¹⁸O isotope tracing study of GeO Desorption from GeO₂/Ge Structure

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1. Introduction

Ge is a promising candidate to replace Si for future beyond scaling devices because of its high mobility [1]. However, a lack of thermodynamic stability at dielectrics/Ge interface hampers the development of Ge-MOS devices. The GeO desorption from GeO₂/Ge but not from GeO₂/SiO₂/Si structure was previously reported [2]. For GeO₂/SiO₂, no GeO decomposition occurs below 1000°C, while the reaction $GeO_2+Ge=2GeO\uparrow$ occurs for GeO₂/Ge. Although the GeO desorption from the GeO₂/Ge interface occurs at 500~600°C, the detailed GeO desorption mechanism is still unclear.

2. Consumption of Ge substrate in GeO desorption

180 nm-thick GeO_2 was partially sputtered on Ge(100)substrate by using photolithography (as seen in Fig. 1(a)). The as-deposited sample was annealed in high-vacuum from 650~800°C for 30 min. Then the surface and cross sectional profiles of the as-annealed sample in high-vacuum were measured by atomic force microscopy (AFM) (as seen in Fig. 1(b) and (c)). It is clearly shown that the surface of initial Ge is about 100 nm higher than the bottom level of the region which was initially covered with GeO₂. This fact directly indicates that 100 nm-thick Ge was consumed through the reaction with GeO₂. 100 nm is close to the calculation result based on the reaction of $GeO_2+Ge=2GeO\uparrow$ by taking account of densities of Ge and GeO_2 . Thus, the results in **Fig.1(b)** and **(c)** are a direct evidence for the reaction $GeO_2+Ge=2GeO_2$.



Fig. 1. (a) Schemtics of initial and final sample structures. **(b)** AFM surface image of as-annealed sample. **(c)** Cross sectional profile of as-annealed sample.

3. Isotope tracing in GeO desorption

GeO₂ (~35 nm) were deposited by sputtering. The peak

temperature of GeO(g) detected in the thermal desorption spectroscopy (TDS) increases with increasing the initial thickness as shown in **Fig. 2**., in which an activation energy was extracted to be less than 1eV. Note that this value is much smaller than the Ge-O bonding energy (4.7eV) in GeO₂ [3]. A lower activation energy suggests an indirect diffusion such as interstitial- or vacancy-mediated one [4, 5].



Fig. 2. The relationship between TDS peak temperature and oxide thickness.



Fig. 3. TDS spectra of GeO desorption for the sample of thermally grown 15nm-GeO₂ in oxygen-18 ambient.

To further investigate the desorption mechanism of GeO, the TDS spectra of GeO desorption for thermally grown 15nm-GeO₂ in ${}^{18}O_2$ is shown in **Fig. 3**. The similar desorption traces between Ge¹⁸O and Ge¹⁶O indicates that the ratio between ${}^{18}O$ tracer and ${}^{16}O$ is 0.6:0.4 after the mass correction, which was also confirmed by SIMS.

Fig. 4(a) shows the TDS spectra of the GeO desorption in Ge¹⁶O₂(15nm, sputtered)/Ge¹⁶O_{0.8}¹⁸O_{1.2}(15nm, thermally grown)/Ge bi-layer structure. The structure is schematically shown in **(b)**, and the corresponding SIMS depth profiles of the samples as–prepared and annealed in TDS chamber at 530°C and 625°C are shown in **Fig. 4(c)**, **(d)** and **(e)**, respectively. In **Fig. 4(a)**, it is found that the Ge¹⁶O desorption is clearly observed whereas no Ge¹⁸O is



Fig. 4(a) TDS spectra of GeO desorption ... $Ge^{16}O_{2}/Ge^{16}O_{0.8}^{18}O_{1.2}/Ge$ structure, (b) Schematic structure of the as-denosited sample, (d) bi-layer structure. (c) depth profiles of the as-deposited sample, (d) the ones annealed in TDS chamber at 530°C and (e) 625°C. Note the surface profile is subject to an SIMS artifact.

observed in a lower temperature region (530~610°C). At a temperature higher than 610°C, both Ge¹⁶O and Ge¹⁸O desorption are detected. Moreover, the depth profiles in Fig. 4(c) and (d) indicate that only a very small amount of O atoms intermix in the bi-layer at 530°C and almost no ¹⁸O reaches the surface of the bi-layer structure.

Thus, it is concluded the oxygen atom of the desorbed Ge¹⁶O comes from the top Ge¹⁶O₂ layer at the lower temperature. By taking account of the facts that no GeO desorption is observed from the GeO₂ film on Si and that the relatively low activation energy was estimated in the desorption as shown in Fig. 2, we infer that the GeO desorption may be due to the Ge diffusion followed by the reaction with oxygen at the top layer rather than due to "knock-on" type diffusion of the GeO molecule. In fact, Ge atoms are continuously injected from the Ge substrate and can diffuse through the GeO₂ layer in the interstitial- or vacancy-mediated process, and "pick up" oxygen atoms near the surface, followed by desorbing out in the form of GeO. On the other hand, at the higher temperature, SIMS result in **Fig. 4(e)** indicates that the oxygen is totally

intermixed and it is hard to clearly distinguish the diffusion mechanism. The important point is that the actual processing temperature of Ge devices is considered to be within the lower temperature range (< 600°C). The model of GeO desorption is illustrated in Fig. 5. The GeO desorption is not through the simple GeO diffusion process at the actual Ge processing temperatures.



Fig. 5 Schematic pictures of GeO desorption mechanism. (a) In the lower temperature range, the Ge¹⁶O desorption from the top layer is limited by the Ge diffusion through the GeO_2 film. (b) Both $Ge^{16}O$ and $Ge^{18}O$ desorption are observed at higher temperature because the oxygen atoms are totally intermixed.

4. Conclusions

The GeO desorption mechanism in GeO₂/Ge has been studied. It was directly confirmed that Ge substrate was consumed through the GeO desorption. The activation energy of less than 1eV was obtained for the GeO desorption. Furthermore, isotope experiments demonstrated that at the actual Ge processing temperature the diffusion species was not the GeO molecule but Ge atom, which reacted with O at the GeO₂ surface. It was also inferred that the low temperature Ge diffusion was with the help of interstitial or vacancy in GeO2 film because of the relatively low activation energy in the GeO desorption.

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References

- C. O. Chui et al., Tech. Dig. IEDM'03, (2003) 437.
- [2] K. Kita et al., *Jpn. J. Appl. Phys.*, **47** (2008) 2349.
 [3] M. Zacharias et al. *Phys. Rev. B* **52** (1995) 14018.
- A. Seger et al., Phys. Status Solidi., 29 (1968) 455.
- [5] W. Frank et al., Diffusion in Crystalline Solids, (Academic New York), (1984) 64.