtering on  $\text{Ge}(001)$ ,  $\text{Si}(001)$ ,  $\text{SiO}_2(100\text{nm})/\text{Si}$  and  $\text{Si}_{0.6}\text{Ge}_{0.4}$ , and ii) SiGe was oxidized in 1atm  $\text{O}_2$  at 650-750°C for 5-120 min.

### (1) GeO desorption in $\text{GeO}_2/\text{SiGe}$ , $\text{GeO}_2/\text{Si}$ , $\text{GeO}_2/\text{Ge}$ and $\text{GeO}_2/\text{SiO}_2/\text{Si}$

GeO desorption induced by the interface reaction in  $\text{GeO}_2/\text{Ge}$  was clearly observed at relatively low temperature as reported [3]. GeO desorption in  $\text{GeO}_2/\text{SiGe}$ ,  $\text{GeO}_2/\text{Si}$  and  $\text{GeO}_2/\text{SiO}_2/\text{Si}$  stacks was inspected as shown in Fig. 1. No GeO desorption is observed from  $\text{GeO}_2/\text{SiGe}$  at low temperature region (LT, 650°C). Instead, a GeO desorption peak appears at higher temperature (HT, 850°C). Interestingly, almost the same amount of GeO desorption at HT is observed from  $\text{GeO}_2/\text{Si}$ , but not from  $\text{GeO}_2/\text{SiO}_2$ . To understand what occurs in  $\text{GeO}_2/\text{SiGe}$  reaction, XPS characterization was carried out at each processing step. Fig. 2 shows that  $\text{SiO}_2$  is newly formed with GeO desorption, and that  $\text{GeO}_2$  is reduced and SiGe surface becomes Ge-rich. These results strongly suggest that HT GeO desorption in  $\text{GeO}_2/\text{SiGe}$  does not result from the reaction between  $\text{GeO}_2$  and Ge but from that between  $\text{GeO}_2$  and Si. Furthermore, note that the integrated GeO desorption intensity from  $\text{GeO}_2/\text{SiGe}$  at HT was slightly less than 50% of that from  $\text{GeO}_2/\text{Ge}$  at LT ( $\text{GeO}_2 + \text{Ge} = 2\text{GeO}\uparrow$ ). It suggests the following reaction:  $2\text{GeO}_2 + \text{SiGe} = 2\text{GeO}\uparrow + \text{SiO}_2 + \text{Ge}$ . Moreover, the remaining  $\text{GeO}_2$  means that this reaction may automatically stop as the process proceeds.

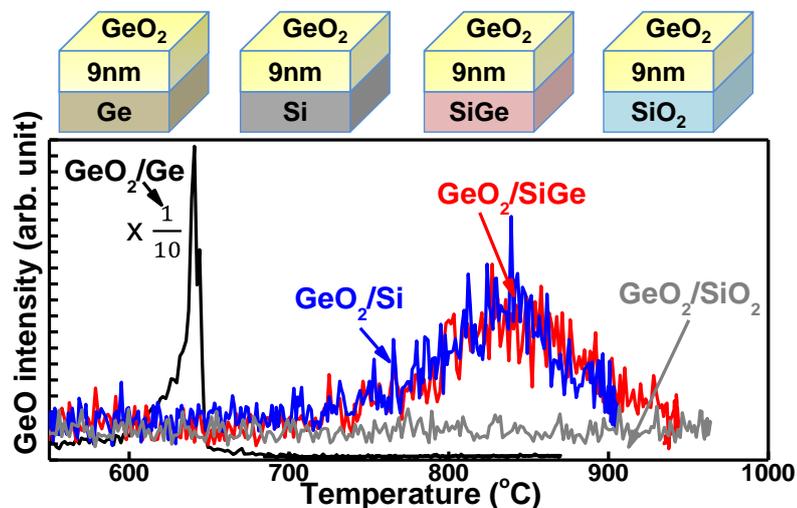


Fig. 1 TDS results of GeO from  $\text{GeO}_2/\text{Ge}$ ,  $\text{GeO}_2/\text{Si}$ ,  $\text{GeO}_2/\text{SiGe}$  and  $\text{GeO}_2/\text{SiO}_2(100\text{nm})/\text{Si}$ . The same amount of GeO desorption is observed from both  $\text{GeO}_2/\text{SiGe}$  and  $\text{GeO}_2/\text{Si}$  at about 850°C, which is different from that from  $\text{GeO}_2/\text{Ge}$  at about 650°C. No GeO desorption occurs from  $\text{GeO}_2/\text{SiO}_2/\text{Si}$  stacks.

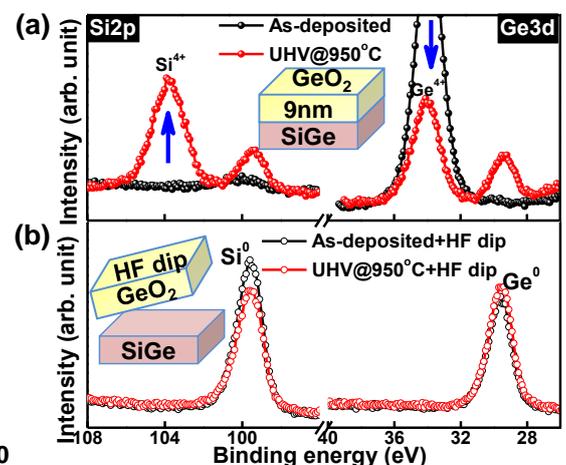
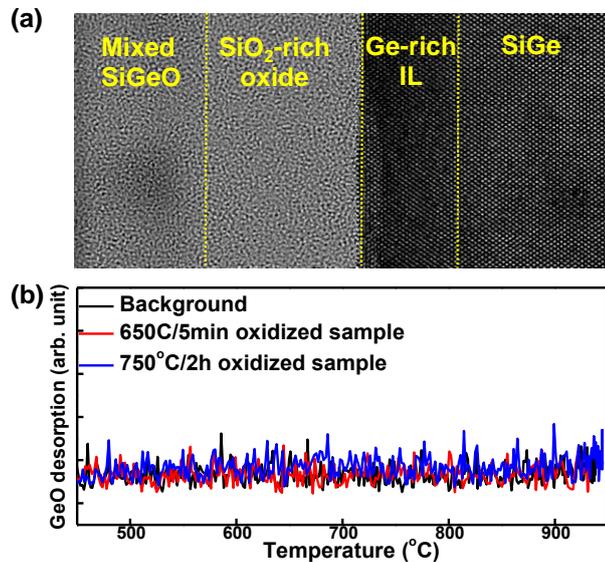


Fig. 2 XPS results of (a)  $\text{GeO}_2/\text{SiGe}$  stacks and (b) their SiGe surface (removing oxide by HF) before and after UHV annealing at 950°C. After UHV annealing,  $\text{SiO}_2$  is newly formed,  $\text{GeO}_2$  is reduced and SiGe surface becomes Ge rich.

## (2) GeO desorption vs. Ge-rich layer formation in SiGe oxidation

Next, GeO desorption in thermally oxidized SiGe stacks was investigated. The structure of oxidized SiGe stacks has been understood that a mixed oxide of  $\text{GeO}_x$  with  $\text{SiO}_2$ , followed by a Ge-rich layer, were formed on SiGe surface by XPS [2] and Raman spectrum [5] in our previous work. In the present work, X-TEM image in **Fig. 3(a)** together with SIMS results (not shown) demonstrate that a Ge rich interfacial layer (IL) with a crystalline structure is formed on SiGe surface, and  $\text{GeO}_x$  is mixed with  $\text{SiO}_2$  mainly near the oxide surface. **Fig. 3(b)** shows no GeO desorption observed at both *LT* and *HT* regions in oxidized SiGe samples with two different oxidation conditions.



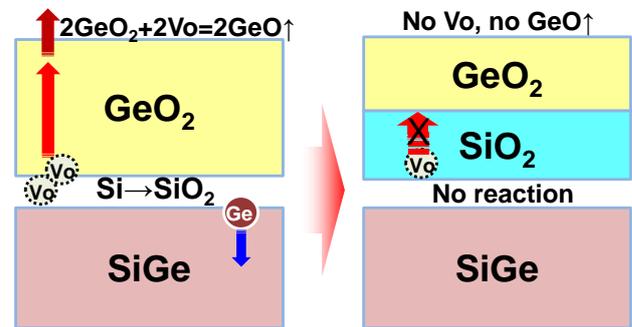
**Fig. 3** (a) X-TEM images of SiGe sample oxidized at 750°C for 2h. A Ge-rich interfacial layer is formed between SiGe and  $\text{SiO}_2$ -rich oxide, and  $\text{GeO}_x$  is mainly mixed near the oxide surface. (b) TDS results of SiGe samples oxidized at 650°C for 5min and 750°C for 2h. No GeO desorption is observed in both cases up to 950°C in UHV annealing.

## 3. Discussion

We recently found that Ge was oxidized mainly by  $\text{GeO}_2$  rather than by  $\text{O}_2$  molecular after the initial oxidation stage [6]. In case of SiGe, the activation energy of Ge oxidation by  $\text{GeO}_2$  should be enhanced due to the higher bond energy of Si-Ge than Ge-Ge. Meanwhile, the reaction between  $\text{GeO}_2$  and Si is thermodynamically more favorable than that between  $\text{GeO}_2$  and Ge. Therefore, *LT*  $\text{GeO}_2$ -Ge reaction is unlikely to occur, instead, *HT*  $\text{GeO}_2$ -Si reaction occurs in  $\text{GeO}_2$ /SiGe. Concerning kinetics of *HT* GeO desorption in Fig. 1, the same amount of GeO desorption in  $\text{GeO}_2$ /SiGe as in  $\text{GeO}_2$ /Si implies that this process is not in a reaction limit at the interface but in a diffusion limit in  $\text{GeO}_2$ . Since GeO desorption requires  $\text{V}_\text{O}$  diffusion from the interface to  $\text{GeO}_2$  surface [3], and it is well known that  $\text{V}_\text{O}$  diffusion in  $\text{SiO}_2$  is quite difficult [7], *HT* GeO desorption will be suppressed in  $\text{GeO}_2$ /SiGe case, as schematically shown in **Fig. 4**. This

view also explains why no GeO desorption is observed in thermally oxidized SiGe gate stacks.

Finally we would like to discuss why the interface is poor in spite of no reaction between  $\text{GeO}_2$  and SiGe in thermally formed gate stacks. Generally speaking, Ge oxidation is kinetically quicker while Si one is thermodynamically more stable. In case of SiGe, Si oxidation may become easier while Ge become harder as indicated by reaction with  $\text{GeO}_2$ . Thus, Si is preferentially oxidized after the initial oxidation, and Ge is diffused into backward, forming Ge rich IL. This means the surface of Ge rich layer is not fully oxygen-terminated, and it is likely that oxide-SiGe interface has many Ge dangling bonds. Thus, in order to make good SiGe gate stacks, the oxidation of SiGe surface should be carefully minimized by using process and/or materials,



**Fig. 5** Schematics of reaction and diffusion in  $\text{GeO}_2$ /SiGe in UHV annealing. The reaction at  $\text{GeO}_2$ /SiGe interface should be:  $\text{SiGe} = \text{SiO}_2 + 2\text{V}_\text{O} + \text{Ge}$ . Generated  $\text{V}_\text{O}$  diffuses through  $\text{GeO}_2$  and GeO desorbs from surface, while Ge diffuses into substrate with  $\text{SiO}_2$  formation. The reaction is suppressed once certain amount of  $\text{SiO}_2$  is formed as  $\text{V}_\text{O}$  diffusion in  $\text{SiO}_2$  is quite hard.

## 4. Conclusion

No reaction of  $\text{GeO}_2$  with Ge at low temperature but appreciable one of  $\text{GeO}_2$  with Si in SiGe at high temperature have been observed in  $\text{GeO}_2$ /SiGe gate stacks. This reaction automatically stops in  $\text{SiO}_2$  formation. Thus, in thermally oxidized samples, Ge-rich IL was formed between  $\text{SiO}_2$ -rich oxide and SiGe. Ge-rich IL resulted from the “struggle for oxygen” between Si and Ge at the interface is not fully O-terminated and should be the dominant origin of the interface states. In order to achieve well-behaved gate stacks, the surface oxidation of SiGe should be minimized.

## Acknowledgment

This work was partly supported by JSPS Grant-in-Aid for Scientific Research (A).

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