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Fluorine Segregation at SiO_2/Si Interface

Yukinori ONO, Michiharu TABE and Yutaka SAKAKIBARA

NTT LSI Laboratories
3-1, Morinosato Wakamiya, Atsugi-shi,
Kanagawa Pref., 243-01,Japan

We demonstrate, for the first time, that the profile of fluorine thermally diffused into SiO_2 film has a peak concentration at the SiO_2/Si interface, though depletion of fluorine at the interface was reported previously. The effects of fluorine on the interface paramagnetic defects are also examined. Electron Spin Resonance measurements indicate that fluorine atoms terminate the trivalent Si dangling bonds at the interface.

1. INTRODUCTION

Recent studies have shown that a suitable amount of fluorine (F) in the oxide film improves MOS device reliability.[1)2)] However, the fundamental properties of F, such as the depth profile near the SiO_2/Si interface, are still not fully understood.

In this paper, the properties of fluorine incorporated into the oxide film by thermal diffusion are examined from the points of view of (1) the detailed fluorine depth profile near the SiO_2/Si interface, and (2) interactions between F atoms and the interface defects.

In the F depth profile measurements, we employed a wet step etching method instead of the conventional sputtering technique to eliminate sputtering-related profile modification. Interactions of F atoms with the interface defects (Pb center) were examined using Electron Spin Resonance (ESR).

2. EXPERIMENTS

Substrates used were mainly CZ phosphorus doped Si with a resistivity of 0.1 Ω cm. For the ESR measurements only, we used FZ boron doped Si wafers with a resistivity of 100 Ω cm.

After 500-Å-thick SiO_2 was thermally grown, F^+ ions were implanted into Si substrate through the SiO_2 film (80keV) except for the ESR samples. For the ESR samples, 5000-Å-thick non-doped amorphous-Si was deposited on the oxide and, then, F^+ ions were implanted into the a-Si layer (30keV). F atoms were introduced into the oxide by thermal diffusion at 1000° C for all samples.

In depth profile measurements, we employed the step-etching of the oxide by a 0.5% HF solution followed by rinsing with DI water for 30 min. Here, the following two experiments were carried out: (a) AES measurements of F intensity near the residual SiO_2 surface at each etching step, (b) O_2^+ beam SIMS measurements of the integrated amount of F by sputtering the entire residual oxide at each etching step, and the depth profile of F was derived by differentiating the amount by depth. In the SIMS measurements, the resultant profile is not influenced by the mixing effects of the sputtering because we focused on only the total amount of F at each etching step. In both AES and SIMS measurements, we confirmed that F absorption from HF solution was negligible.

In ESR measurements, the poly-Si layer (a-Si before annealing) was removed before the measurements in order to eliminate the signal from the amorphous Si center.

3. RESULTS AND DISCUSSION

3.1. Depth Profile

Figure 1 shows the depth profiles of fluorine after 30 min N_2 annealing at 1000° C for the step-etching method. The results by AES (F:$3x10^{16}cm^{-2}$ dose) and

SIMS (F:$1x10^{15}cm^{-2}$ dose) are shown in (a) and (b), respectively. In both measurements, Si substrates used were (111) oriented. The profiles by conventional sputtering techniques are also shown. Ar^+ ions and O_2^+ ions were employed in sputtering of AES and SIMS, respectively.

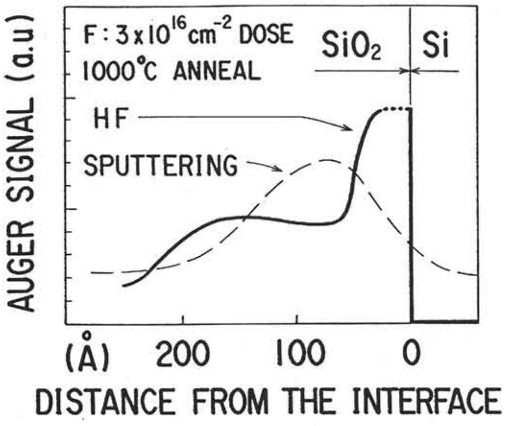

Fig.1(a). F depth profile by AES.

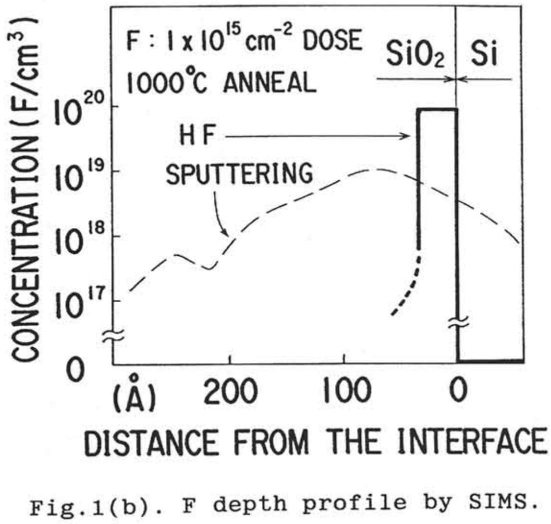

Fig.1(b). F depth profile by SIMS.

In both AES and SIMS, sputtering techniques results in a profile with a broad peak in the oxide and F atoms seem to be depleted at the interface as previously reported.[3] On the contrary, the step-etching method produces a different profile with a peak position at the interface within experimental error (30-40Å). AES measurements, in which F dose was relatively high, show that F depth profile has a maximum peak at the interface and a broad tail towards the SiO_2 bulk. No fluorine was observed when the oxide was completely removed, indicating that F profile is abrupt towards the Si substrate. For the lower dose of fluorine, SIMS was employed because of its high sensitivity. In SIMS measurements, the integrated amount of fluorine was found to be almost unchanged even when the residual oxide thickness was only about 35Å. This shows that most of the F atoms segregate very close to the interface as shown in Fig.1(b).

The profiles of the step-etching method are more likely than the profile obtained by sputtering because step etching prevents the profile modifications caused by the mixing and matrix effects of sputtering.

We also studied the crystalline defects caused by fluorine ion implantation (80keV, $3x10^{16}cm^{-2}$ dose) by XTEM. As shown in Figs.2 (a) and (b), implantation damage near the interface remains after 700° C annealing but disappears after 1000° C annealing. This disappearance evidences that the interface segregation of F shown in Fig.1 is not predominated by extrinsic implantation-damage (trapping sites for F), but determined by intrinsic interface properties. In this experiment, annealing time is 30 min. For shorter annealing time, implantation damage remains even at 1000° C.

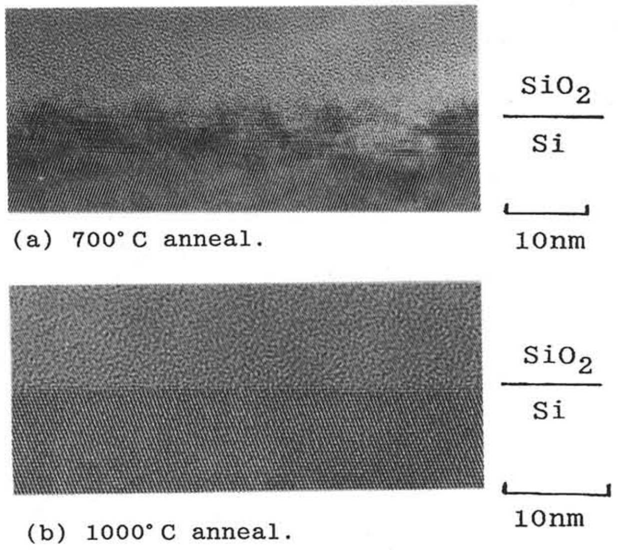

Fig.2. TEM images near the SiO_2/Si interface for F dose of $3x10^{16}cm^{-2}$.

3.2. Substrate Orientation Dependence of F Segregation

Fluorine concentration in the interface region as a function of annealing time are compared between (111) and (100) substrates in Fig.3. In this experiment, F implantation dose was $1x10^{15}cm^{-2}$ and annealing temperature was 1000° C.

Here, we divide annealing time into two regions: A and B. Region A is a intermediate state of the diffusion process. Interface F concentration in this time region must be strongly affected by the supply of F atoms from the substrate and by the recovery rate of implantation damage. On the other hand, Region B is a quasi equilibrium state of interface segregation. In this time region, fluorine segregation must depend only on the intrinsic interface properties. As shown in Fig.3, fluorine concentration in Region B is almost constant and larger amount of fluorine for (111) substrate is observed. The difference suggests that interface segregation of fluorine fundamentally depends on the intrinsic defect density and supports the idea that F atoms terminate them.

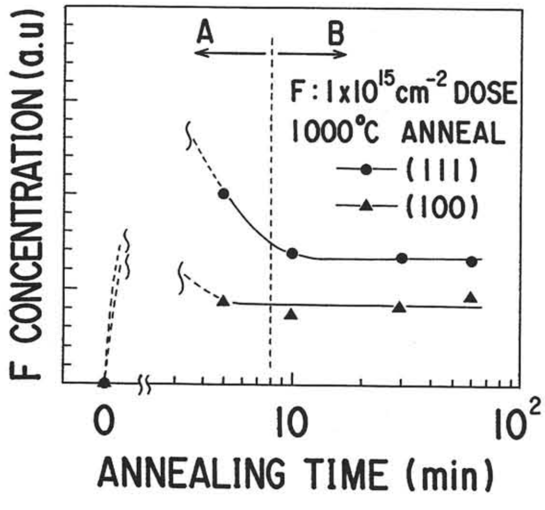

Fig.3. Interface F concentration for (111) and (100) interfaces.

3.3. ESR Measurements

Prior to studying F effects on interface paramagnetic defects, we performed ESR measurements on unimplanted (111) samples. Figure 4 shows the ESR signals of the Pb center after (a) oxidation, (b) a-Si deposition on the oxide, and (c) the N_2 annealing of Sample (b) at 1000° C. The Pb center is observed in (a) but a-Si deposition causes it to disappear. This is probably caused by hydrogen termination to the Si dangling bonds since hydrogen can be supplied from Si source gas (Si_2H_6). The Pb center reappears after N_2 annealing, as shown in (c), indicating hydrogen detrapping. Therefore, similar termination effects of F are expected.

Pb center density and F peak concentration are plotted for (111) substrates as a function of F dose in Fig.5. It can be seen that the number of Pb centers decrease with increasing interface F atoms. These results indicate that segregated F at the interface terminates the interface paramagnetic dangling bonds. However, it is noted that only a small fraction of F atoms in the interface region serve to terminate them.

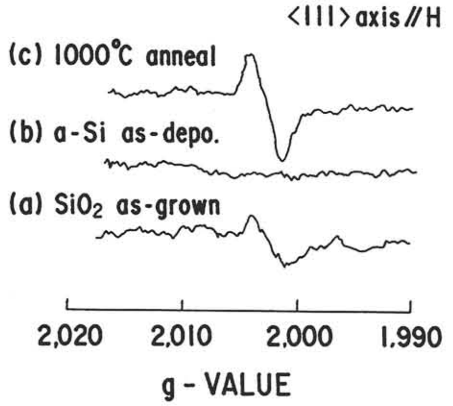

Fig.4. ESR signals of Pb center for the unimplanted samples.

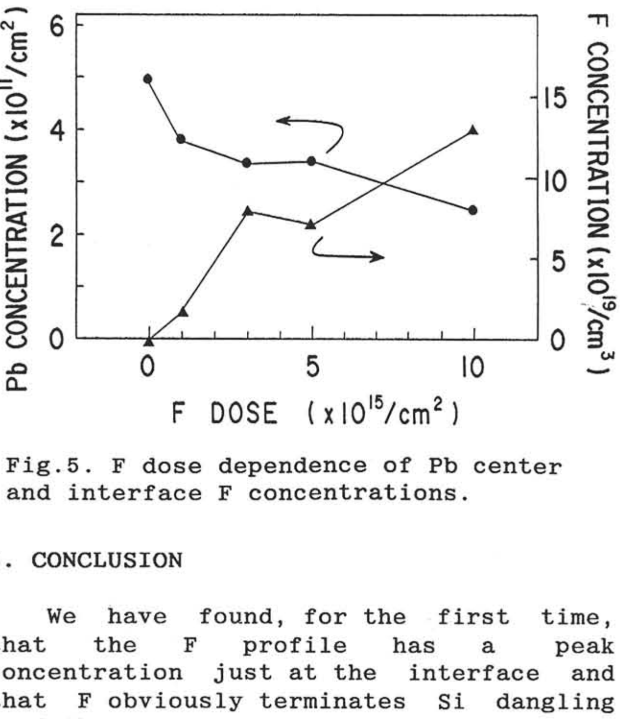

Fig.5. F dose dependence of Pb center and interface F concentrations.

4. CONCLUSION

We have found, for the first time, that the F profile has a peak concentration just at the interface and that F obviously terminates Si dangling bond there.

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