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Defect Termination by Nitrogen Bonding due to NO Nitridation in MOS Structures

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1. Introduction

Using NO nitrided silicon oxide provides higher reliability for hot carrier degradation and stress-induced leakage current (SILC), but not for negative bias temperature instability (NBTI). [1][2][3] To utilize such nitrided films for future-generation MOS devices, it is necessary to understand the role of nitrogen at the interface and inside the SiO_2. To evaluate the bond strength near the nitrided SiO_2/Si(100) interface and inside the SiO_2, and thus clarify the reliability issues, the chemical structure relating to the nitrogen was modeled. The model was confirmed by electron spin resonance (ESR) measurements and by x-ray photoelectron spectroscopy (XPS). We also electrically characterized the interface trap density in MOS capacitors.

2. Experimentals

SiO_2 films with thicknesses of 2 to 9 nm were formed on p-type Si(100) by wet oxidation. The films were annealed in 1 to 100% NO gas ambient at 900 to 950 ℃. For ESR analysis, 2-nm-thick SiO_2 films were grown on wafers polished on both sides and diced into bars. Hidrazine treatment was performed to terminate edge defects. XPS analysis was carried out with a monochromatized AlKα x-ray source. The interface trap density was characterized by high frequency C-V and quasi-static C-V measurements for poly-Si gate capacitors with and without H_2 annealing (450℃, 30 min). The LOCOS was used for isolation. The SiO_2 film thickness for capacitors was 9 nm.

3. Results and Discussion

The results of the ESR measurements are shown in Fig. 1 for an SiO_2 film and an NO nitrided SiO_2 film (NO annealing: 5% NO gas, 950℃, 20 min). Both films showed Pb_0 and Pb_1 centers.[4] The signal intensities are listed in Table 1. Although the intensities of both defects decreased after nitridation, the decrease in the signal for the Pb_0 center was drastic. The decrease in the ESR signals resulted from N-Si bond formation at the interface.

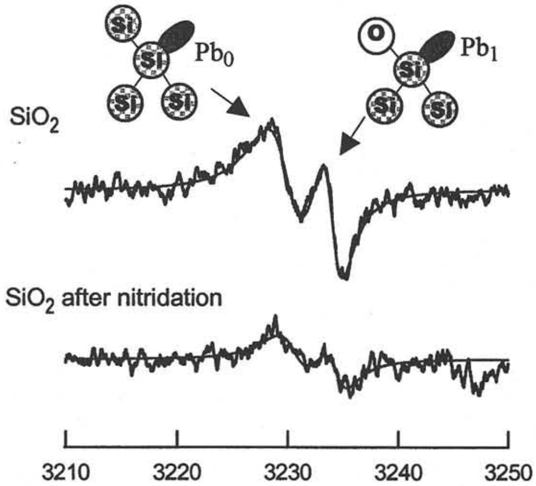

Fig. 1 ESR signals for SiO_2 and nitrided SiO_2

Table 1. Intensities of Pb_0 and Pb_1 centers for SiO_2 and nitrided SiO_2 (a. u.)

	SiO_2	Nitrided SiO_2	Decrease in intensity	
Pb_0	2442	710	1732	79%
Pb_1	831	356	474	21%
			2206	100%

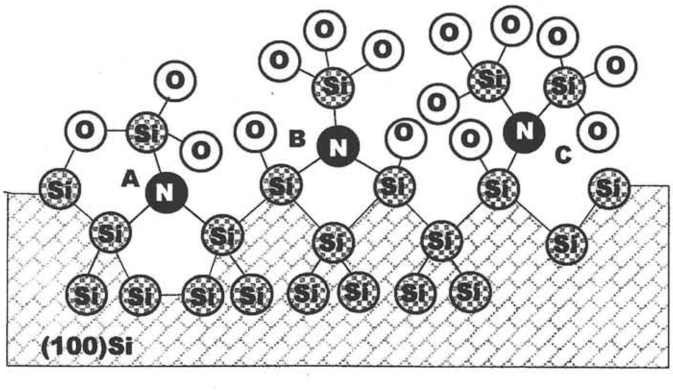

Fig. 2 Model of the chemical structure of NO-nitrided SiO_2/(100)Si.

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By bonding N to the dangling bond, the nitrided interface structure was modeled and is shown in Fig. 2. If the N atom bonds to a Pb_0 center, the structure of the Si-N bond at the interface is like that of **A** in Fig. 2. In this structure, the second nearest neighbors of the N atom are mainly Si, and O to a lesser extent. On the other hand, if the N atom bonds to a Pb_1 center, the structure is like that of **B** or **C** in Fig. 2 and the second nearest neighbors are mainly O.
To determine the chemical structure, XPS analysis was performed on the same samples. The N1s photoelectron spectrum is shown for the NO-nitrided SiO_2 film in Fig. 3. As reported previously, a peak is observed at 398 eV which corresponds to $N\equiv Si_3$ with some O atoms as the second nearest neighbors.[5] However, the peak is asymmetric, showing that two or more energy states exist. The peak can be deconvoluted into two components with an energy difference of about 0.6 eV. Referring to the model shown in Fig. 2, we assigned the lower energy peak N_L as the N in structure **A**, and the higher energy peak N_H as the N in structures **B** and **C**, which have greater numbers of O atoms as second nearest neighbors. The peak intensity ratio of N_L / N_H was about 4, which is in good agreement with the ratio of decrease of the Pb_0/Pb_1 signal.
The decrease in interface trap density by NO nitridation (900℃, 10 min) was electrically characterized in the capacitor with 9-nm SiO_2. The results are shown in Fig. 4. In Fig. 4, the solid and open squares show D_{it} before and after H_2 annealing. As expected from the ESR results, the density of interface traps drastically decreased during NO nitridation. When the NO nitridation was performed in 10% NO gas ambient, more than 90% of the traps were terminated by N.

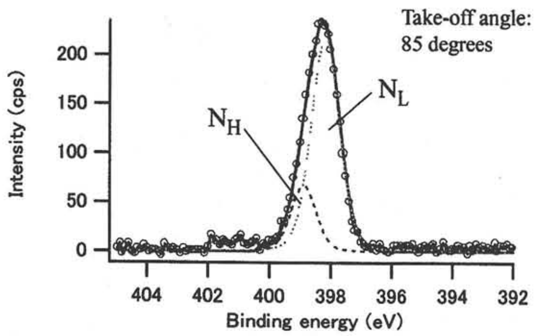

Fig. 3 XPS N1s spectrum for the NO-nitrided SiO_2 film; the dashed lines are curve-fitted peaks with chemical states as labeled. The solid line is the sum of these peaks.

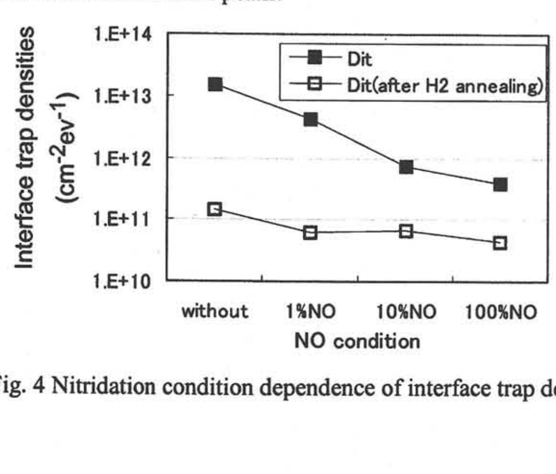

Fig. 4 Nitridation condition dependence of interface trap density.

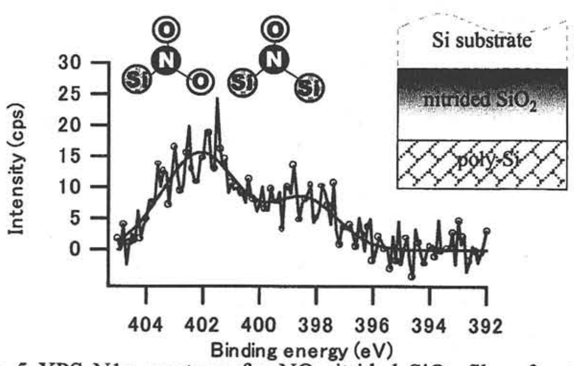

Fig. 5 XPS N1s spectrum for NO-nitrided SiO_2 film after the Si substrate was etched off.

Next, the nitrogen bonding inside the SiO_2 was analyzed. The poly-Si-gate surface was made to adhere to a Si wafer, and the original Si substrate was then polished and etched off in hidrazine. The N spectrum obtained by XPS is shown in Fig. 5. A weak signal with a binding energy of 398 eV and a broad peak with a higher binding energy were detected. According to a calculation using a first-principle approach, [6] the higher energy peak can be assigned to an $N\text{-}Si_2O$ or $N\text{-}SiO_2$ structure. From these results, we found that the NO nitridation not only affects the interface but also creates some nitrogen bonds inside the SiO_2 film.

4. Conclusion

We have successfully modeled the NO-nitrided SiO_2/Si interface, thus explaining on defect analysis obtained by ESR, chemical structure analysis obtained by XPS, and C-V results. At the interface, N atoms are preferentially bonded to Pb_0 centers, which form the dominant Si-N bonds at 398 eV. As a result, more than 90% of the traps are terminated by N at the NO-nitrided SiO_2/Si interface. NO nitridation also creates bonds inside SiO_2 films. The presence of nitrogen may explain reliability issues related to the interface, such as hot-carrier immunity, as well as bulk phenomena, such as SILC suppression.

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