

C-3-4

Plasma Cure Process for Porous SiOCH Films using CF₄ Gas

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Abstract

We investigated a reinforcing technique for porous SiOCH ($k=2.3$) films in which a step process consisting of UV and CF₄ plasma cure followed by hydrogen radical treatment is applied. In order to consider the effect of UV irradiation generated by CF₄ plasma on p-SiOCH film, the plasma condition was selected. This process reduced the k -value of the p-SiOCH film from 2.92 to 2.36 and it was successfully integrated into Cu interconnects, realizing about 10% reduced capacitance and lower leakage current compared with those of conventional Cu/p-SiOCH ($k=2.6$) interconnects.

Introduction

Plasma-enhanced chemical vapor deposited porous SiOCH (p-SiOCH) films are being introduced into Cu/low- k integration for 45-nm node and beyond. However, poor mechanical and electrical properties of the p-SiOCH film cause severe problems such as peeling, increase in k -value and leakage current due to process damage. To improve mechanical properties of the p-SiOCH film, ultraviolet (UV) cure or electron beam cure was introduced as a post-deposition process [1-2].

In this paper, we investigate the effect of CF₄ plasma cure and hydrogen radical treatment as a reinforcing process for p-SiOCH films, and discussed the mechanism of film improvement.

Experimental

Figure 1 shows an experimental process flow for a blanket p-SiOCH film. The PECVD p-SiOCH films were deposited on a 300-mm silicon wafer and treated by UV cure, CF₄ plasma cure and H₂/He down-stream (DS) treatment in series. The UV cure was performed with a wavelength of 172 nm. The CF₄ plasma cure was carried out in an etching chamber that has parallel plates and a dual-electrode system. A remote plasma generation apparatus was used for the H₂/He DS treatment. Hydrogen radical is produced in the H₂ and He mixture gas at a wafer stage temperature of 350°C. Optical emission spectroscopy (OES) was used to analyze intensity of UV light from plasma. The k -value and n -value (refractive index) at 633 nm of the treated p-SiOCH films were measured by a mercury probe and a photo-interferometer, respectively. Electrical performance of 200-nm pitch Cu/p-SiOCH ($k=2.3$) interconnects was evaluated and compared with electrical performance of conventional Cu/p-SiOCH ($k=2.6$) interconnects.

Results and discussion*Blanket film experiment; plasma gas dependency*

Figure 2 compares the k - and square n -values of p-SiOCH films between after UV cure, after CF₄ plasma cure and after H₂/He DS treatment. This also shows the k - and n -values after Ar plasma cure instead of CF₄ plasma cure. The CF₄ plasma

and Ar plasma were excited by applying only top electrode power ($P_{\text{top}} = 1200$ W) without bias power (P_{bias}) to avoid ion assist etching. The n -value decreased after UV cure treatment, which is well known as a means of improving mechanical property of p-SiOCH film [3]. After CF₄ or Ar plasma, no significant change was obtained in the n -values. This indicates these plasmas did not damage to the film. After H₂/He DS treatment, however, the n -value remarkably decreased only after CF₄ plasma, not after Ar plasma. The k -value also decreased from 2.55 to 2.36 after CF₄ plasma, whereas the k -value increased from 2.75 to 2.89 after Ar plasma. This indicates the p-SiOCH film was improved by the step process of UV cure, CF₄ plasma cure and hydrogen radical generated by H₂/He DS treatment. Figure 3 shows FT-IR spectrum of CF₄ plasma cure, Ar plasma and UV cure. Decrease in peak area of C-Hn bond by indicates porogen was effectively removed by CF₄ plasma.

Mechanism of plasma cure

Because several factors are thought to be related to the reduction of the k - and n -values in the conditions of CF₄ plasma and H₂/He DS treatment, we changed the plasma condition in order to understand the mechanism. Figure 3 shows the k -value and etching rate (E.R) of the p-SiOCH film in the case of performing UV cure and CF₄ plasma irradiation. We compared these values between CF₄ plasma and Ar plasma with different bias power of 0 W and 700 W, respectively.

For CF₄ plasma condition, E.R increased with increasing bias power, whereas the k -value did not change depending on the bias power, even though ion or electron bombardment of the surface of the film increased at a high bias power of 700 W. On the other hand, Ar plasma with a bias power of 700 W shows lower E.R and a higher k -value of 2.52. These results indicate that neither physical reaction by ion nor chemical reaction by ion or radical worked to reduce the k -value of the SiOCH film during CF₄ plasma irradiation.

Figure 4 shows the k - and n -square values of the p-SiOCH film CF₄ plasma irradiation and H₂/He DS treatment with and without UV cure. Either condition could reduce n -value, whereas the k -value decreased only in the step process of UV cure, CF₄ plasma and H₂/He DS treatment. On the basis of the above-mentioned experimental results, we investigated the effect of UV light caused by CF₄ plasma on the film improvement. Figure 5 shows the intensity of UV light irradiated from CF₄ plasma and Ar plasma as a function of wavelength from 200 nm to 350 nm. Ar plasma has weak intensity and no significant peak in its spectrum, whereas CF₄ plasma has a strong and wide peak at around 250 nm. We assumed energy of the UV light of CF₄ plasma (470 kJ/mol at around 250 nm) is lower than Si-O bond enthalpy of 800 kJ/mol and slightly larger than Si-C bond enthalpy of 451.5 kJ/mol [4]. Thus, the UV light affected only sub-bond of Si-C, and hydrogen radical could restore the p-SiOCH film during H₂/He DS treatment without damaging the main structure of

Si-O bonds.

200 nm-pitch Cu/p-SiOCH interconnect fabrication

Figure 7 shows line-to-line leakage current of 200-nm pitch capacitor treated by CF4 plasma and H2/He DS and conventional low-k film ($k=2.6$) without plasma cure. Lower leakage current and narrow distribution were obtained in the case of the sample treated by CF4 plasma cure condition. Figure 8 shows dot plots of line-to-line capacitance versus wire resistance for each process. For almost all the Ar plasma cure condition, wire resistance was too high to plot in this figure due to the Cu/p-SiOCH deformation. The CF4 plasma cure condition decreased capacitance by about 10% compared with that of conventional Cu/p-SiOCH ($k=2.6$) interconnects without plasma cure.

We found that p-SiOCH film with a k -value of 2.3 was severely damaged in the damascene process consisting of silicon oxide cap film deposition, etching, ashing, wet cleaning, and pretreatment of metal deposition. As a result, the effective k -value became comparable with that of p-SiOCH film with a k -value of 2.6. Therefore, the authors expect a reinforcing process of p-SiOCH film ($k=2.3$), such as CF4 plasma cure and hydrogen radical treatment, to be a key technology for the next-generation Cu/low- k integration.

Conclusion

Step process of UV cure, CF4 plasma cure and H2/He DS treatment was found to reduce the k - and n -values of p-SiOCH films ($k=2.3$). This method restored process damage of the p-SiOCH film and decreased line-to-line capacitance and leakage current of Cu interconnects compared with those of conventional p-SiOCH.

References

- [1] K. Goto, et al., AMC 2005, p. 30.
- [2] F. Ito, et al., AMC2005, p. 32.
- [3] K. Yoneda, et al., IITC2005.
- [4] CRC Handbook of Chemistry and Physics, 2000.

- p-SiOCH deposition
- UV cure
- plasma cure
- H2/He DS treatment

Fig. 1 Process flow of experiment.

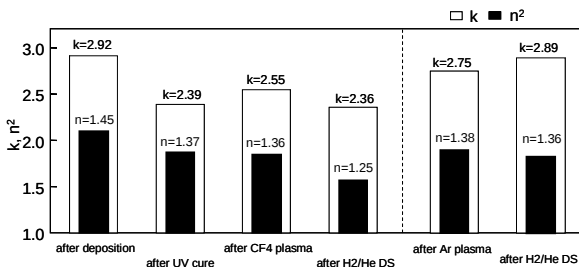


Fig. 2 The k -values after CF4 and Ar plasma with H2/He DS treatment.

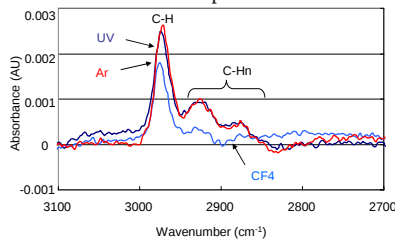


Fig. 3 FT-IR spectrum of CF4 plasma cure, Ar plasma and UV cure.

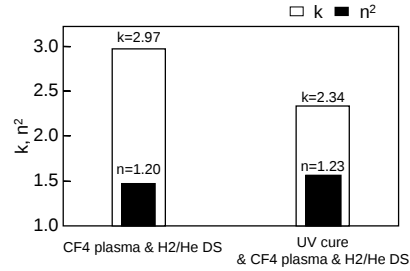


Fig. 4 The etching rate of p-SiOCH by CF4 and Ar plasma and k -value after the plasma cure with H2/He DS treatment.

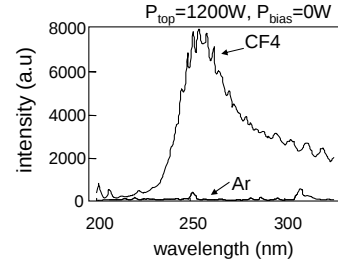


Fig.5 UV light intensity as a function of wavelength for CF4 and Ar plasma.

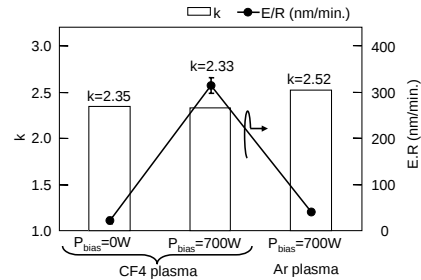


Fig.6 The k - and n -square values of the p-SiOCH film CF4 plasma irradiation and H2/He DS treatment with and without UV cure.

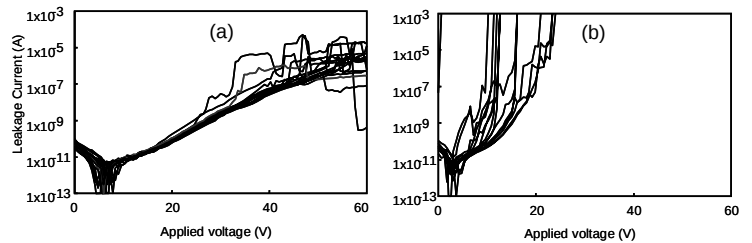


Fig. 7 Leakage current vs. applied voltage for CF4 plasma and H2/He DS treatment (a), conventional low- k (b).

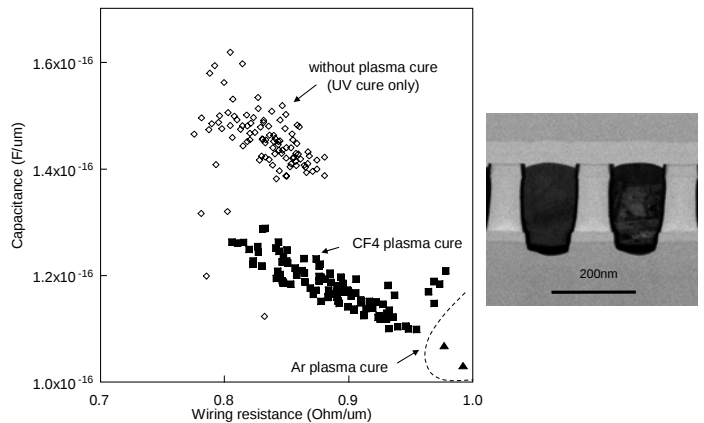


Fig.8 Capacitance vs. resistance of Cu/p-SiOCH ($k=2.3$) after CF4 plasma (cross-sectional TEM view is shown), Ar plasma, and without plasma cure.