

# Impact of reaction kinetics at GeO<sub>2</sub>/Si for high-performance SiGe gate stacks

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## Abstract

An interface layer formation kinetics of SiGe gate stack was studied through a reaction at GeO<sub>2</sub>/Si interface. Although it is understandable that SiO<sub>2</sub> formation is thermodynamically favorable in SiGe oxidation, it is not sure whether the perfectly preferential SiO<sub>2</sub> formation (no Ge oxide formation) is possible or not, and how Ge behaves in that case. This paper discusses above two issues experimentally and thermodynamically.

## 1. Introduction

In the next generation high-performance Si-CMOS, tensile-strained Si *n*MOSFETs and compressively strained SiGe *p*MOSFETs are expected [1]. The interface control of high-Ge-content SiGe is a critical issue, because it is very difficult to prepare a high-quality SiGe gate stacks due to the GeO<sub>x</sub> mixing in SiO<sub>2</sub> [2]. This paper discusses the reaction kinetics of GeO<sub>2</sub> with Si, and report how Ge behaves at the interface and how to prepare SiO<sub>2</sub>/SiGe gate stacks.

## 2. Sample structure

The key point in this work is to understand how GeO<sub>2</sub> is reduced to metallic Ge through the GeO<sub>2</sub>-Si interaction. It is, however, difficult to characterize metallic Ge atoms in the GeO<sub>2</sub>/SiGe system, particularly with XPS, because the chemical shift of Ge in SiGe is too small to differentiate between SiGe and Ge (~0.1 eV) and the peak intensity of reduced Ge is much smaller than that of Ge in the substrate. Therefore, the GeO<sub>2</sub>/Si system was employed to separate the reduced Ge from substrate Ge with XPS.

GeO<sub>2</sub> thin film (~5 nm) was deposited on the HF-last Si surface by rf-sputtering, followed by annealing in the UHV (<10<sup>-7</sup> Pa) at 950°C. Then, samples were dipped in 5% HF solution for 1 min to remove all residual oxide, and were further dipped in the diluted H<sub>2</sub>O<sub>2</sub> solution (0.5%, 1 min.) to selectively remove precipitated Ge on the surface. Finally, both w/ and w/o H<sub>2</sub>O<sub>2</sub> dipped samples were examined by XPS with regard to Ge and Si.

## 3. Results

### (1) Metallic Ge formation at the interface

Fig. 1 schematically shows the possible sample structures for (a) as-deposited, (b) as-annealed with HF, and (c) as-annealed with HF and H<sub>2</sub>O<sub>2</sub> treatments. Since no GeO desorption was observed from in GeO<sub>2</sub>/Si stack by TDS (data not shown), metallic Ge atoms should precipitate at the interface or diffuse into Si substrate. The difference between (b) and (c) was investigated as a function of the initial GeO<sub>2</sub> thickness to differentiate precipitated Ge on the surface from diffused Ge in Si. In the XPS analysis, the Ge2*p*<sub>3/2</sub> spectrum was mainly employed, because it is much more surface sensitive

than the Ge3*d* conventionally used.

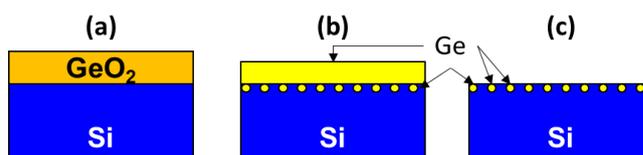


Fig. 1. (a) As-deposited GeO<sub>2</sub>/Si. (b) As-annealed GeO<sub>2</sub>/Si stack with HF treatment. (c) As-annealed GeO<sub>2</sub>/Si stack with HF and further treated with H<sub>2</sub>O<sub>2</sub>.

Fig. 2 shows the GeO<sub>2</sub>/Si stack change from Fig. 1(a) to (b) by the UHV annealing. Two changes are noted. One is that the GeO<sub>2</sub> is mainly converted to SiO<sub>2</sub>. The other is that the metallic Ge newly appears at ~29.8 eV. Since this peak intensity was actually very small, the metallic Ge formation was quantified using Ge2*p*<sub>3/2</sub> peaks in Fig. 2(b). These two facts clearly indicate a dramatic interaction at GeO<sub>2</sub>/Si interface.

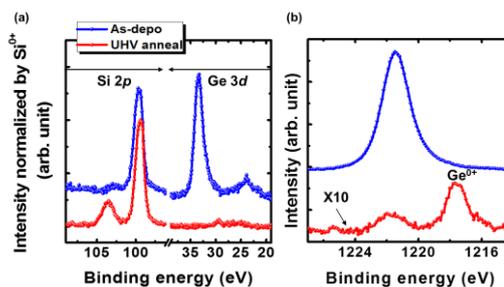


Fig. 2. Si and Ge spectrum of as-deposited (blue) and UHV-annealed (red) GeO<sub>2</sub> (3.3 nm)/Si. (a) Si2*p* and Ge3*d*. (b) Ge2*p*<sub>3/2</sub>. Metallic Ge is clearly observed.

### (2) Two kinds of metallic Ge at the interface

It is expected that two kinds of metallic Ge in Fig. 2(b) may exist. One is the precipitated Ge on Si and the other is diffused Ge in Si. From the viewpoint of gate stack properties, the position of metallic Ge is critically important, because it is directly related to electrical properties of gate stacks.

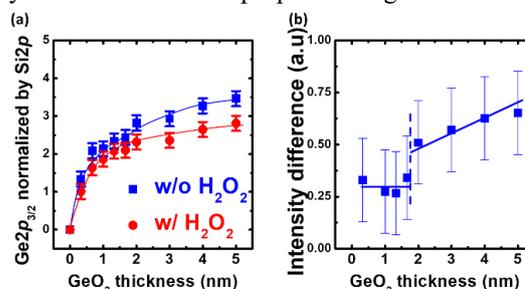


Fig. 3. (a) Ge peak intensity – GeO<sub>2</sub> thickness plot of samples in Fig. 1(b) and (c). Blue solid squares indicate Ge<sup>0+</sup> intensities without H<sub>2</sub>O<sub>2</sub> treatment, while red solid circles are those with further treatment in diluted H<sub>2</sub>O<sub>2</sub>. (b) Intensity difference of blue and red lines in (a). Around 1.8 nm, a distinct jump is observed.

Fig. 3(a) shows Ge XPS results both w/o H<sub>2</sub>O<sub>2</sub> and w/H<sub>2</sub>O<sub>2</sub>,

of as-annealed with HF (Fig.1 (b)). The  $x$ -axis and  $y$ -axis represent the initial  $\text{GeO}_2$  thickness and  $\text{Ge}^{0+}$  peak ( $\text{Ge}2p_{3/2}$ ) intensity normalized by each  $\text{Si}^{0+}$  peak, respectively. The Ge peak intensities w/o and w/  $\text{H}_2\text{O}_2$  etching are shown by blue solid squares and red solid circles, respectively.

A comparison between blue and red curves suggests two different regions with regard to the initial  $\text{GeO}_2$  thickness. In the very thin (below  $\sim 2$  nm)  $\text{GeO}_2$  region, almost no Ge peak intensity decrease is observed with  $\text{H}_2\text{O}_2$ . It indicates that no metallic Ge remains on the substrate surface in this case. While the  $\text{GeO}_2$  thickness becomes thicker above  $\sim 2$  nm, the intensity difference is considerably enhanced. In this region, it is understandable that both Ge diffusion in Si and Ge precipitation on Si occur simultaneously. Fig. 3(b) shows the intensity difference between blue and red points in (a), and indicates a qualitative change at  $\sim 1.8$ -nm-thick  $\text{GeO}_2$  on Si.

#### 4. Discussion

##### (1) Analysis of metallic Ge diffusion into Si

For thin-Ge/Si system, the intensity ratio is described by

$$\frac{I_{\text{Ge}}^{\text{meas}}}{I_{\text{Si}}^{\text{meas}}} = \frac{I_{\text{Ge}}^{\infty} [1 - \exp(-d / \lambda_{\text{Ge}2p_{3/2}}^{\text{Ge film}})]}{I_{\text{Si}}^{\infty} \exp(-d / \lambda_{\text{Si}2p}^{\text{Ge film}})}, \quad (1)$$

where  $\infty$  denotes the intensity of pure material,  $\lambda$  the inelastic mean free path (IMFP) of a given binding energy. Since  $I_{\text{Ge}}^{\infty} / I_{\text{Si}}^{\infty} = 20.231$  was obtained in our XPS, the thickness ( $d$ ) of thin Ge film can be calculated. For the limited-source diffusion, the concentration profile of Ge is described as follows:

$$C(z, t) = \frac{Q}{\sqrt{\pi Dt}} \exp\left(-\frac{z^2}{4Dt}\right), \quad (2)$$

where  $Q$  is the areal density of total Ge atoms, and  $D$  the diffusion coefficient calculated from the data in ref. [3]. The Ge profile  $C$  in Si substrate was calculated as functions of  $z$  and  $t$ , by assuming that the diffusion source  $Q$  was formed from the initial  $\text{GeO}_2$  thickness. The areal density of Ge with given  $\text{GeO}_2$  thickness and its concentration profile with  $t=30$  s at  $950^\circ\text{C}$  was calculated in Fig. 4. It suggests that Ge atoms mainly diffuse deep into  $\sim 0.5$  nm, regardless of initial quantity of Ge atoms.

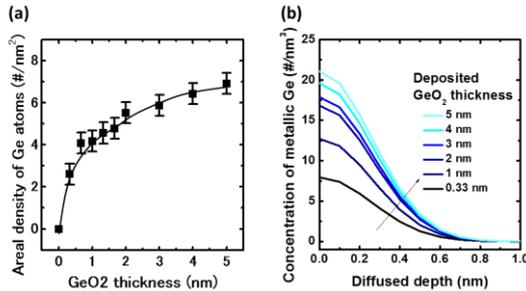


Fig. 4. (a) Areal density of metallic Ge observed in Fig. 3. (b) Concentration profile of metallic Ge atoms diffused into Si substrate ( $t=30$  s), by eq. (2).

##### (2) Ge diffusion into SiGe

Since two different types of Ge could be experimentally verified using the Si substrate, it is worthy to consider Ge diffusion behaviors in case of SiGe substrates. The diffusion flux of metallic Ge,  $J$ , can generally be calculated as follows:

$$J = -D \frac{dC}{dz} = -D \frac{C_z - C_{z=0}}{z - 0}, \quad (3)$$

where  $dC/dz$  depends on the chemical potential gradient and decreases with the increase of  $C_z$ .  $D$  exponentially increases with the increase of Ge fraction in SiGe, as described in Fig. 5(a) [3]. With the fixed quantity of metallic Ge, comparing Ge diffusion flux toward the Si and SiGe substrates ( $J_{\text{Si}}/J_{\text{SiGe}}$ ) suggests that  $J_{\text{SiGe}}$  is  $\sim 100$ -500 times faster than  $J_{\text{Si}}$ , since the diffusion term is more significant than chemical potential gradient in Eq. (3). Therefore, we can expect that the more metallic Ge atoms would diffuse in higher-Ge-content SiGe substrate. Fig. 5(b) shows dramatic decrease of surface concentration of metallic Ge when Ge fraction in SiGe increases, calculated using eq. (3). Considering that metallic Ge atoms that does not diffuse into the substrate become Ge precipitates, it indicates that suppression of Ge precipitation would be stronger for higher-Ge-content SiGe when the same amount of metallic Ge is assumed.

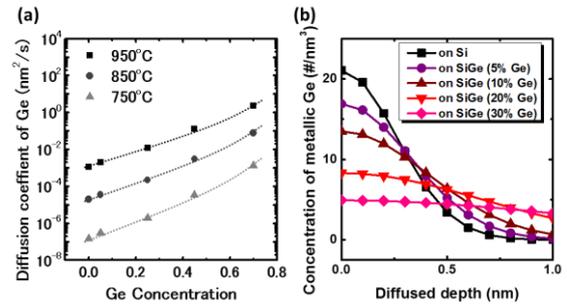


Fig. 5. (a) Ge diffusivity in  $\text{Si}_{1-x}\text{Ge}_x$ . (b) Comparison of metallic Ge profile with the same Ge quantity  $Q$  ( $\sim 6.9$  #/nm²) in Fig. 4(a).

From the discussion above, following three points can be pointed out: (1) Preferential  $\text{SiO}_2$  growth necessarily produces metallic Ge atoms which are accumulated at the interface. (2) Metallic Ge precipitation occurs in case that a critical quantity of Ge exists at the interface. (3) Ge diffusion toward the substrate will be accelerated with an increase of Ge in SiGe substrate.

Finally, it is worthwhile to note one comment. This study employs the UHV-PDA, but even  $\text{O}_2$ -PDA can be used if very low oxygen diffusion dielectrics is pre-deposited [4], since the oxygen potential should be very low at the interface.

#### 5. Conclusion

The reaction kinetics of  $\text{GeO}_2$  with Si substrate was investigated.  $\text{GeO}_2$ -Si interaction causes both  $\text{SiO}_2$  growth and metallic Ge formation. The metallic Ge may diffuse into the substrate and precipitate at the interface. Most importantly, all metallic Ge atoms diffuses into the substrate in very thin  $\text{GeO}_2$  case. According to the simple analysis on the basis of the diffusion kinetics, a considerable amount of Ge atoms diffuse to Si substrate, and the surface Ge concentration is drastically decreased in the SiGe substrate in case of a same amount of metallic Ge atoms on the substrate. It suggests that the perfectly preferential  $\text{SiO}_2$  formation on SiGe is possible by thermodynamic process control.

#### Acknowledgements

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**References** [1] P. Hashemi *et al.*, *VLSI Tech. Dig.* (2015) T16. [2] C. H. Lee *et al.*, *VLSI Tech. Dig.* (2016) p. 36. [3] R. Kube *et al.*, *JAP* **107** (2010) 073520. [4] C.-T. Chang, *et al.*, *IEDM* (2015) p.584.