

Highly Stable Fluorinated Plasma CVD Silicon Nitride Film by SiH₄ Addition for ULSI Passivation

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We have newly developed the highly stable fluorinated Plasma CVD silicon nitride film by SiH₄-Si₂F₆-N₂-H₂ discharge mixtures (P-SiH₄-SiN:F). P-SiH₄-SiN:F stability is superior to that of the other fluorinated Plasma CVD silicon nitride film which is deposited from Si₂F₆-N₂-H₂ discharge mixtures (P-SiN:F), because P-SiH₄-SiN:F composition is controlled with SiH₄ addition, and the stability is sufficient for ULSI passivation. Moreover, P-SiH₄-SiN:F passivation causes no more the reliability degradation of MOS transistor and MOS capacitor than P-SiN:F passivation.

1 Introduction

Plasma CVD silicon nitride film, which is deposited by SiH₄-NH₃ or SiH₄-NH₃-N₂ discharge mixtures (P-SiN), has been widely used as VLSI passivation (1). However, P-SiN causes device reliability degradation, such as enhancement of MOS transistor threshold voltage shift (2) and MOS capacitor interface state generation (3) due to its hydrogen.

Yamazaki et al. has reported that fluorinated silicon nitride film using Si₂F₆-N₂-H₂ discharge mixtures has a smaller amount of hydrogen and hydrogen of this film is tightly bonded nitrogen, and that this film causes less degradation of MOS transistor than P-SiN (4). However, we found that P-SiN:F is unsuitable for ULSI passivation because this film changes into SiO₂ by only 16 hours Pressure Cooker Test (PCT: 121°C, 2kgf/cm²). Compared with P-SiN, P-SiN:F had fluorine and its nitrogen content was smaller. It was considered that fluorine is the center of reaction with humidity and smaller nitrogen content reduces Si-N bonding densities. Therefore, we tried to improve the stability of P-SiN:F by reducing fluorine and increas-

ing nitrogen within the film using SiH₄ addition as feed gas. Moreover, we considered that reducing fluorine causes no device reliability degradation due to hydrogen if fluorine content is enough against hydrogen content.

This paper presents fluorinated silicon nitride film using SiH₄-Si₂F₆-N₂-H₂ discharge mixtures is highly stable, and causes no more the reliability degradation of MOS transistor and MOS capacitor than P-SiN:F.

2 Experiment

2-1 Film Deposition

The deposition flow system is a parallel plate type plasma reactor with 380kHz discharge frequency. P-SiH₄-SiN:F and P-SiN:F were deposited by SiH₄-Si₂F₆-N₂-H₂ discharge mixtures, where N₂ and H₂ gas flow rates were constant, 1000sccm and 290sccm respectively, and the SiH₄/Si₂F₆ gas flow rate ratio was varied (20sccm/10sccm, 10/20, 0/30). P-SiN films were deposited by SiH₄-NH₃-N₂ discharge mixtures as a reference film with the same deposition flow system. All the films were deposited at 300°C.

2-2 Film properties

In order to investigate the film stability of P-SiH₄-SiN:F and P-SiN:F, we observed infrared absorbance spectra of the 100nm films before and after PCT.

Film composition was investigated using X-ray Photoelectron Spectroscopy. Refractive index was measured with an ellipsometer(632.8nm). Hydrogen concentration was measured from infrared absorbance peak by using Lanford methods⁽⁵⁾.

2-3 Device Application

In order to investigate the influence of the passivation film on the device reliability, we measured the n-MOS transistor life time under DC stress and the interface state density of MOS capacitor after constant current stress. These devices each were covered with one of the three types passivation, P-SiH₄-SiN:F, P-SiN:F and P-SiN, subsequently they were annealed at 400°C in N₂ for 60 minutes.

3 Results and Discussion

3-1 Film properties

Infrared absorbance spectra of P-SiH₄-SiN:F and P-SiN:F before and after PCT are shown in Fig.1. Solid line represents infrared absorbance spectra of these films after PCT and broken line represents that of these films before PCT. Fig.1 (a) shows that absorbance peak of P-SiN:F at about 900cm⁻¹ disappeared by only 16 hours PCT, which is regarded as absorbance peak due to Si-N and Si-F bonding⁽⁶⁾, and it changed into absorbance peak at 1080cm⁻¹ due to Si-O bonding. On the other hand, Fig.1 (b) shows that the peak of P-SiH₄-SiN:F still existed after even 256 hours PCT, and Si-O bonding peak is very small. These show that the stability of P-SiN:F is very poor, but the P-SiH₄-SiN:F stability is remarkably improved by SiH₄ addition. It is supposed that the changed film thickness of P-SiH₄-SiN:F by PCT

is a few hundred Å of the surface. P-SiH₄-SiN:F stability is sufficient for ULSI passivation, since the passivation thickness is usually more than several thousands Å.

F/Si and N/Si XPS signal intensity ratio of these films as a function of the SiH₄/(SiH₄+Si₂F₆) gas flow ratio (R) are shown in Fig.2. It shows that F/Si decreases and N/Si increases with increase of the gas flow ratio R. These results in Fig.1 and Fig.2 indicate that this change of film composition caused by SiH₄ addition improves the film stability of P-SiN:F film. The P-SiH₄-SiN:F film stability can be controlled by SiH₄ addition.

Fig.3 shows the refractive index dependence on the gas flow ratio R. The refractive index of P-SiN:F without SiH₄ feed gas is 1.67, while P-SiH₄-SiN:F refractive index increases with increasing the gas flow ratio R and comes up to 1.85. It comes near to 2.0 of stoichiometry Si₃N₄, because of the change of film composition as shown in Fig.2.

The dependence of hydrogen concentration of these films on the gas flow ratio R is shown in Fig.4. For P-SiN:F, no Si-H bonding was observed and N-H bonding is only about 1x10²¹cm⁻³, on the other hand Si-H bonding and N-H bonding of P-SiH₄-SiN:F increase with increase of the gas flow ratio R. Total hydrogen concentration of P-SiH₄-SiN:F is 5x10²¹cm⁻³, when it is deposited with SiH₄=20sccm and Si₂F₆=10sccm (● in Fig.4). It is larger than that of P-SiN:F, however it is less than one thirds of that of reference P-SiN film, which is 15x10²¹cm⁻³.

3-2 Device Application

As shown in Fig.2 and Fig.4, P-SiH₄-SiN:F has smaller fluorine content and larger hydrogen content than P-SiN:F. It was considered that this difference of film composition may cause the device reliability degradation. In order to clarify the device reliability degradation caused by three types passivation, we measured the n-MOS transistor

life time and the MOS capacitor interface state density.

Fig.5 shows the dependences of the MOS transistor life time covered with three types passivation on $1/L_{eff}$ (effective channel length). DC stress condition is $V_d=8V, V_g=3.5V$ and $V_{bb}=-3V$, and transistor life time is defined as the time to 10% reduction of drain current (I_d) at $V_d=5V$ (reverse to V_d of stress), $V_g=5V$ and $V_{bb}=-3V$. It shows that the life time of the MOS transistors with P-SiH₄-SiN:F passivation is longer than that of the MOS transistors with P-SiN:F and P-SiN passivation. The interface state density of MOS capacitors with three types passivation after constant current stress ($-5 \times 10^{-5} A cm^{-2}$ for 2500 seconds) are shown in Fig.6. It shows that the interface state density at the energy of 0.7eV from the valence band edge with P-SiN passivation is nearly $1 \times 10^{13} cm^{-2}$, while that with P-SiH₄-SiN:F passivation is less than $1 \times 10^{12} cm^{-2}$ and it is nearly equal to that with P-SiN:F passivation.

As above results, P-SiH₄-SiN:F passivation causes no more the reliability degradation of MOS transistor and MOS capacitor than P-SiN:F passivation, although it has smaller fluorine content and larger hydrogen content than P-SiN:F. It is considered that fluorine content of P-SiH₄-SiN:F is enough to suppress the device reliability degradation due to hydrogen of this film.

4 Conclusions

We have newly developed P-SiH₄-SiN:F for ULSI passivation. P-SiH₄-SiN:F has the high stability, because its fluorine content and nitrogen content are controlled by SiH₄ feed gas.

P-SiH₄-SiN:F causes no more the reliability degradation of MOS transistor and MOS capacitor than P-SiN:F and P-SiN, because its fluorine content is enough to suppress the device reliability degradation due to

hydrogen. P-SiH₄-SiN:F is promising as ULSI passivation.

Acknowledgment

We wish to thank to I.Kurachi for his help on device reliability analysis, M.Kinoshita and T.Ajioka for their help on XPS studies.

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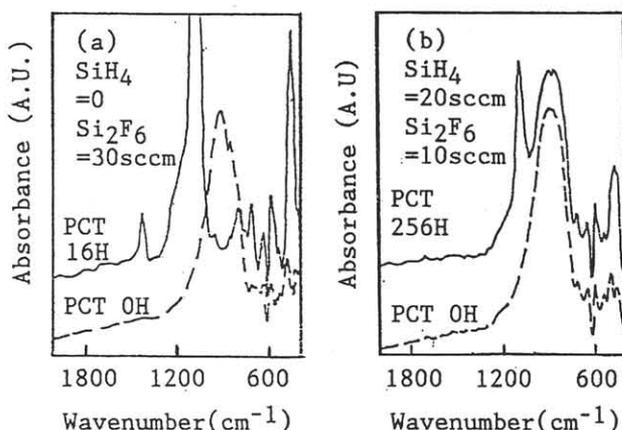


Fig.1 Infrared absorbance spectra of P-SiH₄-SiN:F and P-SiN:F before (broken line) and after (solid line) PCT.

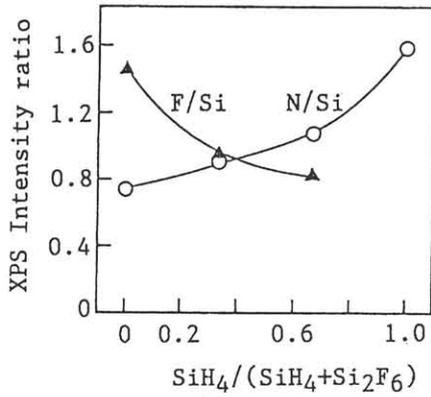


Fig.2 F/Si and N/Si XPS signal intensity ratio of P-SiH₄-SiN:F and P-SiN:F as a function of SiH₄/(SiH₄+Si₂F₆) gas flow ratio.

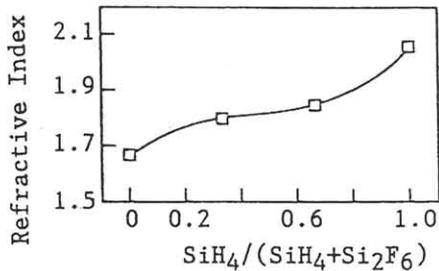


Fig.3 Refractive index of P-SiH₄-SiN:F and P-SiN:F as a function of SiH₄/(SiH₄+Si₂F₆) gas flow ratio.

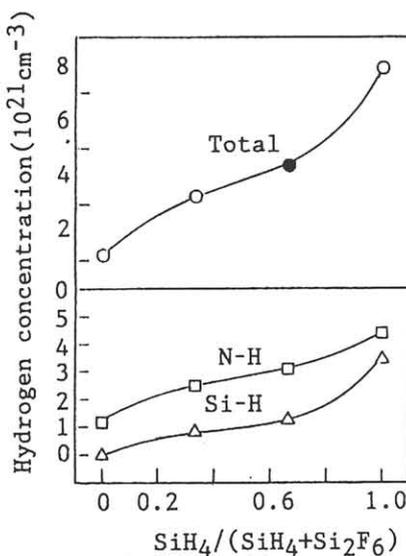


Fig.4 Hydrogen concentration of P-SiH₄-SiN:F and P-SiN:F as a function of SiH₄/(SiH₄+Si₂F₆) gas flow ratio.

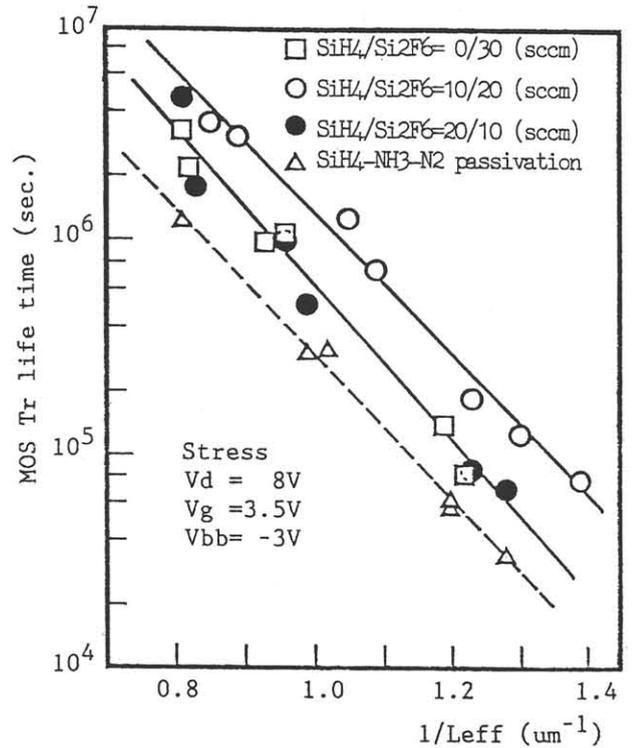


Fig.5 Life time of n-MOS transistors with P-SiH₄-SiN:F passivation, with P-SiN:F passivation and with P-SiN passivation.

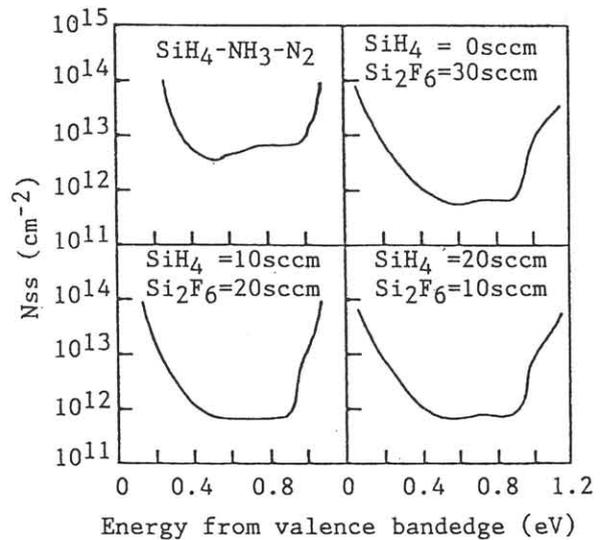


Fig.6 Interface state density of MOS capacitors after constant current stress ($-5 \times 10^{-5} \text{A}/\text{cm}^2$ for 2500 seconds) with P-SiH₄-SiN:F passivation, with P-SiN:F passivation and with P-SiN passivation.