Chapter 2

Study on the impact of plasma treatment and CMP process on low-k Methylsilsesquiazane (MSZ) for interconnection applications

2.1 Introduction

As integrated circuit dimensions continue to shrink, highly-packed multilevel interconnections with low-resistance metal and low-dielectric constant materials have attracted much attention as a method for increased ultra large-scale integrated (ULSI) circuits operating speed [75-76]. Because continued miniaturization of device dimensions and the related need to interconnect an increasing number of devices on a chip is a trend in ULSI technology, this has led to building multilevel interconnections on planarized levels [77-80]. Obviously, surface planarization is a key technology during the manufacture of multilevel interconnections [81-82]. Because the chemical mechanical planarization (CMP) process satisfies the requirement of global topography planarization during integrated circuit (IC) fabrication, this method has been introduced to form interconnections between devices and between devices and outside [83-84]. In the development of CMP low-k dielectrics, Forester et al. [85] found that the polish rate of alkyl siloxane-based spin-on glass (SOG) was lower than that of plasma-enhanced chemical-vapor deposition (PECVD) oxide or thermal oxide using only conventional silica-based slurry. When using conventional oxide slurries, the polish rate of alkyl siloxane-based SOG is dependent on the organic content. A higher Si-R/Si-O ratio in the SOG films induces a lower hydrolysis reaction rate, leading to a lower polish rate. Several reports [86-87] indicate that the use of new

alkaline cerium oxide-based slurry and the introduction of additives could greatly improve the removal rate for organic spin-on materials. However, before adopting new consumables into production, much experimental work should be completed to qualify these consumables.

In this chapter, a novel organic low-k dielectric methylsilsesquiazane (MSZ) provided by Clariant Corp. in Japan was investigated. The low-k MSZ is a methylsilsesquioxane-like (MSQ-like) [88] organic polymer derived from MSZ precursor solution. It was found that the MSZ materials can be degraded by O_2 plasma ashing during photoresist stripping. Therefore, the H_2 plasma and NH_3 plasma pretreatment and TMCS/HMDS post-treatment were proposed to prevent the MSZ dielectric from the damage of O_2 plasma ashing. In addition, in order to explore the impact of CMP process on the MSZ dielectric during Cu and TaN removal processes for Cu damascene structure, the dielectric properties of MSZ after CMP process with Cu and TaN slurries were investigated. Also, the dielectric characteristics of MSZ after CMP process with SS-25 slurry were studied so as to estimate the practicability of MSZ dielectric as a PMD layer in future. Finally, we propose oxygen plasma pre-treatment on low-k methyl-silsesquiazane (MSZ) film to improve the polish rate of CMP MSZ film. Moreover, the investigation of post-CMP characteristics such as electrical performance and leakage behaviors also were emphasized.

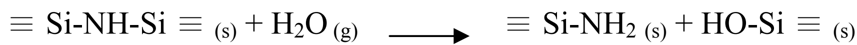
2.2 Experimental procedures

2.2.1 Preparation and intrinsic characteristics of low-k MSZ films

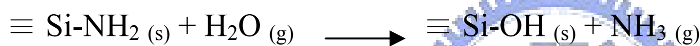
The substrates used in this study were 150-mm p-type (11-25 Ω-cm) single-crystal silicon wafers with (100) orientation. Before film deposition, Si wafers were boiled in

$H_2SO_4 + H_2O_2$ solution and heated to 120 °C for 20 min to remove particles on the surfaces. Then, these wafers were spin-coated with a methyl-silsesquiazane (MSZ) solution at a spin speed of 2000 rpm for 30 s on a model 100CB spin coater. This was followed by a series of sequential thermal baking steps on the hot plate at 150 °C and 280 °C for 3 min. The wafers coated with MSZ precursor solution then received a hydration treatment. The wafers were left in a clean room for 48 hours and the precursor-structure of MSZ films will be transformed to methyl-silsesquiazane through hydrolysis and condensation process, shown as follows [89-90],

Hydrolysis reactions:



$$\equiv \text{Si-NH-Si} \equiv_{(s)} + H_2O_{(g)} \longrightarrow \equiv \text{Si-NH}_2{}_{(s)} + \text{HO-Si} \equiv_{(s)}$$



$$\equiv \text{Si-NH}_2{}_{(s)} + H_2O_{(g)} \longrightarrow \equiv \text{Si-OH}_{(s)} + NH_3{}_{(g)}$$

Condensation reactions:

$$\equiv \text{Si-OH}_{(s)} + \text{HO-Si} \equiv_{(s)} \longrightarrow \equiv \text{Si-O-Si} \equiv_{(s)} + H_2O_{(g)}$$

Afterward, the resultant wafers were thermally cured in a quartz furnace at 400 °C for 30 min under N_2 ambient. The final MSZ films (called as-cured MSZ, marked as sample STD) were formed to a thickness of 400 nm. The final structure is shown in Fig. 2-1. After film formation, by means of light interference effects in films, the thickness of all MSZ films in this experiment was measured using an N&K 1200 analyzer. The structure properties of the MSZ films were studied using fourier-transform infrared spectroscopy (FTIR). The infrared spectrometry was performed from 4000 to 400 cm^{-1} using a Bio-Red QS300 FTIR spectrometer calibrated to an unpatterned wafer and their data were collected in the absorbance mode for studying the chemical structure of films. Electrical characteristics of MSZ films were performed on the metal-insulator-semiconductor (MIS) capacitor with metallic-aluminum deposition as the top electrode and backside electrode. Leakage

current-voltage (I-V) and capacitance-voltage (C-V) characteristics were also used to measure the intrinsic electrical properties of as-cured MSZ films, respectively.

2.2.2 Impact of plasma treatment on dielectric properties of low-k MSZ for interconnection applications

After as-cured films formation, two groups of samples were prepared. The first group of wafers was the as-cured MSZ films with H_2 and NH_3 plasma pre-treatment in plasma enhanced chemical vapor deposition (PECVD) chamber for 3, 6, and 9 min, respectively. Then, the resulting wafers were followed by O_2 plasma treatment for 3 min to investigate the protection ability of H_2 and NH_3 plasma pre-treatment in photoresist stripping process. The parameters of foregoing plasma treatments were list in Table 2-1. The second group of wafers was the as-cured MSZ films subjected to O_2 plasma 3 min and followed by trimethylchlorosilane (TMCS) and Hexamethyldisilazane (HMDS) vapor for 30 min. The TMCS vapor was generated by heating TMCS solution and conveyed into an oven at 60 ^{o}C under 760 torr pressure. The HMDS vapor was generated by the same procedure into an oven with 80 ^{o}C temperature and 760 torr pressure. The chemical structure of all abovementioned MSZ films were analyzed by FTIR. Metal-insulator-semiconductors (MIS) were manufactured to measure the electrical properties of all MSZ films. A Keithley Model 82 CV meter was used to measure the dielectric constant of MSZ films. The capacitors were measured at 1 MHz with an AC small signal. Leakage current-voltage (I-V) characteristics of MSZ were measured using a HP4156 semiconductor parameter analyzer. Thermal desorption spectroscopy (TDS) was carried out to monitor the desorbed elements from post-treated MSZ films during the high temperature process. In the duration of TDS analysis, samples were heated from room

temperature to 600 ^{o} C at a rate of 20 ^{o} C/min in a vacuum chamber. In addition, the outgassing species were collected through the mass spectrometer. In this work, M/e (mass-to charge ratio) = 18 peak attributed to H_2O was monitored.

2.2.3 Impact of CMP processes on low-k MSZ for interconnection applications

In order to investigate the impact of CMP processes on low-k MSZ films, the as-cured MSZ films were polished by CMP processes with various slurries. The CMP experiment was carried out on an IPEC/Westech 372M CMP processor with a Rodel IC 1400 Pad on the primary polishing plated and Rodel Politex regular embossed pad on the final buffering plated. A Rodel R200-T3 carrier film was used to provide buffer between the carrier and wafer. The wafer was mounted on a template assembly for a single 6 in. wafer during the polishing experiment. In this experiment, three slurries were implemented separately to investigate the influence on the characteristics of low-k MSZ films. First was the slurry typically used in polishing Cu metal, provided from National Nano Device Laboratory. This slurries is composed of 2 vol. % HNO_3, 5 x 10^{-2} citric acid, and 3 wt. % Al_2O_3 (0.1 um), labeled as Cu slurry. The pH value of Cu slurry is 0.56. The second is colloidal silicate slurry (marked as TaN slurry), which consists of 10 wt. % colloidal silica and 10 vol. % H_2O_2 in de-ionized (DI) water liquid. Its pH value is 8.5. The third is commercial CABOT^{TM} SS-25 slurry, used to polish SiO_2 extensively, diluted with DI water and TMAH at the ratio of 14:14:5. The first two slurries were used to investigate the influence of Cu and TaN removal processes during Cu damascene manufacture on the low-k MSZ. The last one is used to evaluate the practicability of CMP process on low-k MSZ as a PMD layer in future. In addition, the polishing parameters, such as pad, down force, back pressure, platen

and carrier rotation speeds, and slurry flow rate are shown on Table 2-2 for these three slurries. The thickness of the polished MSZ films was measured at n&k 1200 analyzer by comparing the theoretical reflectance with actual measurement of broad-band reflectance. The surface morphologies of the polished films were investigated by atomic force microscopy (AFM). The structure properties of polished MSZ films were studied by using FTIR. Electrical properties of polished films were implemented on MIS capacitor with metallic copper deposition as the top electrode and aluminum deposition as backside electrode. Leakage current-voltage (I-V) and capacitance-voltage (C-V) characteristics were also used to analyze the leakage current behaviors and to measure the dielectric constants of polished MSZ films, respectively.

2.2.4 A method to improve CMP polishing rate of low-k MSZ for ULSI interconnection applications

In virtue of the fact that the organic materials have been reported to be hardly polished by commercial silica slurries, we propose an O_2 plasma pretreatment to improve the polishing rate of MSZ film during CMP process. Firstly, the as-cured MSZ films were treated with O_2 plasma for 60 s prior to the CMP process (marked as Sample O). The O_2 plasma was operated at a pressure of 650 mtorr and with an oxygen gas flow rate of 900 sccm. A radio frequency (rf) power of 110 W was applied to the upper electrode. Next, the wafers were placed on the grounded bottom electrode, which can be rotated for improving uniformity. The wafers had a substrate temperature up to 250 ^{o}C. Then the CMP process was applied to the plasma-treated MSZ films for 2 min. These post-CMP MSZ films were marked as “Sample C.” The CMP experiment was carried out on an IPEC/Westech 372M CMP processor with a

Rodel IC 1400 pad on the primary polishing platen and Rodel Politex Regular embossed pad on the final buffering platen. A Rodel R200-T3 carrier film was used to provide a buffer between the carrier and wafer. A single 6 in. wafer was mounted on a template assembly. During the polishing experiment, the slurry was commercial CABOT^{TM} SS-25 diluted by de-ionized (D.I.) water with the ratio of 1:1, which is typically used to polish SiO_2. The resultant solution pH value is in the range of 10-11. The polishing parameters, such as down force, back pressure, platen and carrier rotation speeds, and slurry flow rate, were set to be 3 psi, 2 psi, 50 rev./min, 60 rev./min, and 150 ml/min, respectively. By means of light interference effects in films, the thickness of all MSZ films in this experiment was measured using an N&K 1200 analyzer. The structure properties of the MSZ films were studied using fourier-transform infrared spectroscopy (FTIR). The surface morphologies of the polished films were investigated by atomic-force microscopy (AFM). Thermal desorption spectroscopy (TDS) was carried out to monitor the desorbed elements from post-CMP MSZ films during the high temperature process. In the duration of TDS analysis, samples were heated from room temperature to 600 ^{o} C at a rate of 20 ^{o} C/min in a vacuum chamber. In addition, the outgassing species were collected through the mass spectrometer. In this work, M/e (mass-to charge ratio) = 18 peak attributed to H_2O was monitored. Electrical characteristics of post-CMP MSZ films were performed on the metal-insulator-semiconductor (MIS) capacitor with metallic-aluminum deposition as the top electrode and backside electrode. Leakage current-voltage (I-V) and capacitance-voltage (C-V) characteristics were also used to analyze the leakage current behaviors and measure the dielectric constants of post-CMP MSZ films, respectively. In addition, I-V measurements were also conducted for these specimens at different stable temperatures during the temperature rising and cooling procedures to evaluate the practicability of improving the polishing

rate of MSZ films with O_2 plasma pre-treatment for the CMP process. Finally, Auger depth profile analyses were used to investigate the impact of O_2 plasma pre-treatment on low-k MSZ for CMP process.

2.3 Results and discussions

2.3.1 Intrinsic characteristics of low-k MSZ films

For the applications for multilevel interconnects, low-k dielectrics must be carefully characterized for their material and electrical properties. Figure 2-2 represents the fourier-transform infrared spectroscopy (FTIR) spectra of MSZ films during formation processes. After 10 hours of hydration reaction proceeded in a clean room, it was observed that the Si-N peaks almost disappeared, while the Si-O network-like bonds and Si-OH bonds grew gradually. This was due to the hydrolysis process. This result implied that the hydrolysis and condensation process occurred simultaneously during the period. In the periods ranging from 10 to 48 hours, the condensation process resulted in a network-like structure through the bulk MSZ film. Next, the water content was eliminated and the standard MSZ film was obtained after thermal curing in a furnace. Figure 2-3 displays the internal stress variation of MSZ film during thermal cycle. As the temperature is increased, the compressive stress is increased. This means the expansion coefficient of MSZ film is larger than that of Si substrate. Also, the reversible curve is observed due to no damage occurred on the film during thermal cycle test. The thermal stability of MSZ is very reliable up to 550 ^{o}C as shown in Fig. 2-4. There is only slightly change on the FTIR spectra of MSZ films even though undergoing furnace annealing at 550 ^{o}C for 5.5 hours. Figures 2-5(a) and 2-5(b) show leakage current densities and dielectric constant of MSZ film

after undergoing various annealing temperature for 30 min, respectively. It is found that the dielectric constant is slightly increased with raising the annealing temperature. The leakage current densities of MSZ after thermal annealing were almost the same as that of as-cured one. These results are consistent with the FTIR material analyses. In addition, with the imperative of integration of low-k and Cu for interconnection, the influence of thermal stress for Cu electrode on MSZ films must be investigated in detail. Figure 2-6(a) and (b) present the leakage current densities of temperature and time dependence of thermal stress for Cu electrode MIS capacitor. Fortunately, the leakage current is increased slightly with the increase of temperature and periods of time. It is indicated that the MSZ is suitable for the subsequent thermal process during Cu interconnect fabrication.

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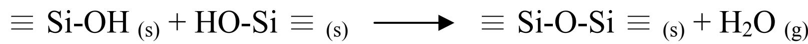
2.3.2 Impact of plasma treatment on dielectric properties of low-k MSZ for interconnection applications

Figure 2-7 exhibits FTIR spectra of the MSZ after O_2 plasma treatment for 3 to 9 minutes. The intensities of Si-OH and H_2O bonds (933, ~3400 cm^{-1}) increased gradually as raising the time of O_2 plasma treatment. The intensities of C-H bond (2974 cm^{-1}) and Si-CH_3 bonds (781, 1273 cm^{-1}) decreased after the MSZ film is subjected to O_2 plasma treatment. The increase in Si-OH and H_2O bonds signal is assumed that the dangling bonds generated from O_2 plasma treatment easily absorb moisture when the sample is exposed to the atmosphere. It is believed that oxygen radicals can react with a large number of Si-CH_3 bonds on MSZ films, which results in the intensity of Si-C and C-H bonds in FTIR spectra decreasing. This reaction will decompose Si-CH_3 bonds and form Si-OH bonds as exposed in atmosphere.

$$\equiv \text{Si-CH}_3\,_{(s)} + 2\,\text{O}_2\,_{(g)} \longrightarrow \equiv \text{Si-OH}\,_{(s)} + \text{CO}_2\,_{(g)} + \text{H}_2\text{O}\,_{(g)}$$

Because the Si-OH group was hydrophilic, it was easy to induce moisture uptake. As a result, after the MSZ film underwent O_2 plasma treatment, the intensities of the Si-OH and H_2O signals would increase. In addition, a partial amount of Si-OH groups might react with each other via a dehydration reaction as exposed to atmosphere [91-92].



$$\equiv \text{Si-OH}\,_{(s)} + \text{HO-Si} \equiv\,_{(s)} \longrightarrow \equiv \text{Si-O-Si} \equiv\,_{(s)} + \text{H}_2\text{O}\,_{(g)}$$

Therefore, the intensity of the absorption bond (1070 cm^{-1}) was increased, which is characteristic of the Si-O-Si vibration in silica. Nevertheless, MSZ film consists of many hydrophobic methyl groups. The hydrophobic groups can resist the oxygen radical approaching into bulk MSZ. This will cause the less degree of hydrolysis reaction than that of inorganic low-k material such as HSQ film. Although the change of MSZ film due to the slight hydrolysis reaction is difficult to observe by FTIR spectra, the TDS and electrical measurement can demonstrate the slight hydrolysis reaction really occurs on MSZ film after O_2 plasma treatment. Figure 2-8 shows the moisture desorption spectra for O_2 plasma-treated MSZ films. The moisture desorption occurs below 200 ^{o}C is due to the release of physically absorbed dipole-dipole reaction. The outgassing from 200 to 400 ^{o}C is due to the break of the hydrogen bonds and the release of moisture from bulk MSZ. As the temperature exceed 400 ^{o}C, the outgassing is attributed to the break of Si-OH bonds resulted from the dehydration reaction. It is obvious that the moisture content is increased with the increase of O_2 plasma treatment time. Electrical properties of MSZ after O_2 plasma treatment can also demonstrate the above inference. Figure 2-9 shows the leakage

current and dielectric constant of MSZ after O_2 plasma treatment for 3 to 9 min. The leakage current increases with the increase of O_2 plasma treatment time. Also, the dielectric constant of O_2 plasma treated MSZ films increased as the O_2 plasma treatment is increased. These results indicate that the O_2 plasma will lead MSZ to absorb moisture quickly and results in the dielectric degradation of MSZ films. In order to enhance the resistance of oxygen plasma damage, H_2 and NH_3 plasma pre-treatment were studied in this chapter. Figure 2-10 presents the FTIR spectra of as-cured and H_2 plasma-treated MSZ after O_2 plasma treatment. It was found that the peaks of Si-OH and H-OH bonds were not observed for the H_2 plasma-treated one. In addition, the electrical properties of these samples were also shown in Fig. 2-11. Both leakage current and dielectric constant of H_2 plasma-treated film after O_2 plasma treatment are lower than that of only O_2 plasma treated one. This implies that H_2 plasma can provide extra active hydrogen radicals to passivate the MSZ either on surface or bulk to avoid the damage of O_2 plasma ashing. On the other hand, the FTIR spectra of NH_3 plasma-treated MSZ after O_2 plasma treatment are illustrated in Fig. 2-12 to investigate the effect of NH_3 plasma pre-treatment on the resistance of O_2 plasma ashing. It was found that Si-OH and H_2O bonds were also not found in the spectra of NH_3 plasma-treated MSZ. The results can be deduced that NH_3 plasma form a nitride-like passivation layer on the surface of MSZ and avoid the damage of O_2 plasma ashing as our previous study in the pass. Figure 2-13 shows the leakage current and dielectric constant of NH_3 plasma-treated MSZ after O_2 plasma treatment. The leakage current and dielectric constant of NH3 plasma-treated MSZ after O_2 plasma treatment are all lower than that of only O_2 plasma ashing. This is consistent with our inference. In addition, we also introduce Trimethylchlorosilane (TMCS) and Hexamethyldisilazane (HMDS) to eliminate the dielectric degradation of MSZ after O_2 plasma ashing. The chemical reaction process is shown as follows:

TMCS:

$Si\text{-}OH + Cl\text{-}Si(CH_3)_3 \longrightarrow Si\text{-}O\text{-}Si(CH_3)_3 + HCl$

HMDS:

$Si\text{-}OH + (CH_3)_3\text{-}Si\text{-}NH\text{-}Si(CH_3)_3 \longrightarrow Si\text{-}O\text{-}Si(CH_3)_3 + NH_2\text{-}Si(CH_3)_2$

$Si\text{-}OH + NH_2\text{-}Si(CH_3)_3 \longrightarrow Si\text{-}O\text{-}Si(CH_3)_3 + NH_3$

The effectiveness of TMCS/HMDS post-treatment on O_2 plasma-treated MSZ can be evaluated by material and electrical analyses. Figure 2-14 shows the FTIR spectra of O_2 plasma-treated MSZ films after TMCS/HMDS treatment. The Si-OH and H_2O bonds of only O_2 plasma-treated MSZ are larger than that of post TMCS/HMDS treated one. From Figure 2-15, it was found that the thickness of O_2 plasma treated MSZ was increased after TMCS/HMDS treatment. This increase of thickness is deduced to be due to the formation of $Si\text{-}O\text{-}Si(CH_3)_3$ which protects MSZ film from moisture absorption. These results can demonstrate the reaction of previous mention. Based on the inference, the leakage current and dielectric constant of O_2 plasma-treated MSZ can be recovered by the TMCS/HMDS post-treatment as shown in Fig. 2-16. In this study, the TMCS and HMDS post-treatment can reduce the Si-OH bonds and moisture absorption resulting from O_2 plasma damage so that the electrical properties of MSZ film can be improved.

2.3.3 Impact of CMP processes on low-k MSZ for interconnection applications

In the Cu damascene manufacture, the detection of end point of metal CMP is difficult due to the complex pattern design in IC chip. Moreover, the thickness of barrier dielectric or etch stop layer must be reduced to meet the requirement of low

effective permittivity in interconnection. Therefore, the influence of metal CMP on low-k material should be investigated for future application. In this study, it was found that the removal rate of low-k MSZ film with TaN slurry is 7nm/min, which is lower than that of TaN (68.1 nm/min) used as barrier metal of Cu damascene structure. Besides, the removal rate of MSZ with Cu slurry is only 2 nm/min, which is much lower than that of Cu (94.6 nm/min) with same slurry. These results indicate that the selectivity of copper or TaN with respect to MSZ is high so that it is easy to avoid the loss of dielectric layer during CMP process. In addition, the dielectric integrity and surface topography of low-k MSZ after metal CMP processes should be evaluated to meet the requirement of interconnection. Figure 2-17 (a) and (b) show the AFM images of MSZ surface after CMP polished with TaN and Cu slurries, respectively. The smooth MSZ surface can be achieved after CMP process with TaN or Cu slurries whose roughness (Ra) is about 0.112 nm and 0.251 nm separately. These results indicate that the high selectivity of Cu and TaN with respect to MSZ and planarization surface can be obtained by using Cu and TaN slurries. As for the practicability of MSZ film as the PMD in future, the CMP of MSZ film with commercial SS-25 slurry was also evaluated in this work. The smooth morphology of MSZ after CMP with SS-25 is shown in Fig. 2-18. The surface roughness and removal rate of MSZ was 0.135 nm and 16 nm/min, respectively. Although the planarization surface can be achieved after CMP, the dielectric properties of MSZ after CMP with various slurries should be considered in detail. Figure 2-19 shows the FTIR spectra of post-CMP MSZ with above-mentioned slurries. It is found that the Si-C and C-H bonds intensity of polished MSZ film are still remained in high level after CMP process. Figure 2-20 (a) and (b) show the leakage current and dielectric constant of MSZ after CMP processes. The leakage current of post-CMP MSZ films is similar to that of as-cured MSZ film. The dielectric constant of post-CMP MSZ films is also kept within an acceptable

region for low-k material. Therefore, the results verify that the dielectric properties of MSZ would not be damaged after CMP process with these slurries.

2.2.4 A method to improve CMP polishing rate of low-k MSZ for ULSI interconnection applications

In order to satisfy the application of CMP process for PMD planarization, the polishing rate of MSZ is too low. Therefore, we proposed a novel method of O2 plasma pre-treatment to improve the polishing rate of MSZ with commercial SS-25 slurry. The experimental results reveal in Fig. 2-21 that the polished rate of MSZ was increased as much as twice in magnitudes compared to that of MSZ without O2 plasma treatment. Also, AFM images of O_2 plasma-treated MSZ film before and after CMP processes are shown in Figs. 2-23 (a) and (b). The roughness (Ra) of O_2 plasma-treated MSZ was 0.341 nm, while the Ra value of post-CMP MSZ with O_2 plasma pretreatment was reduced to 0.227 nm. The results indicate that not only the removal rate can be improved by O_2 plasma pretreatment but also the surface roughness was smooth after CMP process. Figure 2-24 shows FTIR spectra of O_2 plasma-treated MSZ films before and after the CMP process. Prior to the CMP process, both intensities of Si-OH and H_2O groups (at 993 and 3400 cm^{-1}) increased, whereas the intensities of C-H (2974 cm^{-1}) and Si-CH_3 (at 781 and 1273 cm^{-1}) groups decreased when MSZ film underwent O_2 plasma treatment. Moreover, the peak of the Si-O bond at 1070 cm^{-1} was slightly formed in O_2 plasma-treated MSZ. After the CMP process, however, all intensities of functional groups in MSZ films maintained a high level again. These observed phenomena are clearly interpreted as follows.

The decomposition of functional groups in MSZ films, due to O_2 plasma pre-treatment, would lead to forming Si-OH bonds, which easily induced moisture uptake and modified the MSZ surfaces from hydrophobic into hydrophilic ones. It

was believed that oxygen radicals generated from O_2 plasma could react with a large amount of Si-CH_3 groups on MSZ films, which caused the decreasing intensities of Si-C and C-H groups. The phenomena have been explained in previous section of this chapter. The intensity of the absorption band (at 1070 cm^{-1}), which was characteristic for the Si-O-Si vibration in silica, was thereby increased after O_2 plasma treatment. The hydrophilic surfaces consisting of oxide facilitated CMP of MSZ films and a rapid CMP polish rate was obtained, just with only the conventionally-used CMP oxide slurry CABOT™ SS-25. The hydrophilic Si-OH bonds would be removed after the CMP process. Thus, Si-OH bonds disappeared in FTIR spectra. After the removal of the oxide layer on the surface of O_2 plasma-treated MSZ, organic function groups such as Si-C and C-H bonds maintained a high level of peak intensity. The temperature dependence of moisture desorption is shown in Fig. 2-25. After being subjected to the O_2 plasma treatment, the moisture content of MSZ film was increased, while it decreased after the CMP process. This was consistent with our inference that oxide layers on MSZ surfaces could induce moisture and be easily polished away just with oxide slurry used typically. Once the surface oxide layers were absent, the surfaces of MSZ would return to being hydrophobic-like, resulting in less moisture content. The oxidation phenomena can also be demonstrated by auger depth profile analysis. Figure 2-26 (a) and (b) shows the auger depth profile of as-cured and 1 min O_2 plasma treated MSZ films, respectively. It was found that that the C element distribution in O_2 plasma-treated MSZ would approach to stable level when the sputter time arrives at about 300 sec. However, the Si substrate can be reached until the sputter time arrives at about 1550 sec. Moreover, the thickness of as-cured MSZ film was about 400 nm measured by n&k analyzer. Therefore, we can evaluate the thickness of oxygen plasma effectively penetrated into MSZ film by the ratio of sputter time of MSZ films with and without O_2 plasma treatment and the thickness of

the as-cured MSZ film. As a result, the depth of the oxygen plasma penetrating into MSZ is about 77.4 nm. Furthermore, the electrical characteristics were investigated to evaluate the impacts of the CMP process on O_2 plasma-treated MSZ films. Figure 2-27 (a) and (b) show the leakage current and dielectric constant of O_2 plasma-treated MSZ before and after the CMP process. The electrical properties of MSZ with O_2 plasma treatment were degraded. After the CMP process, however, the leakage current and dielectric constant of MSZ were recovered significantly. In order to explore the leakage behaviors of MSZ films with O_2 plasma pre-treatment before and after CMP process, we tried to conduct I-V measurement at different temperatures during the temperature rising and cooling procedure. Figure 2-28 shows the leakage current density of sample O and sample STD measured at 25 ^{o}C (curve I, II, and IV) and 150 ^{o}C (curve III), respectively. Owing to O_2 plasma treatment, the leakage current of sample O was larger than that of sample STD. The O_2 plasma could modify the surface of MSZ film, leading to formation of defects and inducing moisture uptake. Both the hydrophilic defects and the defect-induced moisture often result in an increase of leakage current. In order to recognize the effect of moisture uptake on the O_2 plasma-treated MSZ film, leakage-current measurement was performed before and after 150 ^{o}C bake, respectively. In comparison with sample STD, after O_2 plasma ashing, the leakage current density increased about 1 to 2 orders of magnitude due to defects-induced moisture uptake, as shown for sample O (curve II). After the 150 ^{o}C baking process (curve III), an amount of water molecules were desorbed from the sample O so that the leakage current of the sample O (measured at the 150°C baking temperature) decreased about 1 order of magnitude. Nevertheless, when the measured temperature of sample O was cooled from 150 ^{o}C to 25 ^{o}C, the leakage current of sample O increased significantly again (curve IV), which resulted from the moisture re-uptake during the temperature-cooling processing. In addition, the moisture

re-uptake may be due to the remainder of hydrophilic defects caused by O_2 plasma damage in the surface of the MSZ film. Figure 2-29 shows the leakage current density of sample C and sample STD measured at 25 ^oC (curve I, II, and IV) and 150 ^oC(curve III), respectively. Because the modification surface layer of O_2 plasma-treated MSZ was polished away by the CMP process, the leakage current of sample C (curve II and IV) was close to that of as-cured MSZ film (curve I) at 25 ^oC. Moreover, the leakage current of sample C (curve III) increased by 1 order of magnitude compared to that of the as-cured MSZ film (curve I) at 150 ^oC. This indicates that the leakage current mechanism could be dominated by a thermionic field emission procedure at the high temperature I-V measured condition. Our results reveal that the hydrophilic surface layer made due to the O_2 plasma treatment would result in the increase of leakage current of MSZ film. However, the leakage current of O_2 plasma-treated MSZ could be recovered after polishing the most of hydrophilic layer by CMP process. These electrical results were consistent with aforementioned FTIR, temperature desorption spectroscopy (TDS), and auger depth profile analyses data.

2.4 Conclusion

In this study, we investigated the intrinsic properties of low-k MSZ films and the effect of various plasma treatments on MSZ film in detail. The MSZ film has a high thermal stability up to 550 ^oC. Its dielectric properties will be degraded by O_2 plasma ashing during photoresist stripping process. The H_2 and NH_3 plasma pre-treatments and TMCS/HMDS chemical post-treatments can effectively avoid the dielectric degradation during O_2 plasma ashing process. In addition, we also evaluated the impact of CMP process on MSZ with various slurries. It was found that the dielectric

characteristics were not damaged during metal CMP process in Cu damascene fabrication. However, the polishing rate was so slow with SS-25 slurry for PMD planarization application. Therefore, we have proposed an effective method to improve the CMP polish rate of organic MSZ films. The oxygen plasma was used to make the surface of the MSZ film more hydrophilic and to facilitate the CMP of MSZ films. As a result, the polish rate of O_2 plasma-treated MSZ was as large as twice the magnitude of MSZ without O_2 plasma pre-treatment. In addition, the electrical properties of O_2 plasma-treated MSZ films could be recovered almost to a similar state as the as-cured MSZ after CMP process. This indicated that most of damage surfaces of O_2 plasma-treated MSZ films could be removed during the CMP process. Also, the dielectric properties of MSZ could maintain the low-k quality. The results were consistent with those of material analyses. Therefore, O_2 plasma pre-treatment will be a promising method to increase the polish rate of organic MSZ films.