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Diffusion of Carbon in SiO_2 Films and Its Segregation at Si/SiO_2 Interface

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Diffusion of carbon and its segregation at Si/SiO_2 interface were investigated using carbon-incorporated BPSG films and carbon-implanted SiO_2 films. It was found that carbon atoms diffuse in SiO_2 film at a temperature as low as 500°C, and they segregate at the Si/SiO_2 interface. Annealing in oxidizing ambient stimulates the carbon diffusion in SiO_2 and is effective for removing carbon from the films and for the suppression of carbon segregation. FE-TEM and EELS observations revealed that carbon atoms exist on the SiO_2 side of the interface and another carbon-rich phase is formed in SiO_2.

1. INTRODUCTION

Interlayer-dielectrics, such as SiO_2 and BPSG films, have come to be deposited with organic sources, such as TEOS, by LPCVD, because it provides better coverage than films deposited with non-organic sources, such as SiH_4, by APCVD. However, in the case of films with organic sources, carbon cannot be eliminated from the films during the deposition. It has been pointed out that carbon atoms segregate at the Si/SiO_2 interface and degrade the isolation characteristics, because segregated carbon atoms act as positive charge[1)]. Therefore, it is important to investigate the characteristics of carbon in SiO_2 films on Si substrates. In this paper, diffusion characteristics of carbon in SiO_2 films and the state of segregated carbon at the Si/SiO_2 interface were investigated.

2. EXPERIMENT

LP-BPSG films were deposited on thermally grown SiO_2 films using TEOS ($Si(OC_2H_5)_4$), TMB ($B(OCH_3)_3$), phosphine (PH_3) and oxygen (O_2) at 600°C by LPCVD at 0.8torr. Carbon ion implanted SiO_2 films were also fabricated. The samples were annealed in a nitrogen or oxygen ambient. Diffusion characteristics of carbon in BPSG and in SiO_2 were measured by SIMS. Electrical influence of carbon was examined with C-V measurements for capacitors and with Id-Vg measurements for Al-gate field transistors. Cross-sectional FE-TEM and EELS were performed for the analysis of segregated carbon at the interface.

3. EFFECT of CARBON SEGREGATION

Figure 1 shows a typical SIMS profile for as-deposited and annealed samples with LP-BPSG films. In as-deposited films, a concentration of about $10^{20}cm^{-3}$ of carbon atoms was incorporated in the BPSG films. However, after annealing, most of the carbon atoms were segregated at the Si/SiO_2 interface. Figure 2 shows the positive charge and surface state density induced by the interfacial carbon in the annealed samples. Samples were fabricated by the deposition of various thickness of BPSG films on thermally grown SiO_2. Positive charge was generated by the segregation of carbon[1)], and the charge density was proportional to the carbon concentration, while surface state density did not depend on the carbon concentration.

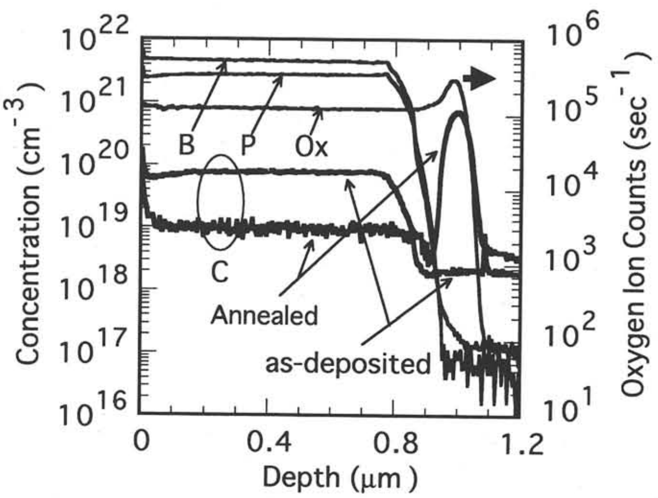

Fig.1 SIMS profiles for as-deposited and annealed samples. 900nm-thick BPSG was deposited on 100nm-thick SiO_2 films. The sample was annealed at 900°C for 30 min.

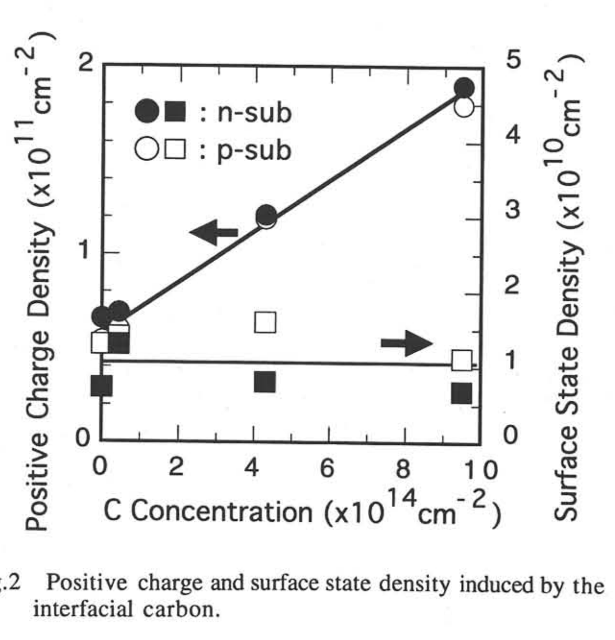

Fig.2 Positive charge and surface state density induced by the interfacial carbon.

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4. DIFFUSION of CARBON in SiO_2

Diffusion of carbon in SiO_2 was examined with carbon implanted samples in order to examine the diffusion characteristics in a wide temperature range. Carbon ions were implanted with a dose of $3x10^{15}cm^{-2}$ at 50keV into thermally grown SiO_2 films. Figure 3 shows depth profiles of carbon for samples annealed in a nitrogen ambient for 30 minutes. Some amount of carbon diffuses from the initial depth to the surface and to the Si/SiO_2 interface. This suggests that carbon atoms can make stable bonds at the surface and the interface. Figure 4 shows the segregated carbon concentration at the Si/SiO_2 interface for the samples annealed in the temperature range between 500°C and 800°C. Figure 4 indicates that even at a temperature as low as 500°C, carbon atoms diffuse in SiO_2 films and segregate at the interface.

Annealing in oxygen ambient showed quite different diffusion characteristics. Figure 5 shows carbon profiles for samples annealed in oxygen ambient. Concentrations of carbon atoms at the surface and in the SiO_2 film were much lower than those shown in Fig.3, when the annealing temperature was higher than 700°C. Bonds between carbon and silicon atoms in SiO_2 films were broken and carbon atoms were eliminated as CO or CO_2 molecules. Thus, the carbon at the surface disappeared and the interfacial carbon density was lowered.

Adopting this oxygen annealing process, the influence of carbon on the positive charge can be suppressed. Figure 6 shows the threshold voltages for field transistors using LP-BPSG films. Without the annealing in an oxygen ambient, the interfacial carbon concentration was about $4x10^{15}cm^{-2}$, and the threshold voltages for NMOS field transistors were lowered to about 0 V due to the carbon segregation even though the oxide thickness was 1.4μm. On the other hand, almost the same threshold voltages about 40 V were obtained for both PMOS and NMOS transistors, belonging to the low carbon concentration group, which were fabricated with the oxygen annealing process.

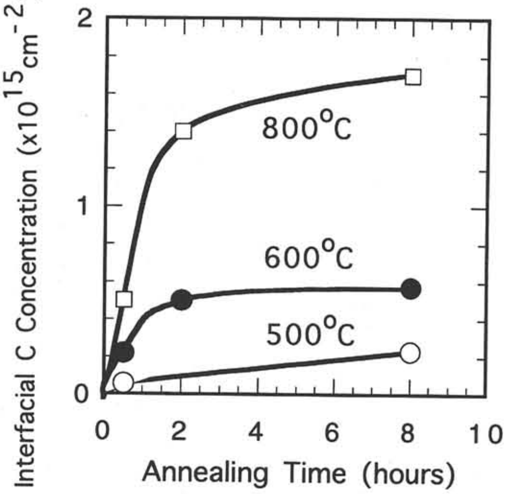

Fig.4 Segregated carbon concentration at the Si/SiO_2 interface for the annealed samples.

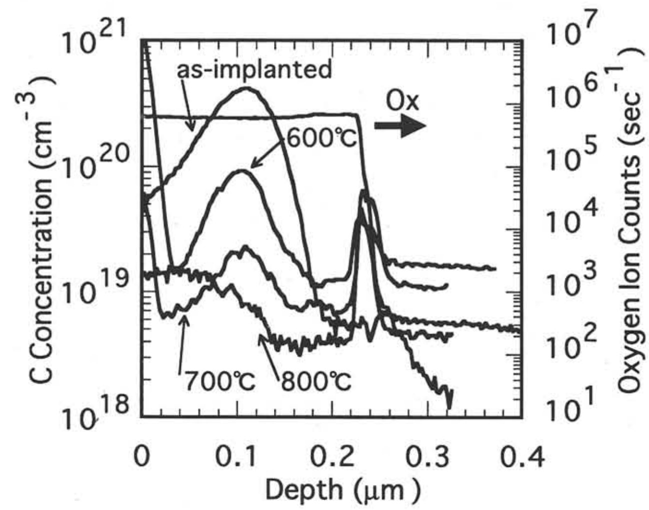

Fig.5 Depth profile of carbon for samples annealed in an oxygen ambient.

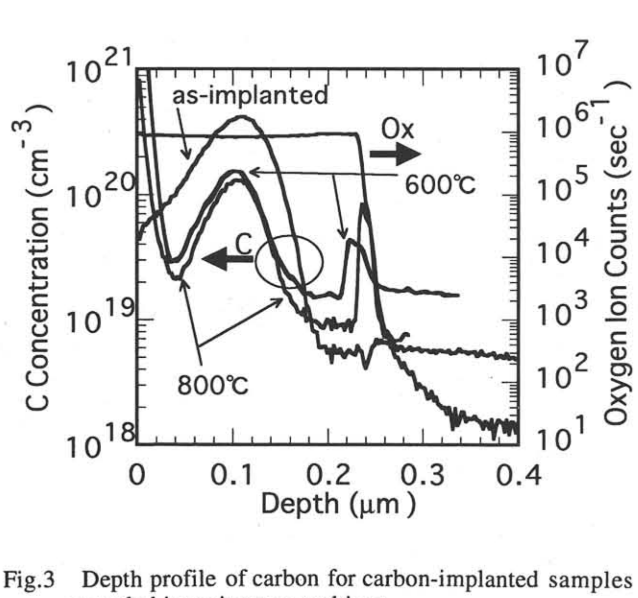

Fig.3 Depth profile of carbon for carbon-implanted samples annealed in a nitrogen ambient.

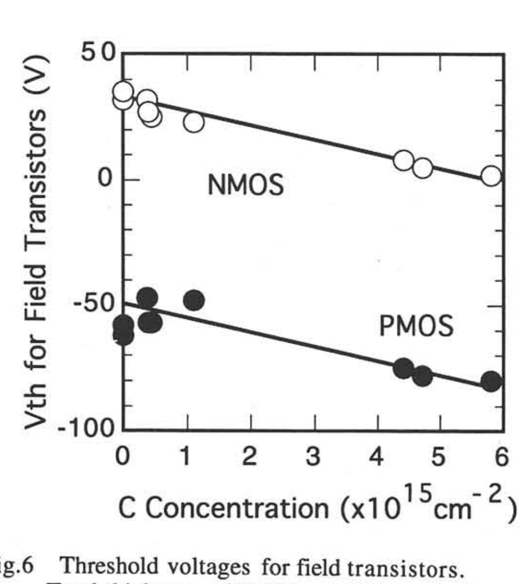

Fig.6 Threshold voltages for field transistors. Total thickness of BPSG and SiO_2 was 1.4μm.

5. SEGREGATED CARBON at Si/SiO_2 INTERFACE

FE-TEM and EELS measurements by HITACHI HF-2000 clearly indicated that carbon atoms segregate on the SiO_2 side and that another carbon related phase is formed. Figure 7 (a) and (b) shows the cross-sectional TEM at the Si/SiO_2 interface, where the interfacial carbon density was $1.9x10^{16}cm^{-2}$ and $2.2x10^{16}cm^{-2}$, respectively. Round areas having different contrast to the surrounding SiO_2 are found for both samples. The diameter of the area was about 5nm for the higher carbon concentration sample, while smaller areas were observed for the sample with lower segregated carbon concentration. EELS spectra were measured at the three points, as indicated in Fig.8: (A) Si side of the interface, (B) SiO_2 side of the interface and (C) round area observed in SiO_2. On the Si side of the interface, no carbon was observed as shown in Fig.9(A). On the contrary, on the SiO_2 side, carbon atoms were detected as a peak at 284 eV, as shown in Fig.9(B). Much higher intensity of carbon was detected at the round area as shown in Fig.9(C). There results indicate that carbon atoms segregate on the SiO_2 side of the interface and some carbon atoms form another carbon-rich phase, such as SiC, in SiO_2 films.

6. CONCLUSION

Carbon atoms diffuse in SiO_2 films at a temperature as low as 500°C. Annealing in oxygen stimulates the carbon diffusion in SiO_2 and is effective for removing carbon from the films and for decreasing the positive charges. They segregate on the SiO_2 side of the Si/SiO_2 interface, and a part of carbon atoms form carbon-rich phase in SiO_2.

Reference

1) H.Mori et al., Ext.Abst. SSDM p.904 (1994).

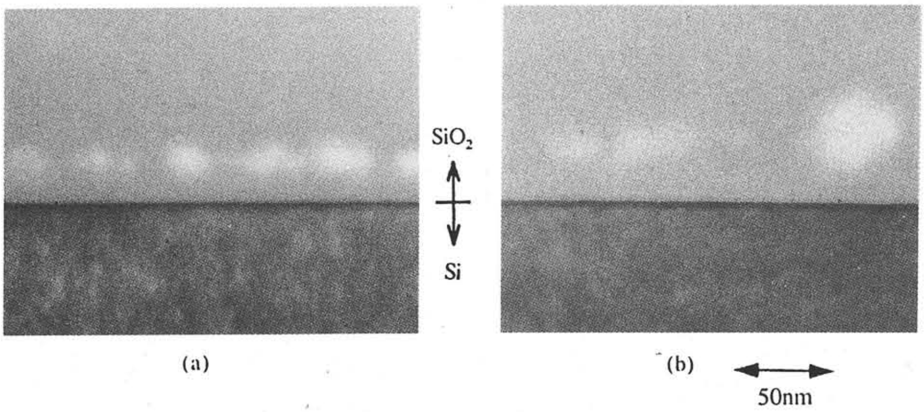

Fig.7 Cross-sectional TEM at the Si/SiO_2 interface for two samples with different interfacial carbon concentration: (a) $1.9x10^{16}cm^{-2}$ and (b)$2.2x10^{16}cm^{-2}$.

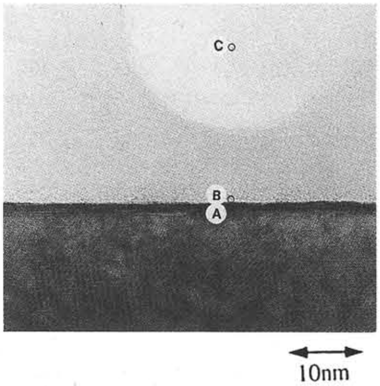

Fig.8 Cross-sectional TEM at the Si/SiO_2 interface where carbon atoms are segregated. Three points indicated as A, B and C were analyzed by EELS.

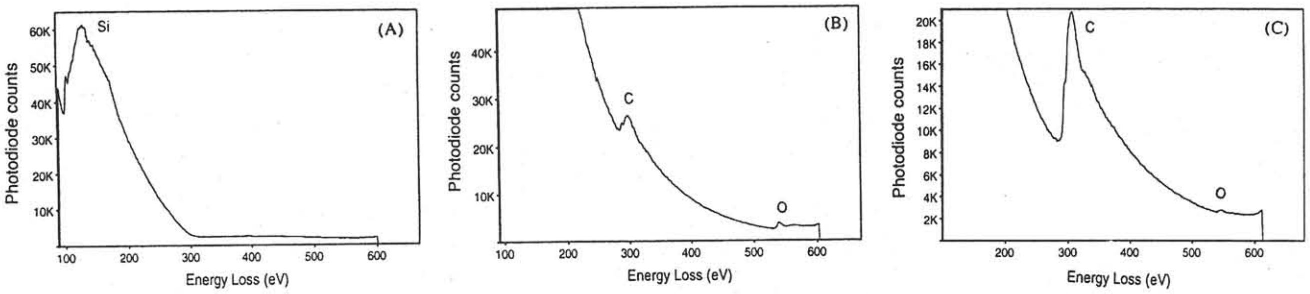

Fig.9 EELS spectra of (A) the Si side, (B) the SiO_2 side of the interface and (C) the round area in SiO_2.