Studies of the Thin Oxide of Epitaxial SiGe/Si Film by High Resolution Grazing Angle Rutherford Backscattering Spectrometry and Channeling

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Grazing angle Rutherford Backscattering Spectrometry/Channeling (RBS/C) with an improved depth resolution (2-3 nm) in combination with X-ray photoelectron Spectroscopy (XPS) was used to investigate the thin oxide of $Si_{1-x}Ge_x$ (x=0, 0.2 and 0.3) films oxidized at elevated temperatures in a dry chlorinated ambient atmosphere (O_2/Cl). Experimental results showed that after oxidation, only SiO_2 was formed while Ge was completely rejected from the oxide to form Ge-rich layers. The effect of the oxidation enhancement of the SiGe alloy with an increase in the Ge content was also found in this study. The strain of the unoxidized SiGe layer underneath the oxide layer characterized by channeling angular scans indicates that these rejected Ge atoms during oxidation have less influence on the integrity of the SiGe layer due to diffusion of the Ge atoms.

Keywords: grazing angle rutherford backscattering spectrometry, strain, SiGe/Si heterosystem

1. INTRODUCTION

Owing to both the enhanced hole mobility in a compressively strained SiGe layer on Si substrate and compatibility with the state-of-the-art Si processing technology, strained SiGe/Si materials have attracted considerable interests interest[1,2]. The need for high-quality oxides on SiGe/Si (100) for the fabrication of MOS devices has prompted researchers to attach great importance to the oxidation of SiGe. A range of studies has been conducted regarding the oxidation of SiGe alloys to form thicker oxide films[3-6]. These studies have revealed that Si in the alloy is selectively oxidized, accompanying the pileup of Ge atoms underneath oxides and the undesired strain relaxation at the alloy/substrate interface. However, owing to the depth resolution limitation of related to characterization techniques for thinner oxide films, few reports[7,8] involving to a thinner SiGe oxide of SiGe have been published thus far. On the other hand, as the dimensions of MOSFETs have scaled down into the deep submicron regime, the characteristics of a thinner oxide for SiGe is expected to become a topic of future investigations in this area[9,10].

In the aforementioned publications related to thin-oxide SiGe, Nayak et al.[7] reported that the oxidation rate of the SiGe layer is identical to that of Si in the thin oxide regime (<10 nm). They also found and that the rate is independent of the Ge content and that the oxide is only composed of SiO_2. However, Terrasi et al. [8] pointed out that when SiGe is oxidized to form a thin oxide (<10 nm) layer, even if Si in the alloy is preferentially oxidized and there is a pileup of Ge atoms, GeO_2 is also found. Moreover, novel oxide growth rate enhancement (GRE) with respect to pure Si is demonstrated. It was found that the experimental conditions (rapid thermal oxidation at an elevated temperature) of the oxidation of SiGe (x<0.5) alloys in the aforementioned studies were identical. However, there were such evident differences in their experimental results that it is necessary to investigate the characteristics of thinner oxides for SiGe further.

In the present article, thin-strained $Si_{1-x}Ge_x$ (x=0, 0.2 and 0.3) layers were oxidized at elevated temperatures in dry chlorinated ambient (O_2/Cl) to obtain thinner oxide layers (<10 nm). Grazing angle Rutherford Backscattering Spectrometry/Channeling (RBS/C) with an improved depth resolution (2~3 nm) together with XPS were used to characterize the thinner oxide on the SiGe films. Channeling angular scans were used to investigate the influence of the rejected Ge atoms during oxidation on the strain relaxation properties of unoxidized SiGe layers underneath the oxide.

2. EXPERIMENTAL

Samples used in this study had a 10 nm strained $Si_{1-x}Ge_x$ (x=0, 0.2, 0.3) layer grown on Si (100) substrates via a com-

mercial ASM Epsilon 2000 chemical vapor deposition (CVD) reactor. The growth details are described elsewhere [11]. Before they were loaded into an oxidation furnace, the $Si_{1-x}Ge_x$ samples were cleaned by a standard RCA approach with a HF-vapor pretreatment [12]. These $Si_{1-x}Ge_x$ (x=0, 0.2 and 0.3) samples were oxidized by conventional furnace thermal oxidation in chlorinated oxidizing ambient (O_2/Cl) with a 10:1 ratio of O_2 and Cl gas under dual conditions of 750°C for 60 min and 800°C for 1 min. The choice of O_2/Cl over pure O_2 as an oxidant was made in order to simulate a valid device fabrication process and to improve the interface characteristic between SiO_2 and the Si substrate.

The chemical states of each component in the thin oxide films were identified by means of XPS. All of the XPS spectra were obtained using Mg K_α radiation (1253.6 eV). The Si2p, Ge3d and O1s spectra were recorded. The binding energies for these core levels were calibrated using the C1s peak positioned at 284.6 eV. 2.0 MeV $^4He^+$ glancing angle Rutherford backscattering spectrometry (RBS/C) (with a backscattering angle of 93 degrees) with an improved depth resolution was used to determine the thickness, composition and Ge redistribution after oxidation. The magnitudes of the strain in unoxidized SiGe layers were characterized by channeling angular scans along an inclined <110> axis.

3. RESULTS AND DISCUSSIONS

Figure 1 shows the XPS spectra of the Si2p (Fig. 1a, Ge 3d (Fig.1b) and O1s (Fig. 1c) core levels for these SiGe samples (x=0.2, 0.3) oxidized at 750°C in chlorinated oxidizing ambient (O_2/Cl) for 60 min. The formation of SiO_2 is evidenced by the chemical shift of the Si2p core level peak from 98.9 eV (pure Si^{0+} state) to 103.5 eV (Si^{4+}). The 28.9 eV peak position of the Ge3d core level corresponding to pure Ge, i.e. Ge^0, is shown in Fig. 1b. The O2s photoelectron peak was also found in Fig. 1b. A prominent O1s photoelectron peak centered at 532.3 eV is shown in Fig. 1c, which corresponds to SiO_2. As a consequence, the oxide film of the SiGe samples (x=0.2, 0.3) oxidized at 750°C for 60 min in an O_2/Cl ambient is only composed of SiO_2.

Figures. 2a and 2b exhibit the XPS spectra of the Si2p (Fig. 2a), Ge3d (Fig. 2b) and O1s (Fig. 2c) core levels for these SiGe samples (x=0.2, 0.3) oxidized at 800 in chlorinated oxidizing ambient (O_2/Cl) for 1 min. Only the formation of SiO_2 is evidenced by the chemical shift of the Si2p core level peak from 98.9 eV (pure Si^{0+} state) to 103.5 eV (Si^{4+}). The ratio of the Si^{4+} to Si^{0+} peak intensities shown in Fig. 2a is lower than that observed in Fig. 1a, which indicates that the thickness of the oxide formed at 800°C for 1min is less than that generated at 750°C for 60 min. The peak position at 108.5 eV near the Si 2p peak (104.2 eV) in Fig. 2a come from the LMM Auger peak of Ge. It is also shown that the thickness of the oxide formed at 800°C is less
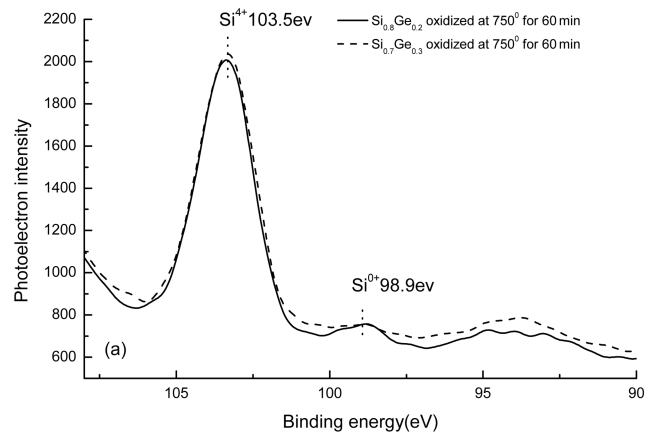

Fig. 1a. The XPS spectra of the Si 2p core level for $Si_{1-x}Ge_x$ (x=0.2, 0.3) film oxidized at 750°C for 60 min in Chlorinated ambient (O_2/Cl).

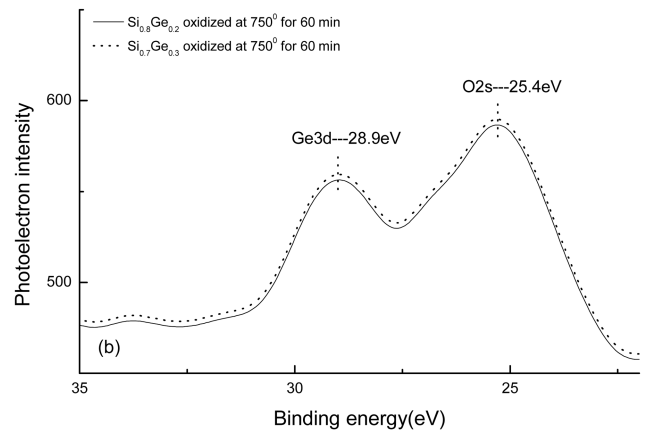**Fig. 1b.** The XPS spectra of the Ge 3d core level for $Si_{1-x}Ge_x$ (x=0.2, 0.3) oxidized at 750°C for 60 min in Chlorinated ambient (O_2/Cl).
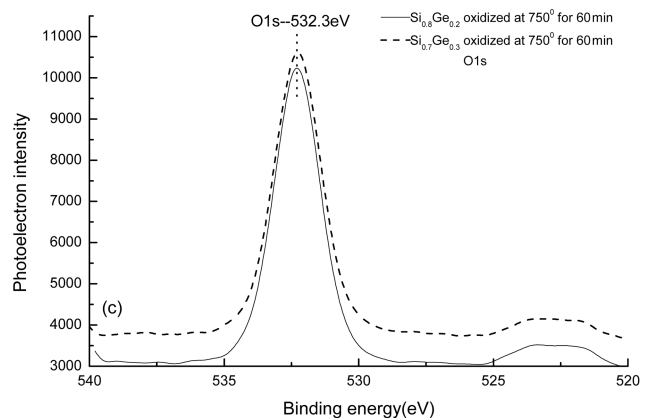

Fig. 1c. The XPS spectra of the O1s core level for for $Si_{1-x}Ge_x$ (x=0.2, 0.3) oxidized at 750°C for 60 min in Chlorinated ambient (O_2/Cl).

than that formed at 750°C. Both the Ge 3d signal in Fig. 2b and the O1s signal in Fig. 2c demonstrate that only SiO_2 is formed on the surface of the SiGe films.

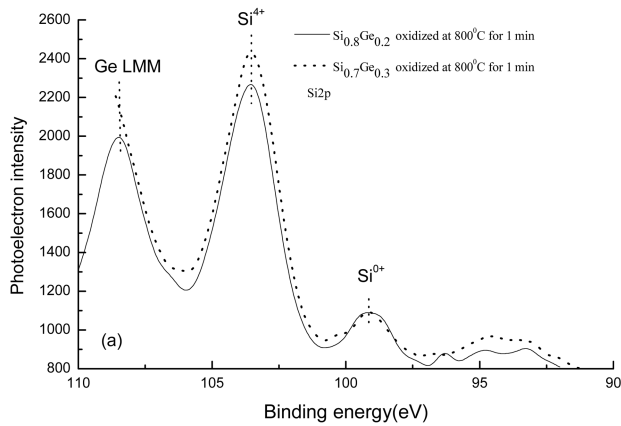For these strained $Si_{1-x}Ge_x$ films (x=0.2, 0.3) oxidized at

Fig. 2a. The XPS spectra of the Si 2p core level for $Si_{1-x}Ge_x$ (x=0.2, 0.3) oxidized at 800°C for 1 min in Chlorinated ambient (O_2/Cl).
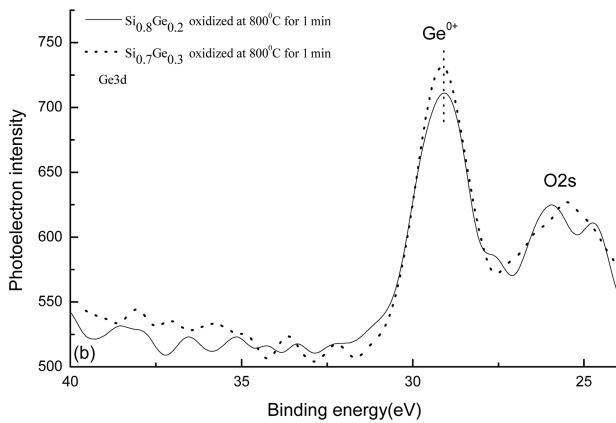
Fig. 2b. The XPS spectra of the Ge3d core level for $Si_{1-x}Ge_x$ (x=0.2, 0.3) oxidized at 800°C for 1 min in Chlorinated ambient (O_2/Cl).
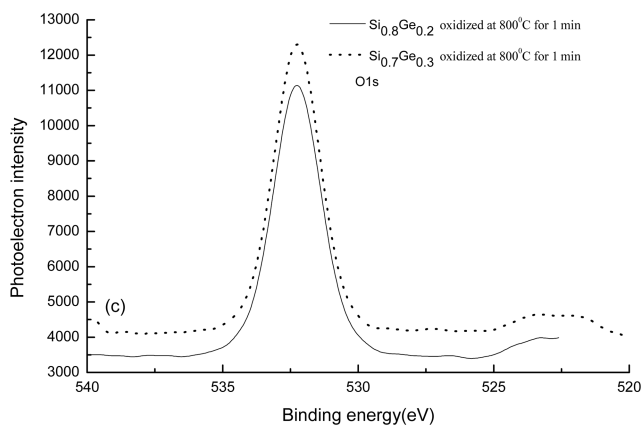
Fig. 2c. The XPS spectra of the O1s core level for $Si_{1-x}Ge_x$ (x=0.2, 0.3) oxidized at 800°C for 1 min in Chlorinated ambient (O_2/Cl).

750°C for 60 min and 800°C for 1 min, the thicknesses of the oxide and Ge re-distributions as determined by grazing angle Rutherford Backscattering Spectrometry/Channeling (RBS/C) are shown in Figs. 3a and 3b, respectively. The total amount of oxygen atoms obtained by the RBS/C analysis could be
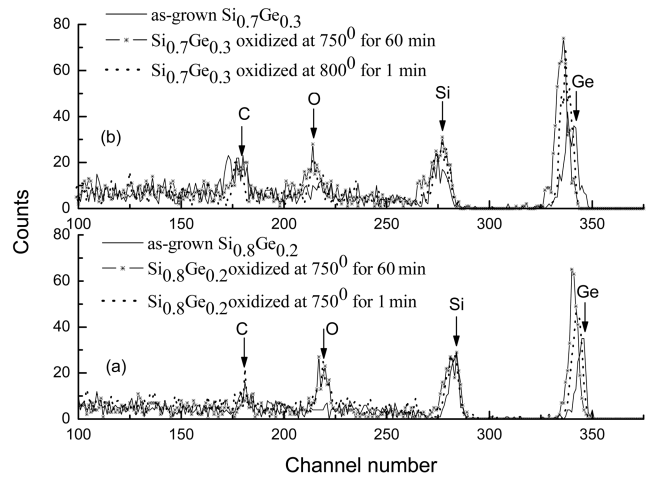
Fig. 3. High resolution grazing angle RBS/Channeling spectra for as-grown $Si_{1-x}Ge_x$, strained $Si_{1-x}Ge_x$ film oxidized at 750°C for 60 min and 800°C for 1 min with different Ge content (a) x=0.2, (b) x=0.3, respectively.

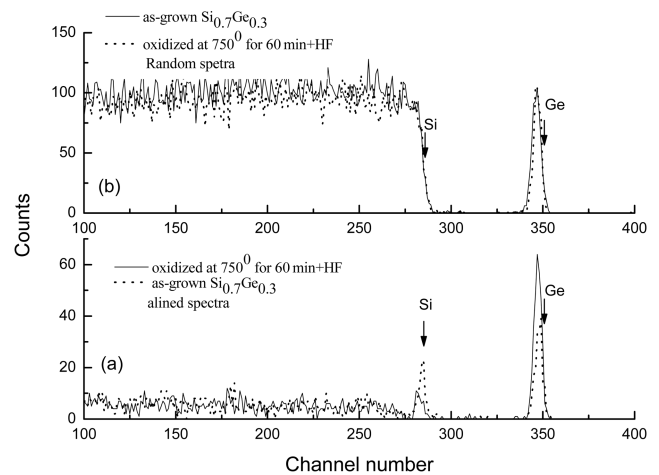**Fig. 4.** The glancing angle RBS random spectra and aligned spectra for as-grown ($Si_{0.7}Ge_{0.3}$)and as-etched samples labeled in (b) and (a), respectively.

easily converted into the oxide thickness, as only SiO_2 formed on the surface of the SiGe layer, as evidenced by the foregoing XPS results. Oxide thicknesses of 6.9 nm and 4.8 nm or 7.1 nm and 5 nm for these $Si_{1-x}Ge_x$ film with x=0.2 or 0.3 oxidized at 750°C for 60 min and 800°C for 1 min can be determined from Figs. 3a and 3b, respectively. The surface positions of the C, O, Si and Ge signals are labeled with arrows. The introduction of carbon signals is due to $^4He^+$ analysis beams. When decreasing the acquisition time of the RBS spectra or changing the position of the beam dot in a sample, the magnitudes of the C signals will decrease or disappear. The inward movement of Ge while the $Si_{1-x}Ge_x$ films (x=0.2, 0.3) were oxidized at 750°C for 60 min and 800°C for 1 min can be determined from Fig. 3 from the shift of the Ge signal towards the low channel side, which is compared

to that of the as-grown $Si_{1-x}Ge_x$ films (x=0.2, 0.3).

For the $Si_{0.7}Ge_{0.3}$ sample oxidized at 750°C for 60 min in O_2/Cl ambient, a 7.1 nm oxide layer was etched by an HF acid solution (hereafter termed the as-etched sample). The grazing angle Rutherford backscattering/Channeling spectra of the as-grown $Si_{0.7}Ge_{0.3}$ and the as-etched samples are shown in Figs. 4a and 4b, respectively. The complete superposition of the Ge signals in the RBS random spectra between the as-grown and the as-etched samples shown in Fig. 4b indicate that Ge atoms are completely rejected from the oxide and that no loss of Ge occurs during oxidation. It is worth noting that the surface peak of the Ge-aligned peak of the as-etched sample is larger than that of the as-grown sample (by nearly a factor of two) according to Fig. 4a. This can be attributed to the rejected Ge atoms from the oxide not
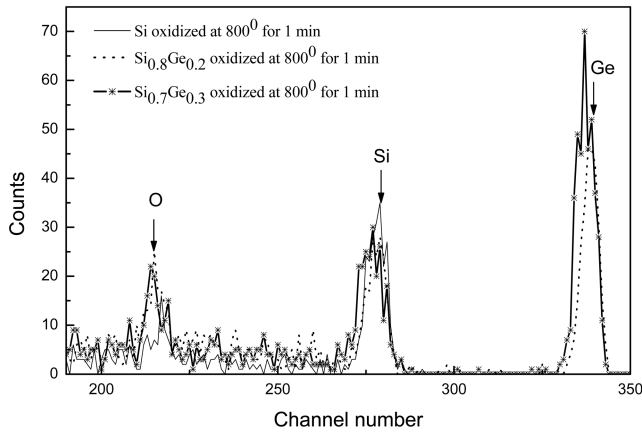

Fig. 5. The grazing angle channeling spectra of $Si_{1-x}Ge_x$ films with x=0, 0.2 and 0.3 oxidized at 800°C for identical duration (1 min).

fully taking up the position of the Si lattice. In other words, the crystalline quality of Ge in the as-etched sample is inferior to that in the as-grown sample.

To verify if the GRE effect with respect to pure Si as initially reported by Terrasi et al.[8] also appears in the present study, the grazing angle channeling spectra of $Si_{1-x}Ge_x$ films with x=0, 0.2 and 0.3 oxidized at 800°C for 1 min are displayed in Fig. 5. The thicknesses (2.4 nm, 4.8 nm and 5.1 nm) of the oxides for these $Si_{1-x}Ge_x$ (x=0, 0.2 and 0.3) samples corresponding to different Ge fractions were determined. Both the surface peaks of Si and the aligned peak of Ge for the $Si_{0.8}Ge_{0.2}$ sample have smaller values compared to those of $Si_{0.7}Ge_{0.3}$. This is consistent with the different oxide thicknesses of these SiGe samples, as determined by XPS. The experimental results of this study demonstrate that the oxidation rate of $Si_{1-x}Ge_x$ (x=0.2 or 0.3) is higher than that of pure Si oxidized in chlorinated oxidizing ambient (O_2/Cl). The effect of the oxide growth rate enhancement of SiGe with respect to pure Si is shown to exist.

A channeling angular scan for the as-grown sample ($Si_{0.8}Ge_{0.2}$/Si) is shown in Fig. 6a. The angular difference of $\Delta\theta = -0.40°$ between the minima of the two angular scan dips for the SiGe layer and the Si substrate was obtained. -1.4% of tetrogonal distortion ε_T stored on the SiGe layer can be computed as[13]: $\varepsilon_T = \Delta\theta/\sin\theta\cos\theta$, where θ is the angle between the <100> and <110> directions in the substrate, and $\Delta\theta$ is the shift of the center of the angular yield curves between the SiGe layer and the Si substrate. The negative value indicates that the strain in the SiGe layer is compressive. For the $Si_{0.8}Ge_{0.2}$ sample oxidized at 800°C for 1min, ε_T in the unoxidized SiGe layer underneath the oxide is nearly
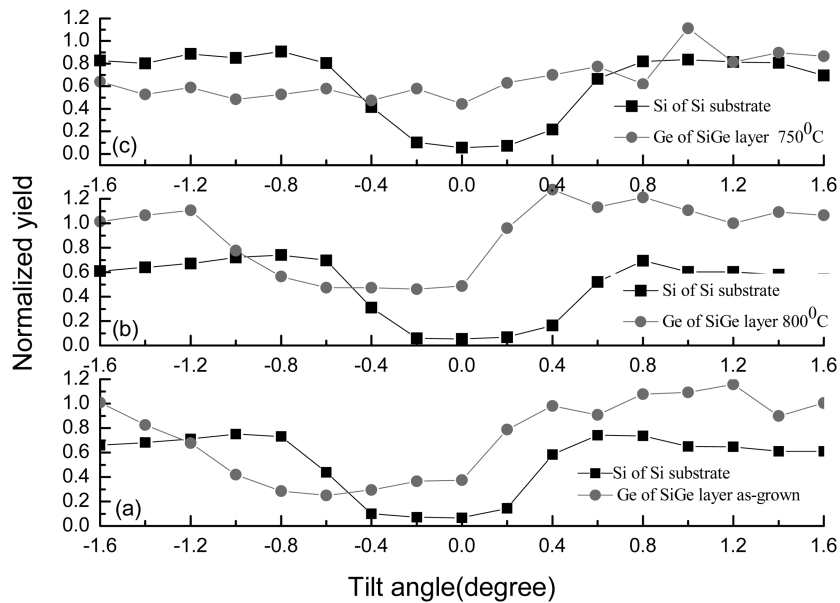

Fig. 6. The channeling angular scan dip curves for the as-grown sample ($Si_{0.8}Ge_{0.2}$/Si), sample oxidized at 800°C for 1 min and sample oxidized at 750°C for 60 min in chlorinated ambient (O_2/Cl) shown in (a), (b) and (c), respectively.

equal to that of the as-grown sample, as shown in Fig. 6b. In addition, for the $Si_{0.8}Ge_{0.2}$ sample oxidized at $750^{\circ}C$ for 60 min, the channeling angular scan dip curve is shown in Fig. 6c, as an unoxidized SiGe layer could not be achieved, making it impossible to characterize the strain. This is in good agreement with the very thin unoxidized SiGe layer that is beyond the scope of conventional MeV channeling angular scan detection[14].

The formation of SiO_2 and the rejection of the Ge from the oxide during oxidation as determined by XPS and RBS/Channeling in this study can be explained in terms of an existing model[10]. When the SiGe layer is oxidized at an elevated temperature, simultaneous oxidation of both Si and Ge will occur. However, owing to the instability of GeO_2 at high temperatures ($>700^{\circ}C$) in the presence of Si, the reaction of $Si+GeO_2 \rightarrow SiO_2+Ge$ would be instantaneous. In addition, owing to the thinner oxide film, there will be a large amount of free Si available to participate in the reaction. Therefore, in the very thin oxide regime, the SiGe oxide is composed of SiO_2, and Ge is completely rejected from the oxide to take up the SiGe lattice sites in place of Si atoms that escape from the SiGe lattice, which in turn participate into the oxidation process.

The effect of the oxidation enhancement observed in this study may be attributed to the following factors: First, the breaking of the weak Si-Ge bond is easier than the breaking of the Si-Si bond. Secondly, the Ge layer generated by SiGe oxidation, as reported by LeGoues *et al.*[15], suppresses Si interstitials. The suppression of Si interstitials to some extent would increase the number of Si atoms that could react with the incoming oxidant. Another possible explanation is the creation of excess vacancies involved in the removal of Si atoms from the SiGe layer during oxidation[16]. Finally, when the SiGe layer was oxidized in this study, Ge atoms are rejected from the oxide layer, which is accompanied by the diffusion of the Ge atoms. The final distribution of rejected Ge atoms depends on the diffusion coefficient of Ge in the $Si_{1-x}Ge_x$ alloy as well as the diffusion time. According to the diffusion coefficient value reported by Mc Vay *et al.*[17], the diffusion length ($X_0=(Dt)^{1/2}$) of the Ge in the $Si_{0.8}Ge_{0.2}$ sample oxidized at $750^{\circ}C$ for 60 min or at $800^{\circ}C$ for 1min is estimated to be 0.7 nm or 0.3 nm, respectively. Therefore, the Ge distribution in the unoxidized epilayer, except the Ge-rich region generated during oxidation, should remain intact due to the very small diffusion length of Ge in the SiGe layer under these two temperatures and times. The lower diffusion of rejected Ge atoms would have little influence on the strain of the unoxidized SiGe layer, as confirmed by Fig. 6.

4. CONCLUSION

The thin oxides (<10 nm) of $Si_{1-x}Ge_x$ films were investigated by high-depth resolution grazing angle Rutherford Backscattering Spectrometry/Channeling (RBS/C) together with XPS. Experimental results show that only SiO_2 is formed, and that Ge is completely rejected from oxide. Strain in the unoxidized SiGe layer characterized by channeling angular scans shows that the rejection of Ge during oxidation has little influence on the integrity of the unoxidized SiGe layer. In addition, the phenomena of the oxidation rate enhancement of SiGe compared to pure Si in chlorinated ambient (O_2/Cl) was double-checked.

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REFERENCES

1. J. C. Bean, L. C. Feldman, A. T. Fiory, S. Nakahara, and C. K. Robinson, *J. Vac. Sci. Technol, A* **2**, 436 (1984).
2. H. Daembkes, H.-J. Herzog, H. Jorke, H. Kibbel, and E. Kaspar, *IEEE. Trans. Electron Devices* **33**, 633 (1986).
3. O. W. Holland, C. W. White, D. Fathy, *Appl. Phys. Lett.* **51**, 520 (1987).
4. J. E. Pfiester and P. B. Griffin, *Appl. Phys. Lett.* **53**, 471 (1988).
5. F. K. LeGoues, R. Rosenberg, and T. Nguyen, *Mater. Res. Soc. Sym. Pro.* **105**, 313 (1988).
6. A. R. Srivatsa, S. Sharan, O. W. Holland, *J. Appl. Phys.* **65**, 4028 (1989).
7. D. Nayak, K. Kamjoo, C. S. Woo, and K. L. *Wang, Appl. Phys. Lett.* **56**, 66 (1990).
8. A. Terrasi, S. Scalese, and R. Adorno, *Mat. Sci. Eng. B* **89**, 269 (2002).
9. A. Kling, J. C. Soares, A. C. Prieto, J. Jiménez, A. Rodríguez, J. Sangrador, and T. Rodríguez, *Nucl. Instr. and Meth. B* **240**, 405 (2005).
10. A. Muñoz-Martín, A. Climent-Font, A. Rodríguez, J. Sangrador, and T. Rodríguez, *Nucl. Instr. and Meth. B* **240**, 395 (2005).
11. A. C. Lindgren, C. C. Chen, S. L. Zhang, and Dezhang Zhu. *J. Appl. Phys.* **91**, 2708 (2002).
12. P.-E. Hellberg, S.-L. Zhang, and C. S. Petersson, *J. Appl. Phys.* **82**, 5773 (1997).
13. M. F. Wu, A. Vantomme, G. Langouche, H. Vanderstraeten, and Y. Bruynseraede, *Nucl. Instr. and Meth. B* **54**, 444 (1991).
14. S. V. S. Nageswara Rao, A. P. Pathak, A. M. Siddiqui, D. K. Avasthi, and C. Muntele, *Nucl. Instr and Meth. B* **212**, 442 (2003).
15. F. K. LeGouses, R. Rosenberg, and B. S. Meyerson, *Appl. Phys. Lett.* **54**, 644 (1989).
16. F. K. LeGouses, R. Rosenberg, T. Nguyen, and B. S. Meyerson, *J. Appl. Phys.* **65**, 1724 (1989).
17. G. L. McVay and A. R. DuCharme, *Phys. Rev. B* **9**, 627 (1974).