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Process Induced Damage Analysis of Low-k SiOCH Films Focusing on Siloxane Network and Methyl End Group

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1. Introduction

Signal propagation delay determined by interconnect capacitance is a key factor for high-speed ULSI operation. Skillful porous low-k dielectric application is essential beyond 45 nm node. Recently, concern for process induced damage becomes larger, because porous low-k material is damaged by following BEOL processes easily. However, we have not understood what a "damage" is. The Purpose of this paper is discussing the process induced damage through RIE, ashing, and wet cleaning processes. Investigations on the Si-CH₃ depletion, moisture uptake, and film densify due to process induced damage were already reported [1-4]. This study has clarified the structural change of siloxane networks in SiOCH films through RIE, ashing and wet cleaning processes, and dependence of process induced damages on material structures.

2. Experiments

Table I shows the basic properties of low-k SiOCH films evaluated in this study. Two types of spin-on porous methyl-silsesquioxane (MSQ) films were evaluated. MSQ-A contains much Si-CH₃ functional group and exhibits high hydrophobic property. However, much end group existence limits the efficient growth of Si-O-Si network and poor mechanical strength is concerned. Though, mechanical strength improvement using such as UV cure process is suitable for MSQ-A [5]. On the other hand, Si-CH₃ density of MSQ-B is lower than that of MSQ-A. MSQ films were deposited on p-type, 10-15 Ω·cm, 300 mm wafers. MSQ films were coated and soft-baked using a SOD coater and thermal or UV cured subsequently. Thermal cure was executed using a conventional vertical furnace in N₂ ambient, 400°C, 60 minutes. UV cure was treated with ~200 nm single wavelength UV irradiation on 350°C heated wafer stage. UV cure process time (30 sec.) was fixed with the MSQ film shrinkage of 5%.

Figure 1 shows test scheme of the process induced damage evaluation. 150 nm MSQ films were etched to 100 nm using a RIE process, and then ashing and wet cleaning process were treated subsequently. Process conditions of RIE, ashing, and wet cleaning were the same as a mature process flow. CF₄/Ar/N₂ gases were used in RIE process, and H₂/He remote plasma with 350°C heated stage was

used in ashing process. A conventional organic wet solution was used in wet cleaning.

Film thickness, refractive index and film structure were in-line measured by spectroscopic reflectometer and Fourier transform infrared spectroscopy (FTIR), respectively. Dielectric constants of MSQ films before and after RIE, ashing, and wet processes were measured by Hg probe.

3. Results and Discussion

Figure 2(a) shows the subtracted FTIR spectra between before and after RIE process. The intensity of subtracted spectrum was normalized by film thickness. Peak and valley spectrum indicates the bond increase and decrease respectively. If the RIE process only removes the 50 nm SiOCH film and "fresh" 100 nm SiOCH film has been remained, the subtracted FTIR spectrum should be flat. However, Fig. 2(a) indicates that there were Si-CH₃ (1280 cm⁻¹) end group decrease and cage, ladder (1140 cm⁻¹), and network (1030 cm⁻¹) Si-O-Si structure decrease in both MSQ-A, -B films after RIE. These were due to bond breaking by RIE process and low process temperature (40°C) that should not be able to repair the broken bonds. Process induced damage at the via/trench sidewall is more important for the process/material development. However, in this study, simplified blanket evaluation was performed for the primal understanding.

Figure 2(b) shows the subtracted FTIR spectra between RIE and ashing process. After ashing process, Si-O-Si network growths were observed in both MSQ-A, -B. This might be due to bond repair enhance by ashing process at high temperature of 350°C. H₂/He ashing used in this study was characterized by low process damage and did not affect the film properties of porous SiOCH film [6]. However, the film structure changes were observed even after the H₂/He ashing as shown in Fig. 2(b). This is because of the existence of broken bond due to RIE process. Film thickness decrease was also observed after ashing process (Fig. 3). This was thought to be due to Si-O-Si network growth shown in Fig. 2(b). In the Fig 2(b), no Si-CH₃ decrease was detected although Si-O-Si structure was changed. This indicates that this film thickness decrease were film shrinkage but etching. Film shrinkage in MSQ-B after ashing was smaller than that of MSQ-A (Fig. 3). This is because density of Si-O-Si network in the MSQ film

Table I Basic Properties of SiOCH Films

Low-k Film	MSQ-A	MSQ-B
Cure Method	UV	Thermal
Dielectric Constant	2.27	2.43
Young's Modulus	3.4 GPa	6.7 GPa
Relative Si-CH ₃ Density	1.00	0.83

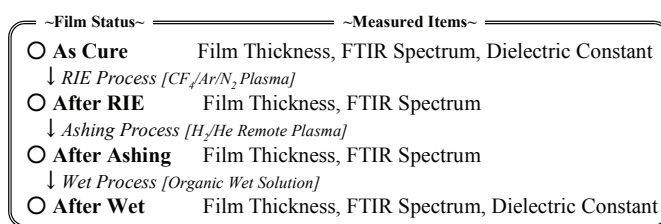


Figure 1. Test Scheme of Process Induced Damage Evaluation

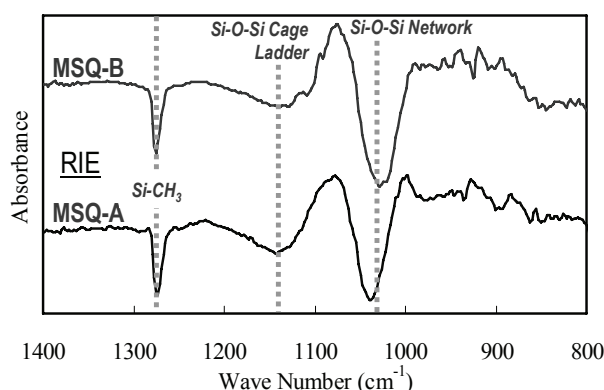


Figure 2(a). Subtracted FTIR Spectra between before and after RIE

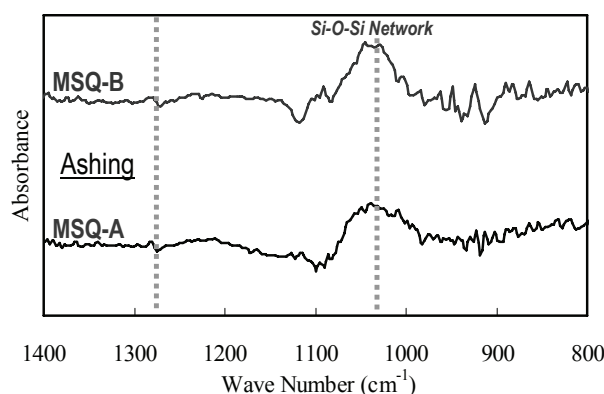


Figure 2(b). Subtracted FTIR Spectra between RIE and Ashing

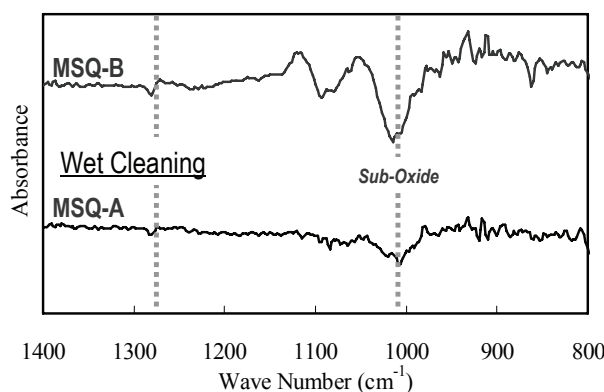


Figure 2(c). Subtracted FTIR Spectra between Ashing and Wet Cleaning

determines the film toughness.

Figure 2(c) shows the subtracted FTIR spectra between ashing and wet cleaning process. After wet cleaning, there was no significant change on film thickness and refractive index. However, valley spectra (1000cm^{-1}) were observed in the subtracted FTIR spectra that suggests the sub-oxide decrease. This sub-oxide decrease might be an etching by wet cleaning solution that penetrates in the porous SiOCH film easily. Sub-oxide region was thought to be formed through RIE~ashing process.

Figure 4 compares the dielectric constant increase through RIE~ashing~wet cleaning process. The reasons of dielectric constant increase were thought to be film structure change, film densify, moisture uptake, and so on. However, cause-and-effect relationship has not been clear yet. There is a material dependence on dielectric constant

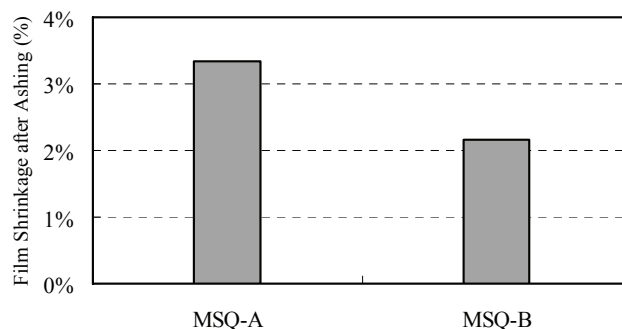


Figure 3. Film Shrinkage after Ashing Process

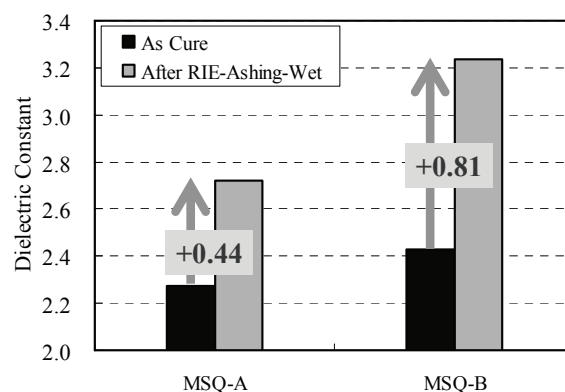


Figure 4. Dielectric Constant Comparison through RIE~Ashing~Wet Processes

increase. MSQ-A shows the smaller dielectric constant increase. Much Si-CH_3 end group should prevent the moisture uptake and dielectric constant increase was suppressed. In terms of SiOCH material structure, as shown in Fig. 3, 4, there is a trade off relationship between film shrink resistance after ashing and dielectric constant increase resistance.

4. Conclusion

Process induced damage through RIE~ashing~wet cleaning on SiOCH films were discussed. After RIE process, not only film etching but also Si-CH_3 decrease and Si-O-Si breaking were observed. 2~3% film thickness shrinkage was observed after ashing process. This is due to repair of broken Si-O-Si bond. Wet etching of sub-oxide region was observed after wet cleaning. Dielectric constant increase was observed though RIE~ashing~wet cleaning process. Si-O-Si network rich SiOCH film was able to prevent the film shrinkage after ashing, and Si-CH_3 end group rich SiOCH film was able to prevent the dielectric constant increase.

Acknowledgement

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