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Relationship between Water Diffusivity of Dielectric Films and Accelerated Hot Carrier Degradation Caused by Water

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The relationship between the water diffusivity of dielectric films evaluated by use of D₂O and the accelerated hot carrier degradation caused by water is presented. The diffusion coefficient of D₂O in a tetraethylorthosilicate-based plasma CVD SiO₂ (P-TEOS) film was about one tenth that of a SiH4-based (P-SiO) film. The P-TEOS film did not block the water diffusion, while a P-SiO film only 200nm in thickness was sufficient to block the water diffusion and suppress accelerated hot carrier degradation. FT-IR measurement suggested that the Si-H, Si-NH or Si-NH₂ included in P-SiO film efficiently trapped the diffusing water.

1. INTRODUCTION

In submicron ULSI technology, spin-on glass (SOG) or O3 and tetraethylorthosilicate (TEOS)-based CVD SiO2 are used for planarization. These dielectric films contain large amounts of water, which diffuses into the gate oxide film during annealing to form many traps. The traps accelerate hot carrier degradation. (1)-(5) To suppress accelerated hot carrier degradation, a dielectric film with low water diffusivity is required. Hence, quantitative evaluation of the water diffusivities of dielectric films is important.

In this work, the authors investigated the water diffusivities of dielectric films by use of heavy water (D₂O) instead of water in order to distinguish between water which permeated from outside and that which was included in the dielectric film. Based on the results, this paper describes the relationship between the water diffusivities of dielectric films and accelerated hot carrier degradation caused by water, and presents a mechanism explaining immunity to water diffusivity of dielectric films.

2. EXPERIMENTAL PROCEDURE 2-1. Sample Preparation

A PSG film with a thickness of 800nm was deposited on a Si substrate using SiH4, PH3, and O2 under atmospheric pressure at 400°C. The purpose of this PSG film was absorb D2O permeating through the evaluation films. The evaluation films were P-SiO and three kinds of P-TEOS films 300 nm in thickness deposited on the PSG film. The P-SiO film was deposited using SiH4 and N2O in plasma at 350°C. The three kinds of P-TEOS films were deposited using TEOS and O2 in plasma at 400°C at three different mixing ratios of TEOS and O2 (TEOS/O2), namely, 0.4, 0.67, and 0.9. Samples were cut into rectangular plates about 12.5 mm x 25 mm. After soaking in D2O for 24 hours at 80°C, the depth profiles of deuterium, hydrogen concentration and phosphorus secondary ion intensity were analyzed using secondary ion mass spectrometry (SIMS). In order to clarify the mechanism of immunity to water diffusivity of dielectric films, Fourier transform infrared (FT-IR) analysis was performed, and the densities of dangling bonds in the P-SiO and P-TEOS films were estimated by electron spin resonance (ESR) measurement.



Fig. 1 Schematic cross sections of nMOS transistors.

2-2. Measurement of Hot Carrier Life Time

The value of hot carrier life time (τ_{HC}) of conventional LDD and nMOS transistors with gate lengths of 0.5µm and widths of 15 µm, and a gate oxide thickness of 10nm was measured at the maximum substrate current. Here, τ_{HC} was defined as the stress time when the transconductance (Gm) degraded 10% from the initial value. Two nMOS transistor structures were evaluated, as shown in Fig. 1-(a) and (b). Structure (a) contained an SOG film sandwiched by P-TEOS films. The P-TEOS film on the SOG was deposited at a TEOS/O₂ of 0.67. The P-TEOS film under SOG was deposited at a TEOS/O₂ of 0.2 or 0.67. Structure (b) had an SOG film sandwiched by P-TEOS films deposited at a TEOS/O₂ of 0.67, and in addition, a P-SiO film on the metal lines. The SOG films were used as a diffusion source of water.

3. RESULTS AND DISCUSSION 3-1. Diffusion Coefficient of D₂O

Figures 2 and 3 show the depth profiles of deuterium and hydrogen concentration, and phosphorus secondary ion intensity in the P-TEOS and P-SiO films, respectively. The depth variation of the diffusion coefficients of D2O in the P-SiO and P-TEOS films is shown in Fig.4. The diffusion coefficients of D2O in the P-TEOS film decreased as TEOS/O2 decreased. Permeation of D2O is thought to be suppressed because the P-TEOS film becomes more dense as the O2 concentration increases. The diffusion coefficient of D2O in the P-SiO film was about one tenth of that in the P-TEOS film with a TEOS/O2 of 0.4. Hence, the P-SiO film had better immunity to water diffusivity than that of the P-TEOS film.

3-2. Hot Carrier Life Time

Figure 5 shows the 1/Vd dependence of τ_{HC} , where Vd is the drain voltage. The THC of an nMOS transistor with a P-SiO film 200nm thick on the metal lines was about ten times longer than that with P-TEOS. Device characteristics such as substrate current showed the same values with both the nMOS transistor types. Hence, τ_{HC} depends on the density of the traps for carriers injected into the gate oxide, which implies that the occurrence of traps is attributable to water permeating into the gate oxide. The P-TEOS film failed to block water diffusion, which could be sufficiently suppressed only by the 200nm P-SiO film. This result shows good agreement with the results from the diffusion coefficients of D2O. A previous researcher reported that a large amount of hydrogen atoms included in the plasma CVD SiN film accelerated hot carrier degradation.(6) However, the hydrogen concentration in the P-SiO film was higher than that in the P-TEOS film, as shown in Figs. 2 and 3. Hence, accelerated hot carrier degradation could not have been caused by the diffusion of hydrogen absorbed by the dielectric film during deposition, but rather was caused by water diffusion from the SOG film. Water in the SOG film diffuses toward the gate oxide film, resulting in the formation of many traps, which accelerated hot carrier degradation. Furthermore, in structure (a), the THC values of the nMOS transistors with a P-TEOS film deposited at a TEOS/O2 of 0.2 or 0.67 under the SOG film were nearly equal. This result means that the high water diffusivity of the P-TEOS film at a TEOS/O2 of 0.2 makes it impossible to block permeation by water. Figure 6 shows the TEOS/O2 dependence of the diffusion coefficient of D2O in the P-TEOS films and that of the P-SiO film at 0.1 µm depth after soaking for 24 hours at 80°C.



The diffusion coefficients of D₂O in the P-TEOS film were extrapolated in order to find the TEOS/O₂ at which the diffusion coefficient of D₂O in the P-TEOS film has the same value as that in the P-SiO film. The result, however, was a negative value, indicating that it may be difficult to block the diffusion of water only by decreasing the TEOS/O₂ of P-TEOS films. A dielectric film with very low water diffusivity such as the P-SiO film must therefore be laid under the P-TEOS film in order to block the water diffusion.



Fig. 6 TEOS/O₂ dependence of diffusion

coefficient of D_2O in the P-TEOS films at 0.1 μ m

depth at 80 °C. Diffusion coefficient of D_2O in the P-SiO films is also indicated by the dotted line.

3-3. Mechanism of Immunity to Water Diffusivity of Dielectric Films

Takahashi et al. pointed out that dangling bonds of Si trap protons from water, which can block water diffusion.⁽⁷⁾ The densities of the dangling bonds in the P-SiO and P-TEOS film are shown in Table I. Clearly, the density of the dangling bonds in the P-SiO film is about twenty times larger than that in P-TEOS. In addition, the intensity of infrared (IR) absorption spectra attributed to the Si-H bond of the P-SiO film decreases after soaking in D2O, and the intensity of the IR absorption spectra which can be assigned to a Si-NH or Si-NH₂ bond also decreased after soaking. On the other hand, neither IR absorption spectra attributable to Si-H, nor Si-NH bond and Si-NH₂ bonds were observed in the P-TEOS film. Therefore, water which diffuses from the SOG film appears to react with Si-H and Si-NH or Si-NH₂ in dielectric films, preventing water diffusion. Conversely, this mechanism explains why the P-TEOS film has a high water diffusivity, namely, because it has no Si-H, Si-NH or Si-NH₂ bond.

Table I. Density of the dangling bonds in the dielectric films. The measurement was performed at 150K.

P-TEOS film (TEOS/O ₂ =0.67)	5.1×10^{17} spins/cm ³
P-SiO film	$1.1 \times 10^{19} \text{ spins/cm}^3$

4. CONCLUSION

A dielectric film with very low water diffusivity such as P-SiO must be deposited under a P-TEOS film in order to block water diffusion and thus suppress accelerated hot carrier degradation. As the mechanism preventing water diffusion, water reacts with Si-H, Si-NH, or Si-NH₂, which thus block permeation by water.

5. REFERENCES

- N. Lifshitz and G. Smolinsky: IEEE Electron Device Lett. <u>12</u> (1991) No. 3, 140.
- K. Shimokawa, T. Usami, S. Tokitou, N. Hirashita, M. Yoshimaru and M. Ino: 1992 Symposium on VLSI Technology Digest of Technical Papers (1992) 96.
- Chun Jiang, Chenming Hu and C. H. Chen, and P.N. Tseng: Proceedings of International Reliability Physics Symposium (1992) 122.
- M. Takagi, I. Yosii and K. Hashimoto: International Electron Devices Meeting Technical Digest (1992) 703.
- K. Fujino, Y. Nishimoto, N.Tokumasu, S. Fisher and K. Maeda: Proceedings of VLSI Multilevel Interconnection (1993) 96.
- R. C. Sun, J. T. Clements, and J. T. Nelson: Proceedings of International Reliability Physics Symposium (1989) 244.
- J. Takahashi, K.Machida, N. Shimoyama, and K. Minegishi: Appl. Phys. Lett. <u>62</u> (1993) No.19, 2365.