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Dry Oxidation of Germanium (100) and (111) Surfaces - Impact of Oxidation Temperature on Ge Oxide Growth -

A. Ohta[1], S. K. Sahari[1], M. Ikeda[1], H. Murakami[1], S. Higashi[1], and S Miyazaki[2]

[1]Grad. School of AdSM, Hiroshima University, Kagamiyama 1-3-1, Higashi-Hiroshima, Hiroshima 739-8530, Japan
Phone: +81-82-424-7648, FAX: +81-82-422-7038, E-mail: semicon@hiroshima-u.ac.jp
[2]Grad. School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Aichi 464-8603, Japan

1. Introduction

Control of interfacial reaction between gate dielectric and Ge channel and the reduction of defects in the gate stack are the most critical issues for the development of Ge-channel MISFETs. Although the high-k dielectric/Ge gate stack is indispensable to achieve EOT scaling down to below 1 nm [1], understanding of the Ge oxidation kinetics is of great importance to fabricate the high-quality dielectric/Ge interface. In particular, a formation of ultrathin GeO_2 layer at high-k/Ge interfaces and the suppression of GeO desorption during the post deposition annealing are thought to be crucial issues to reduce the defect in the gate stack [2, 3]. As for the GeO desorption, it has been clarified that thermal desorption is derived from the reduction reaction at the Ge-oxide/Ge interface [2, 4]. At all rates, the understanding of the oxidation mechanism is very limited because there are few published reports of the thermal oxidation of Ge surface with taking into account of both Ge oxidation and GeO desorption, which is presumably related to the fact that GeO_2 is chemically and thermally unstable in contrast to SiO_2 [5].

In this paper, the influences of the oxidation temperature and the crystallographic orientation on Ge oxide growth have been investigated systematically by using spectroscopic ellipsometry (SE) and x-ray photoelectron spectroscopy (XPS) utilizing monochromatized AlKα radiation (hν = 1486.6 eV).

2. Experimental Procedure

Ge (100) and (111) wafers with a resistivity of ~20 Ω·cm were first dipped in de-ionized pure water to dissolve the native oxide and followed by immersing them in 15% H_2O_2 to re-oxidize the surface intentionally. Then, the wafers were rinsed with de-ionized pure water and subsequently dipped in 30% HCl solution to remove the surface oxide layer. Finally, the Ge wafers were shortly dipped in de-ionized pure water to minimize residual Cl atoms. After that, a Ge oxide layer was grown in the temperature ranging from 375 to 575 °C in a quartz furnace with flowing dry-O_2 at a rate of 4L/min under atmospheric pressure.

3. Results and Discussion

Ge oxide thickness grown on wet-chemically cleaned Ge surface was evaluated from SE analysis. Figure 1 shows the Ge oxide growth on Ge(100) with oxidation time at different oxidation temperatures ranging from 375 to 575 °C. In the region of oxidation time over 10 min, the oxide growth rate clearly shows a linear relationship in a log-log plot at a fixed temperature, and it was characterized by the slope n and pre-factor A at each oxidation temperature which are given by the following equation:

$$T_{ox} = A \cdot t^{n} \qquad (1)$$

where T_{ox} and t are Ge oxide thickness and oxidation time, respectively. From the best fitting result, obtained n and A values at each oxidation temperatures were summarized in Table 1. The n value of the 375 °C oxidation is close to that of the native oxide growth (0.12) in clean room air exposure at 24 ºC [6], which implies that the rate-limited of Ge surface reaction with O_2 molecules by network structure change in the Ge-oxide and/or near the Ge-oxide/Ge interface. Obviously, this n value was linearly increased with oxidation temperatures and reached to 0.56 at oxidation temperature of 575 ºC (as shown in Fig. 2). Also, these results are very different from the thermal oxidation of Si surface [7].

Ge oxide growth on Ge(100) and (111) were compared in Fig. 3. Thermal oxidation at 375 °C shows no significant difference between (100) and (111) surfaces, which indicates that overall reaction rate of the O_2 molecules with Ge in (100) and (111) orientations is almost the same. On the other hand, for the oxidation at temperatures over 450 °C, the growth of Ge oxide on Ge(100) is faster than that on Ge(111) although the slope at each oxidation temperatures almost remains unchanged irrespective of the orientations as show in Table 1. Considering the fact that the oxide growth rate of Si(100) surfaces by thermal oxidation in dry-O_2 is slower than that of (111) surface [8, 9], the thermal desorption of GeO may be involved in the orientation dependence of oxide growth on Ge being different from Si oxidation.

To get an insight into the GeO desorption during thermal oxidation, 11nm-thick SiO_2/Si was placed nearby Ge(100) or Ge(111) in the oxidation furnace and oxidized simultaneously as schematically illustrated in Fig. 4, and then XPS analysis of SiO_2 surface was carried out. Figures 5(a) and 5(b) show the $Si2p_{3/2}$ and $Ge2p_{3/2}$ spectra taken for the SiO_2 surface after oxidation at 550 °C for 60 min. In each spectrum, the binding energy calibration and the photoelectron intensity normalization were made by $Si2p_{3/2}$ signals. Obviously, for both samples oxidized with Ge(100) and Ge(111), $Ge2p_{3/2}$ signals originating from attached GeO_x on SiO_2 were observed clearly. Also, it was found that the amount of GeO desorption from Ge(100) surface was higher in comparison to the Ge(111) case as shown in Fig. 6. Taking into account of the crystallographic orientation dependence of Ge-oxide

growth as discussed in Fig. 3, some of GeO units (or oxygen vacancies) generated at the oxide/Ge interface are likely to be re-oxidized (or annihilated) with O_2 flux through the oxide until reaching the oxide top surface, which results in enhanced oxide growth.

In summary, we found that Ge oxide growth on both Ge(100) and (111) in region of the oxidation time over 10min shows a linear relationship in a log-log plot at a fixed temperature. It is likely that GeO units generated and emitted at the oxide/Ge interface, as a result of a balance in reaction rates between oxidation and reduction at the interface, are re-oxidized prior to the desorption from the top surface and contribute to the GeO_2 network formation.

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References [1] International Technology Roadmap for Semiconductor 2011. [2] K. Kita, et al., Jpn. J. Appl. Phys. **47** (2008) 2349. [3] R. Zhang, et al.,IEEE Trans. on Elec. Dev., **59** (2012) 335. [4] S. K. Wang, et al., J. Appl. Phys., **108** (2010) 054104. [5] A. Ohta, et al., Jpn. J. Appl. Phys., **50** (2011) 10PE01. [6] S. K. Sahari, et al., Jpn. J. Appl. Phys., **50** (2011) 04DA12. [7] B. E. Deal, et al, J. Appl. Phys., **36** (1965) 3770. [8] J. P. Meindl, et al., in F. Van de Wiele, W. L. Engl, and P. O. Jespers, Eds., Process and Device Modeling for Integrated Circuit Design, Noordhoff, Leyden, 1977. [9] S. M. Sze, Physics of Semiconductor Devices, 2nd ed., p.66, Willey, New Jersey, 1981.

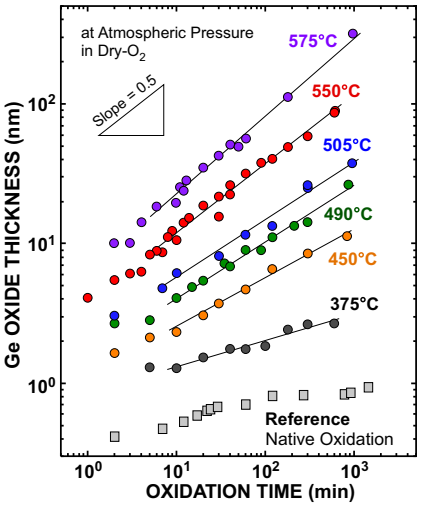

Fig. 1 Thermal oxidation of p-type Ge(100) in dry-O_2 ambience at different temperatures as functions of oxidation time. Ge oxide growth at room temperature is also shown as a reference [6].

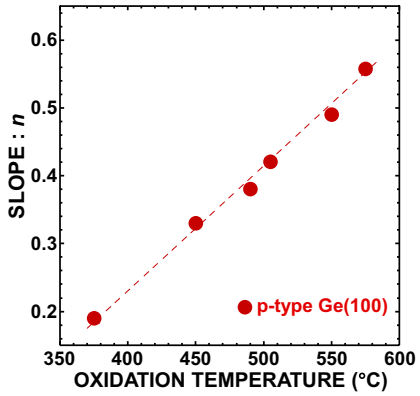

Fig. 2 The slope *n* indicated in Fig. 1 as a function of oxidation temperature.

Table. 1. Extracted *n* and *A* values from the Ge oxide growth on (100) and (111) surfaces in the oxidation time range over 10min shown in Figs. 1 and 3.

	Ge (100)		Ge (111)	
	n	*A*	*n*	*A*
375°C	0.19	0.84	0.18	0.90
450°C	0.33	1.21	0.34	1.08
490°C	0.39	1.73	0.38	1.49
505°C	0.41	2.18		
550°C	0.49	3.79	0.51	3.07
575°C	0.56	6.24		

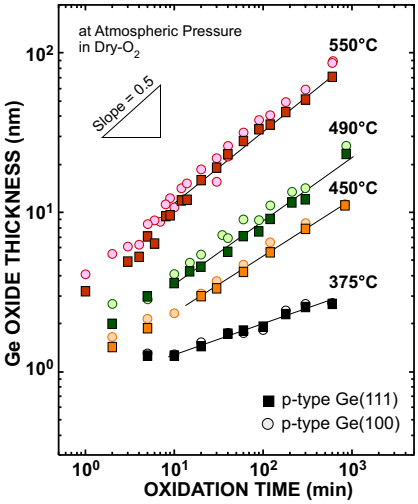

Fig. 3 Thermal oxidation of p-type Ge(111) in dry-O_2 ambience at different temperatures as functions of oxidation time. Ge oxide growth on Ge(100) is also shown .

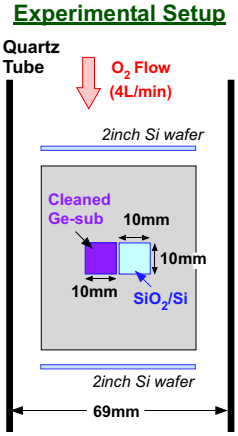

Fig. 4 Schematic image of experimental setup to evaluate the GeO desorption during Ge thermal oxidation.

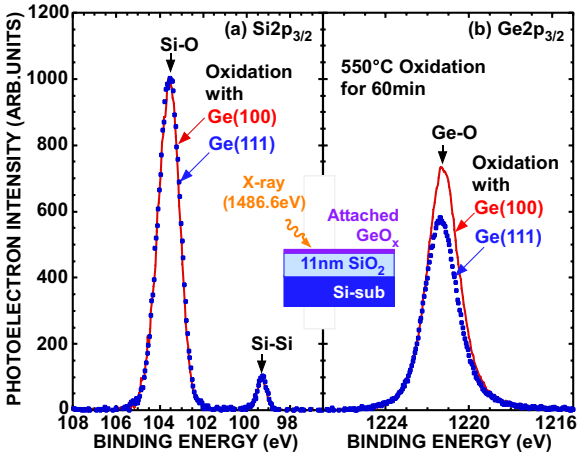

Fig. 5 (a) $Si2p_{3/2}$ and (b) $Ge2p_{3/2}$ spectra for 11 nm-thick SiO_2/Si set nearby Ge(100) or Ge(111) during oxidation at 550 ºC for 60 min. The experimental set up was shown in Fig. 4. Photoelectron take-off angle was set at 90º.

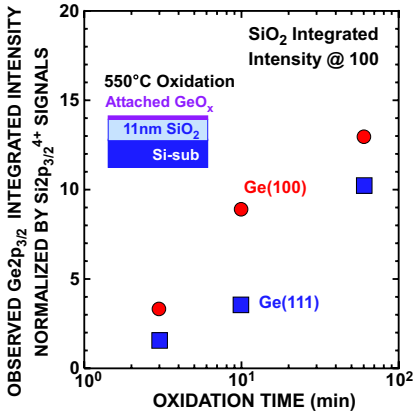

Fig. 6 Observed $Ge2p_{3/2}$ integrated intensities on SiO_2 surface after oxidation at 550 ºC with Ge(111) or (100) substrate. $Ge2p_{3/2}$ photoelectron intensity in each spectrum was normalized by the integrated intensity of $Si2p_{3/2}^{4+}$ signals to be 100.