

Enhancement of Carbon Diffusion Caused by Thermal Oxidation on $\text{Si}_{1-x}\text{C}_x$ Alloy Layer / Si(001) Surfaces

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1. Introduction

A strained-Si CMOS is developed as one of the high speed operation devices. In such CMOS devices, the strained-Si channel is formed on a relaxed $\text{Si}_{1-x}\text{Ge}_x$ alloy layer. The concentration of Ge, x , can be increased above 0.3 without dislocations by oxidation of a $\text{Si}_{1-x}\text{Ge}_x$ alloy layer. In this process, it is reported that no Ge is oxidized at all and condensed in the $\text{Si}_{1-x}\text{Ge}_x$ alloy layer [1]. Recently, we reported that a similar condensation phenomenon took place for the $\text{Si}_{1-x}\text{C}_x$ alloy layer as well as $\text{Si}_{1-x}\text{Ge}_x$ [2]. However, the condensation mechanism of not only Ge but also C due to oxidation is still an open question.

In this study, to clarify the behavior of C on the basis of the oxide growth kinetics, the oxidation reaction kinetics of a $\text{Si}_{1-x}\text{C}_x$ alloy layer was investigated by real-time photoelectron spectroscopy. The $\text{Si}_{1-x}\text{C}_x$ alloy layer was formed by exposing a Si(001) surface to ethylene (C_2H_4). Although the solubility of C in Si bulk is as small as $\sim 3.5 \times 10^{17} \text{ cm}^{-3}$, it is reported that the solubility of C can be increased by $\sim 10^4$ times due to the dimerization-induced strain, making it possible to form a $\text{Si}_{1-x}\text{C}_x$ alloy layer on Si(001) with x up to ~ 0.2 but within only the first several Si layers below the surface [3]. From a comparison between the changes in the depth profile of C and oxygen uptake, the enhancement of C diffusion is considered in terms of the oxidation-induced strain [4].

2. Experiment

Experiments were performed using the surface reaction analysis apparatus (SUREAC2000) installed at BL23SU of SPring-8, Japan. The p-type Si(001) wafer with a resistivity of $1 - 10 \text{ } \Omega\text{cm}$ of resistivity was used. After the annealing at $\sim 1000^\circ\text{C}$ for 10 min, Si(001) surface was carbonized at 640°C with C_2H_4 diluted by adding He (2.65%) for 1000 s at $\sim 10^{-6} \text{ Pa}$. The partial pressure of C_2H_4 was $3.5 \times 10^{-5} \text{ Pa}$. Following the carbonization, the sample was annealed for 2000 s at 640°C . When changing the sample temperature from 640°C to 500 and 660°C for the surface oxidation manner of Langmuir-type oxidation and two dimensional (2D) oxide island growth, respectively, the $\text{Si}_{1-x}\text{C}_x$ alloy layer was oxidized using O_2 gas of 99.995% purity. During carbonization and oxidation, Si 2p, O 1s and C 1s photoe-

lectron spectra were measured alternately for 42, 5, and 10 s, respectively, at photon energy of 710 eV.

3. Result and discussion

Figure 1 (a) shows the image plot of C 1s photoelectron spectra obtained *in situ* as a function of the reaction time during the carbonization, annealing and 2D oxide island growth at 660°C , and the C 1s spectrum at the end of oxidation is demonstrated in Fig. 1(b). To begin with, it is apparently recognized that the peak position of C 1s remains almost unchanged up to $\sim 7000 \text{ s}$ after introducing O_2 gas but then shows a significant shift to the high binding energy side. As shown in the curve-fitting analysis of Fig. 1(b), this is ascribed to the appearance of SiC_xO_y component with a shift of $\sim 0.8 \text{ eV}$ [5]. On the other hand, the C 1s in-

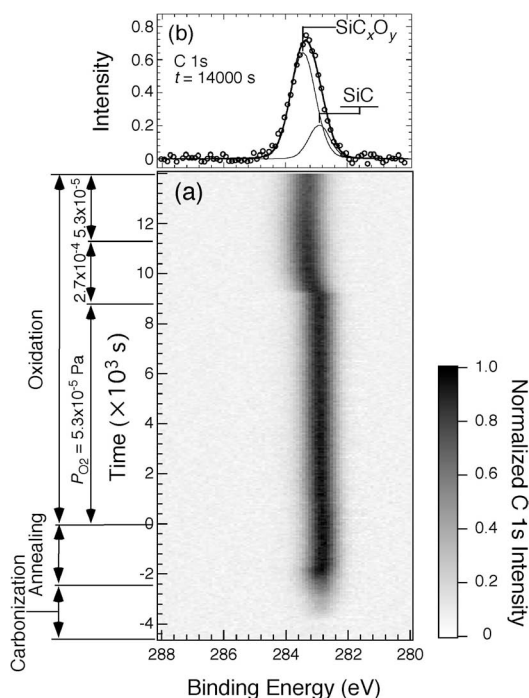


Fig.1 (a) Image plot of C 1s photoelectron spectra taken *in situ* during carbonization, subsequent annealing and oxidation on a Si(001) surface. (b) C 1s photoelectron spectrum obtained after the background subtraction at the end of oxidation ($t = 6950 \text{ s}$).

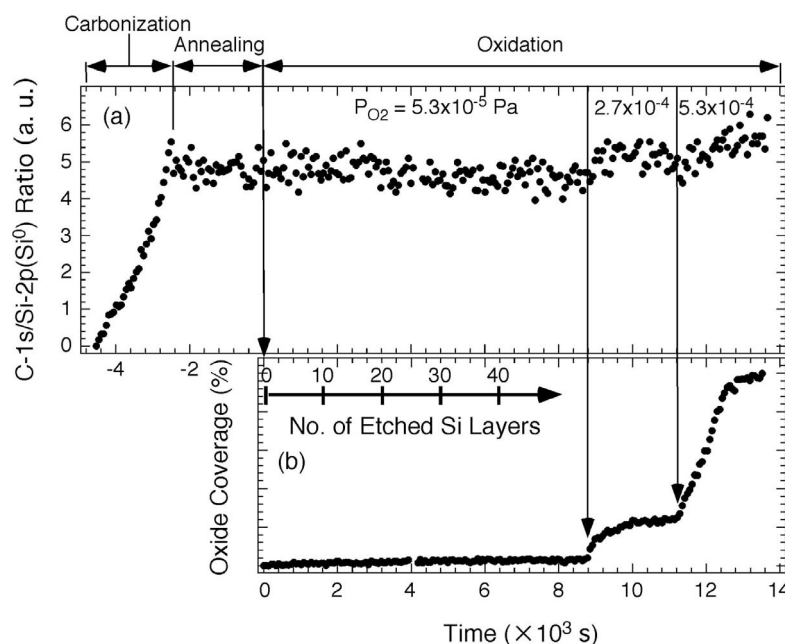


Fig.2 (a) Time evolution of C-1s/Si-2p(Si⁰) intensity ratio measured during carbonization, subsequent annealing at 640°C, and oxidation after raising the temperature from 640°C to 660°C. The O₂ pressure in oxidation was increased from 5.3×10^{-5} Pa to 2.7×10^{-4} Pa and 5.3×10^{-4} Pa. (b) Time evolution of oxide coverage obtained from O 1s photoelectron intensity. The number of etched Si layers in the inset indicates that the Si surface is etched by SiO desorption as well as two-dimensional oxide island growth.

tensity normalized by the Si 2p intensity of the bulk component I_{C-1s} increases in proportion to C₂H₄ dosage and then remains almost unchanged up to ~8000 s as seen in Fig. 2(a). After ~8000 s, when the O₂ pressure was increased, I_{C-1s} shows a slight increase in accordance with a rapid increase of oxide coverage depicted in Fig. 2(b). Here, the initial value of x before oxidation was estimated as 0.06. Therefore, the 2D oxide island growth kinetics is divided into two regions at ~8000 s.

In the region below ~8000 s, etching due to SiO desorption dominantly occurs with a very slow growth of oxide. As indicated in the inset of Fig. 2(b), the number of etched Si layers was estimated in terms of the O₂ pressure and sticking probability of O₂ molecule on Si(001). In spite of removing more than 40 Si layers, the almost constant value of I_{C-1s} implies that C atoms of the Si_{1-x}C_x alloy layer do not desorb as CO and/or CO₂ together with SiO but still remains near the surface. Namely, C diffusion is enhanced by the oxidation with the significant desorption of SiO. Similar enhancement in C diffusion was also observed for the Langmuir-type adsorption at oxidation temperature of 500°C, where oxide growth exclusively occurred with no SiO desorption. Therefore it is likely that C atoms can be diffused down to the subsurface by oxidizing the Si_{1-x}C_x alloy layer with and without SiO desorption.

At oxidation times above ~8000 s, on the other hand, a considerable shift of C 1s peak position observed in Fig. 1(b) suggests that oxidation of the Si_{1-x}C_x alloy layer leads to the formation of SiC_xO_y layer. This is consistent with the slight increase of I_{C-1s} . The reason is that the SiC_xO_y layer lies closer to the surface than the Si_{1-x}C_x alloy layer, result-

ing in an increase of I_{C-1s} . Such an agreement indicates that some of C atoms of the Si_{1-x}C_x alloy layer are incorporated to oxide layers rather than diffusing to the subsurface. In the case of Langmuir-type adsorption at 500°C, no C atoms are included in the oxide layer up to thickness of ~1 nm while the C concentration at the interface between the oxide and Si_{1-x}C_x alloy layer is maintained almost constant. Thus C diffusion can be caused corresponding to the progress of oxide growth at oxidation temperature as low as 500°C. It is noted that oxide growth rate is influenced by the presence of C on the surface for both the surface oxidation manners. Therefore, the observed enhancement of C diffusion as well as the changes in oxide growth rate is thought to be concerned with the point defect generation (emitted Si atom and vacancy) caused by the oxidation-induced strain [4].

4. Conclusions

The oxidation reaction kinetics on the Si_{1-x}C_x alloy layer / Si(001) surface was monitored in real time by photoelectron spectroscopy. We have found that significant enhancement of C diffusion is caused by oxidation with and without SiO desorption. It is suggested that the oxidation-induced strain plays an important role in both phenomena of C diffusion and oxide growth.

References

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