Kinetics of thermally oxidation of Ge(100) surface

S K Sahari1, A Ohta1, M Matsui1, K Mishima1, H Murakami1, S Higashi1, and S Miyazaki2
1Graduate School of Advanced Sciences of Matter, Hiroshima University, Higashihiroshima, Hiroshima, 739-8530 Japan
2Graduate School of Engineering, Nagoya University, Nagoya, Aichi, 464-8603 Japan
1semicon@hiroshima-u.ac.jp, 2miyazaki@nuee.nagoya-u.ac.jp

Abstract. Thermal oxidation of a Ge(100) surface was investigated by using spectroscopic ellipsometry (SE) and x-ray photoelectron spectroscopy (XPS). Ge oxide was grown in the temperature range of 375 to 550°C in dry-O2 ambience at atmospheric pressure. Although the Ge-oxide growth rate shows a linear relationship in a log-log plot at a fixed temperature, and the slope indicates an enhancement of GeO desorption at oxidation temperatures over 490°C. The GeO desorption was also confirmed from the XPS analysis of the Si surface which was oxidized simultaneously with the Ge(100) surface. Thus, the Ge thermal oxidation at atmospheric pressure cannot be explained simply by the Deal-Grove model, in which the contribution of thermal desorption of Ge monoxide must be taken into account.

1. Introduction

As Ge has higher carrier mobilities than those of Si [1-3], it is a promising channel material for metal-oxide-semiconductor (MOS) field effect transistors (FETs). Controlling the MOS interface and minimizing the generation of defect state densities in the gate dielectric and at the dielectric/Ge interface are the most critical issues for the development of Ge-channel MOSFETs [4, 5]. The detailed mechanism of Ge oxidation and the nature of the interfaces between Ge and GeO2 are still research matters, which are presumably related to the fact that GeO2 is chemically and thermally unstable in contrast to SiO2 [6, 7]. In particular, the suppression of Ge oxide desorption is a key to obtaining a high FET performance. So far, the GeO desorption has been intensively studied [8-12]. Thermal desorption spectroscopy (TDS) measurements of thermally grown GeO2 films on Ge(100) clarify that the film desorbs mainly in the form of GeO and the peak temperature depends on the GeO2 film thickness [10]. In addition, the GeO desorption is thought to be enhanced by the reaction at the interface between GeO2 and Ge substrate [11, 12]. Since there are few published reports of the thermal oxidation of Ge surface with taking into account of both Ge oxidation and GeO desorption, the understanding of the oxidation mechanism is very limited.

In our preliminary report, chemical bonding features of thermally-grown Ge oxide/Ge(100) were investigated by using high-resolution x-ray photoelectron spectroscopy (XPS). It is found that Ge sub-oxides signals due to Ge2+ and Ge3+ components slightly increased with increasing thermal oxidation temperatures from 375 to 490°C, which indicates that oxygen deficient region in Ge-O network increased with oxidation temperatures. In addition, the amount of these sub-oxides decreases by 60% after being annealed at 375°C in dry oxygen ambience at atmospheric pressure [13]. In this work, we have studied the Ge oxide growth on Ge(100) surface at different oxidation temperatures in dry oxygen ambience at atmospheric pressure by spectroscopic ellipsometry (SE) and XPS.
2. Experimental Procedures
A p-type Ge(100) with a resistivity of ~10 Ω·cm was used. The Ge wafers were first dipped in deionized pure water to dissolve the native oxide and followed by immersing them in 15% H₂O₂ to re-oxidize the surface intentionally. Then the wafers were rinsed with deionized pure water and subsequently dipped in 30% HCl solution to remove the surface oxide layer. Finally, the Ge wafers were briefly dipped in deionized pure water to minimize residual Cl atoms. After the wet-chemically cleaning, a Ge oxide layer was grown at the temperature ranging from 375 to 550°C in a quartz furnace with flowing dry-O₂ at a rate of 4 L/min under atmospheric pressure. The thicknesses of thermally-grown Ge oxide were evaluated with an accuracy of ±0.1 nm by SE with wavelengths ranging between 192 and 1000 nm. The chemical bonding features of thermally grown Ge oxides so-prepared were characterized by XPS under monochromatized AlKα (hv = 1486.6 eV) radiation.

3. Results and Discussion
The Ge oxide growth on Ge(100) by thermal oxidation for 10 min in the temperature ranging from 375 to 550°C is shown in figure 1. At oxidation temperatures below 490°C, the Ge oxide thickness is almost exponentially increased with temperature. Further increase in oxidation temperature significantly enhances the growth rate of Ge oxide, implying that the oxygen diffusion to the Ge surface through Ge oxide becomes significant. To get a better understanding of Ge thermal oxidation, the Ge oxide growth with different oxidation temperatures was summarized as a function of oxidation time (Figure 2). As indicated in figure 2, we have extracted the slope n at each oxidation temperature from linear extrapolation in the log-log plot, and found that the n value of the 375°C oxidation is close to that of the native oxide growth (0.12) [14], where in an air-exposure time within 10 min at 24°C, native Ge oxide with a thickness as low as 0.6 nm is formed. The result suggests that the oxidation at 375°C and below is rate-limited by surface reaction. With increasing oxidation temperature from 490 to 550°C, the n value decreases slightly from 0.38 to 0.36, which implies evolving thermal desorption of Ge oxide.

To investigate the GeO desorption during the thermal oxidation at temperatures over 500°C, both Ge(100) and Si(100) were oxidized at the same time as schematically illustrated in figure 3. In this experiment, wet-chemically cleaned p-type Si(100) wafer with a resistivity of 8-12 Ω·cm was used. The Si2p3/2 and Ge3d spectra taken for the Si(100) surface after oxidation at 505 and 550°C for 10 min are shown in figure 4. With an increase of oxidation temperature from 505 to 550°C, not only...
Figure 3. Experimental setup to confirm GeO desorption during Ge thermal oxidation.

Figure 4. (a) Si 2p$_{3/2}$ and (b) Ge 3d spectra taken for Si(100) surfaces after oxidation at 505 and 550°C in the experimental setup as shown in figure 3. The photoelectron take-off angle was set at 30°. The photoelectron intensity in each set of the spectra was normalized by Si 0+ signals.

increase in chemically-shifted Si 2p$_{3/2}$ signals due to the Si oxide components but also a significant increase of Ge 3d signals was clearly observed. The result of figure 4 indicates that the GeO desorption occurs even at 505°C oxidation and is enhanced with increasing oxidation temperatures, which is consistent with the results of SE analysis (Figure 2). Notice that Ge3d signals observed on oxidized Si(100) surfaces consist mainly of metallic Ge (Ge$^{0+}$) and Ge oxide (Ge$^{4+}$) components. It is likely that, in the deposition of Ge-rich oxide from the thermal decomposition of Ge monoxide thermally-desorbed from oxidizing Ge substrate, reduction of Ge oxide layer and/or phase separation into two thermally stable states (Ge$^{0+}$ and Ge$^{4+}$) proceed. The detailed chemical bonding features of this metallic Ge component on Si surface were evaluated from the Auger parameter without influence of the positive charge-up during the XPS measurement as shown in figure 5 [15]. The Auger parameter was calculated by using the following equation.

$$\text{Auger Parameter} = \text{Ge3d}_{5/2} (B.E) + \text{Ge L}_{3}M_{45}M_{45} (K.E)$$

As a result, the Auger parameter of a metallic Ge component observed on the oxidizing Si surface was obtained to be 1174.6 eV, which is higher than the reference value of Ge-Ge bonding units (1173.8 eV). This energy shift can be interpreted as a formation of Si-Ge bonding units. Also, the formation
of Si-Ge bonding units in the oxide layer was confirmed from photoelectron take-off angle dependence of XPS core-line signals.

Next, to get an insight into the mechanism of Ge thermal oxidation, we made a trial estimation by applying the general oxidation equation proposed by Deal and Grove [16] to experimentally-obtained results. In the Deal-Grove model which is well-known to explain Si thermal oxidation well, the growth of oxide thickness of $x_0$ with oxidation time of $t$ is given by

$$x_0^2 + Ax_0 = B(t+\tau) \quad (2)$$

$$x_0 = \frac{B(t+\tau)/x_0 - A}{\tau} \quad (3)$$

where the quantity $\tau$ corresponds to a shift in the time coordinate which corrects for the presence of the initial oxide layer. Furthermore, the coefficients of $A$ and $B$ are the positive value in the Si oxidation case. In figure 6, the obtained Ge oxide thickness shown in figure 2 is replotted as a function of $(t+\tau)/x_0$ based on the eq. (3). In each oxidation temperature, the $\tau$ value was estimated by using the same method as described in Ref. 16. The oxidation at 375°C only shows a linear relationship but has a negative value of intercept of $A$, which is different from the situation of the Si oxidation. For the higher oxidation temperature from 490 to 550°C, a logarithmic relationship was obtained. Obviously, the Deal and Grove model cannot be applied to the Ge thermal oxidation at atmospheric pressure in all temperature range. Thus, the contribution of GeO desorption must be considered in thermal oxidation of Ge surface and particularly for oxidation over 400°C at atmospheric pressure.

To gain a better understanding of thermal desorption process, the time-dependent model as described in Ref. 17 was applied, in which nonsteady-state oxidation in the early stages is taken into account. Based on the model, the Ge oxide growth rate, $dx_0/dt$, was evaluated as a function of oxide thickness in the consideration of the thickness dependent GeO-desorption [18]. Figure 7 shows the results obtained at 490°C, where the oxidation rate was calculated from $(x_0-x_i)/t$, where $x_i$ is the initial thickness of oxide at $t=0$ min. The oxidation rate increases at with an increase in oxidation thickness until it reaches its maximum at ~5 nm in thickness and then decreases with increasing oxide thickness. In the case of Si thermal oxidation at atmospheric pressure, oxidation proceeds with no desorption and the oxidation rate in the early stages show an exponential decay with progressive oxidation [17], which is theoretically explained the oxidation reaction rate at the interface is controlled by the
behavior of the emitted Si atoms. [19]. Taking into account of this fact, the observed increase in the Ge oxide growth rate in the early stages indicates that the GeO desorption proceeds simultaneously during thermal oxidation at atmospheric pressure.

4. Conclusion
The thermal oxidation of the Ge(100) surface was investigated. The slope of Ge oxide growth at 375°C with oxidation time shows the same value as native oxide growth and this slope gradually decreases with increasing temperatures over 490°C. The rate constant for Ge oxidation at 375°C is a linear relationship while oxidation at temperatures over 490°C shows a logarithmic relationship. The GeO desorption during thermal oxidation was confirmed from the XPS analysis of Si substrate placed next to the Ge during oxidation over 505°C. Also, the GeO desorption involves in thickness dependent oxidation rate for Ge thermal oxidation at temperatures over 490°C.

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References
[1] Sze S M and Ng K K 2007 Physics of Semiconductor Devices (New York, Wiley 3rd ed) p.786.
[2] Chui C O, Kim H, McIntyre P C and Saraswat K C 2003 IEDM Tech. Dig. p.437.
[3] Shang H, Okorn-Schmidt H, Chan K K, Copel M, Ott J A, Kozlowski P M, Steen S E, Cordes S A, Wong H-S P, Jones E C and Haensch W E 2002 IEDM Tech. Dig. p.441.
[4] Murakami H, Fujioka T, Ohta A, Bando T, Higashi H and Miyazaki S 2010 ECS Trans. 33 253
[5] Ohta A, Fujioka T, Murakami H, Higashi H and Miyazaki S 2011 Japan. J. Appl. Phys. 50 10PE01
[6] Murakami H, Miura M, Ohta A, Yogauchi R, Higashi S and Miyazaki S 2008 Ext. Abst. of 4th Int. SiGe Technol. and Device Meeting p.165
[7] Prabhakaran K, Maeda F, Watanabe Y and Ogino F 2000 Appl. Phys. Lett. 76 2244.
[8] Nagashio K, Lee C H, Nishimura T, Kita K and Toriumi A 2009 Mater. Res. Soc. Symp. Proc. 1155-C06-02
[9] Wang S K, Kita K, Nishimura T, Nagashio K and Toriumi A 2011 *Japan J. Appl. Phys.* **50** 04DA01

[10] Toriumi A, Wang S K, Lee C H, Yoshida M, Kita K, Nishimura T and Nagashio K 2010 *ECS Trans.* **28**(2) 171

[11] Kita K, Suzuki S, Nomura H, Takahashi T, Nishimura T and Toriumi A 2008 *Japan J. Appl. Phys.* **47** 2349.

[12] Kita K, Lee C H, Nishimura T, Nagashio K, and Toriumi A 2009 *ECS Trans.* **19** 101.

[13] Sahari S K, Ohta A, Matsui M, Murakami H, Higashi S, Miyazaki S 2011 *Ext. Abst. of 2011 SSDM* p. 14

[14] Sahari S K, Murakami H, Fujioka T, Bando T, Ohta A, Makihara K, Higashi S, Miyazaki S 2011 *Japan J. Appl. Phys.* **50** 04DA12

[15] Wagner C D, Gale L H and Raymond R H 1979 *Anal. Chem.* **51** 466.

[16] Deal B E and Grove A S 1965 *J. Appl. Phys.* **36**(12) 3770

[17] Massoud H Z, Plummer J D and Irene E A 1985 *J. Electrochem. Soc. Solid-State Science and Technology* **132** (11) 2685

[18] Wang S K, Kita K, Lee C H, Tabata T, Nishimura T, Nagashio K and Toriumi A 2010 *J. Appl. Phys.* **108** 054104

[19] Kageshima H, Shiraishi K and Uematsu M 1999 *Japan. J. Appl. Phys.* **38** L971