

# GeO Desorption Mechanism from GeO<sub>2</sub>/Ge Stack Determined by <sup>73</sup>Ge Labeling Technique in Thermal Desorption Spectroscopy (TDS) Analysis

Sheng Kai Wang<sup>1</sup>, Koji Kita<sup>1,2</sup>, Tomonori Nishimura<sup>1,2</sup>, Kosuke Nagashio<sup>1,2</sup> and Akira Toriumi<sup>1,2</sup>

<sup>1</sup>Department of Materials Engineering, The University of Tokyo, <sup>2</sup>JST-CREST  
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

Phone: +81-3-5841-7161, Fax: +81-3-5841-7161 E-mail: skwang@adam.t.u-tokyo.ac.jp

## 1. Introduction

Ge is a promising candidate to replace Si for beyond scaling devices because of its high mobility. However, the GeO desorption from the high- $\kappa$ /Ge system hampers the development of Ge-MOSFETs. Therefore, understanding the GeO desorption mechanism is important for us to realize the interface control of Ge-based devices. For GeO<sub>2</sub>/Ge, we have previously revealed [1-3]; (i) GeO<sub>2</sub> films desorbs mainly in the form of GeO; (ii) between 400~700°C, GeO desorption is not derived from the decomposition of GeO<sub>2</sub> itself but from the reaction between GeO<sub>2</sub> and Ge; (iii) during GeO desorption, Ge substrate is consumed; (iv) GeO desorption follows the reaction GeO<sub>2</sub>+Ge→2GeO(g); (v) GeO desorption is limited by a diffusion process in the GeO<sub>2</sub> films; (vi) the oxygen in the desorbed GeO comes from the GeO<sub>2</sub> surface. But the whole GeO desorption mechanism is still unknown.

In this work, to further clarify the GeO desorption mechanism, <sup>73</sup>Ge labeling technique [4] was used to investigate the GeO desorption from GeO<sub>2</sub>/Ge system.

## 2. Experimental

Two samples, <sup>Nat</sup>GeO<sub>2</sub>/<sup>73</sup>Ge/SiO<sub>2</sub>/Si which was denoted by **A** and <sup>73</sup>GeO<sub>2</sub>/p-<sup>Nat</sup>Ge (100) which was denoted by **B**, were used in our experiments. The superscript Nat is short for Ge with natural abundance. For sample **A**, a 65nm-thick amorphous <sup>73</sup>Ge layer was deposited on SiO<sub>2</sub> (1 $\mu$ m)/Si substrate by thermal evaporation in vacuum. Then, 17 nm-thick <sup>Nat</sup>GeO<sub>2</sub> was sputtered onto the <sup>73</sup>Ge layer. For sample **B**, 12 nm-thick <sup>73</sup>Ge was deposited on HF-last p-<sup>Nat</sup>Ge (100) substrate by thermal evaporation in vacuum. Then it was annealed in 1atm O<sub>2</sub> at 550°C for 15min. The GeO<sub>2</sub> thickness was confirmed to be 17nm by ellipsometry. Considering the physical densities of GeO<sub>2</sub> and amorphous Ge [5], we concluded that the <sup>73</sup>Ge layer was slightly over oxidized to the <sup>Nat</sup>Ge substrate. Since the self diffusivity of Ge in Ge [6] was very small at 550°C, so the GeO<sub>2</sub> layer in sample **B** was mainly <sup>73</sup>GeO<sub>2</sub>. Then, isothermal TDS measurements were performed on A and B at 540°C and 555°C, respectively.

## 3. Results and Discussion

Fig. 1 (a) and (b) show the isothermal TDS spectra of the GeO desorption for sample **A** and **B**, respectively. The spectra are divided into two regions by dash lines which are denoted by region I and region II, respectively. In Fig. 1 (a), the desorption rate of <sup>Nat</sup>GeO in region I is higher than that of <sup>73</sup>GeO, while in Fig. 1 (b), the desorption rate of <sup>73</sup>GeO is higher than that of <sup>Nat</sup>GeO in region I. These results

clearly indicate that the Ge in the desorbed GeO in the region I comes from the GeO<sub>2</sub> surface. Consider the diffusion process in the GeO<sub>2</sub> films during GeO desorption, we conclude the diffusion species should not be the directly diffused GeO molecule from the GeO<sub>2</sub>/Ge interface.

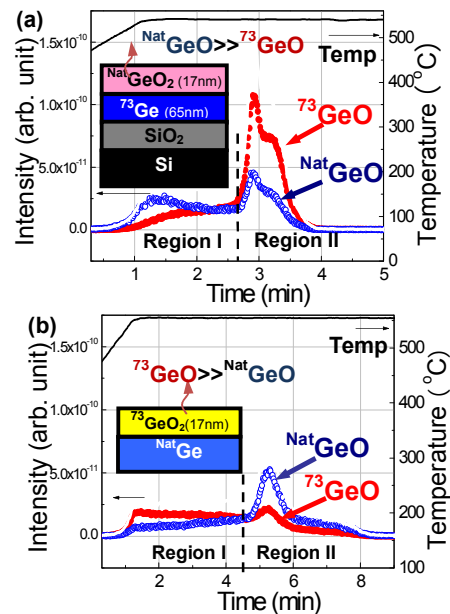
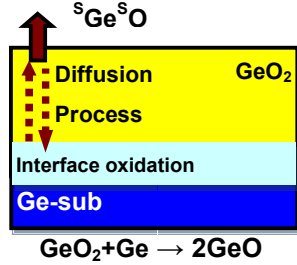


Fig. 1 Isothermal TDS spectra of (a) <sup>Nat</sup>GeO<sub>2</sub>/<sup>73</sup>Ge/SiO<sub>2</sub>/Si (sample **A**) and (b) <sup>73</sup>GeO<sub>2</sub>/Ge (100) (sample **B**). The schematic of each sample is shown in the inset. <sup>Nat</sup>GeO and <sup>73</sup>GeO desorption signals are plotted by blue dots and red dots respectively. The GeO desorption spectra are divided into region I and II by dash lines. In Fig. 1 (b), desorption of <sup>Nat</sup>GeO at the beginning of the spectra is attributed to the intermixing of <sup>73</sup>GeO<sub>2</sub> and the over oxidized <sup>Nat</sup>GeO<sub>2</sub> during sample preparation.

We have already revealed that the GeO desorption is initiated by the GeO<sub>2</sub> surface, and that the GeO desorption is closely related to the reaction at the GeO<sub>2</sub>/Ge interface [3]. But the relationship between the interface reaction and the surface initiated GeO desorption is still unclear.

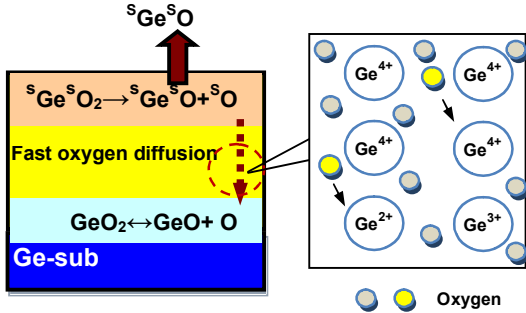
Although the initial GeO<sub>2</sub> thickness in sample **B** is the same as that in sample **A**, and the annealing temperature (555°C) for **B** is a little higher than that for **A** (540°C), the GeO desorption rate from **B** is smaller than that from sample **A**. Since the substrate in sample **A** is amorphous and that in sample **B** is (100)-oriented single crystalline, it is concluded that the GeO desorption is also sensitive to the Ge substrate. When TDS measurements were also performed on Ge (111) substrate, the desorption rate was

much lower than those from Ge (100) and amorphous Ge substrates (data not shown). Such orientation dependent desorption behavior is in a good agreement with the interface oxidation kinetics, strongly indicating that GeO desorption is derived from the interface oxidation reaction.



**Fig. 2** Schematic which summarize the experimental results of GeO desorption from GeO<sub>2</sub>/Ge system so far. <sup>s</sup>Ge and <sup>s</sup>O denote the surface Ge and O, respectively.

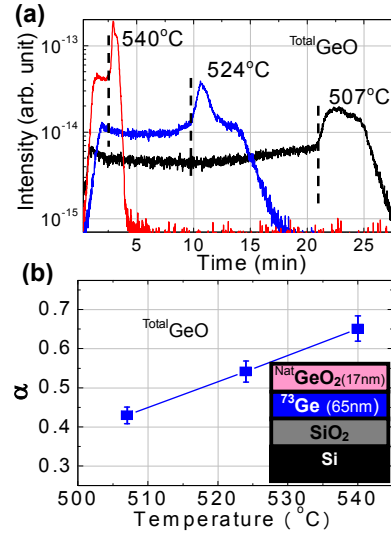
**Fig. 2** depicts the phenomenological picture of GeO desorption on the basis of the results obtained so far [1-3], we have developed a GeO desorption model by mainly considering the interface oxidation and the motion of oxygen, as schematically shown in **Fig. 3**. Once the reaction of GeO<sub>2</sub>+Ge→2GeO takes place at the interface, the interface region becomes oxygen poor. According to theoretical calculation [7], the diffusivity of oxygen is much faster than Ge in GeO<sub>2</sub>. Therefore, oxygen will move to the oxygen-poor region promptly. Resultantly, the oxygen motion will finally form the oxygen poor region at the GeO<sub>2</sub> surface. Compared with the desorption from the GeO<sub>2</sub> network, it should be easier for GeO to desorb from the oxygen-poor surface region prior to the compensative diffusion of oxygen.



**Fig. 3** Schematic of GeO desorption model from GeO<sub>2</sub>/Ge. Oxygen concentration change induced by the interface reaction is a driving force for the atom motion.

On the other hand, it is also necessary to understand the desorption behavior in a macroscopic scale. In region I, GeO desorption is considered to follow a uniform way [2]. However, for the desorption peaks in the region II of the isothermal TDS spectra, as shown in Fig. 1 (a) and (b), they were attributed to the non-uniform desorption with voids formation from the AFM observations [3]. To further discuss this behavior, we define  $\alpha$  by  $\alpha = I_N/I_0$  to evaluate the non-uniform degree of the GeO desorption. Where,  $I_N$  and  $I_0$  are the integration areas of region II and the total area, respectively. **Fig. 4 (a)** shows the isothermal TDS spectra

of GeO desorption from sample A, in which region I and II are divided by dash lines for each temperature. The  $\alpha$  as a function of annealing temperature is shown in **Fig. 4 (b)**. It indicates that lower temperature is more likely to follow the uniform desorption mechanism (a smaller  $\alpha$ ). Since the voids formation in GeO<sub>2</sub> is generally considered harmful to the device performance, we can assess that a lower processing temperature is required to suppress the formation of voids from Fig. 4 (b).



**Fig. 4 (a)** Isothermal TDS spectra of GeO desorption from <sup>Nat</sup>GeO<sub>2</sub>/<sup>73</sup>Ge/SiO<sub>2</sub>/Si stacks at 540 °C, 524 °C and 507°C, respectively. The region I and II are divided by dash lines. **(b)** The  $\alpha$  value as a function of annealing temperature. Note <sup>Total</sup>GeO is the total desorption signal including both <sup>73</sup>GeO and

#### 4. Conclusions

GeO desorption mechanism has been further clarified by using <sup>73</sup>Ge labeling technique. We conclude that the GeO desorption initiates from the GeO<sub>2</sub> surface by using <sup>73</sup>Ge labeling technique. An oxygen diffusion to equilibrate the oxygen potential in the film might make the surface oxygen poor. In addition, two kinds of GeO desorption (uniform and non-uniform) has been demonstrated, and the uniform one is likely occur at lower temperature.

#### References

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