Chapter 3

The effect of CMP process on ultra low-k porous-polysilazane (PPSZ) for ULSI application

3.1 Introduction

Shrinking device dimensions associated with ultra large scale integrated (ULSI) circuits is highly effective in achieving high speed performance and in increasing yields at lower cost per chip. In order to assure the performance of the high-speed circuits, continuous efforts have been devoted to incorporating copper or low-dielectric constant (low-k) materials into multilevel interconnections for reducing the major part of circuit delay, cross talk, and power consumption [93-95]. For integrating Cu and low-k materials into integrated circuits (ICs), the damascene technique with chemical mechanical polishing (CMP) is the most suitable approach towards using copper in a multilevel metallization scheme [96-97]. Furthermore, it was reported that Cu is easily diffused into most low-k materials no matter at interconnect manufacture process and reliability testing procedure [98-99]. Therefore, the barrier metal such as TaN should be used between Cu and low-k materials to protect Cu from diffusing into low-k materials. As a result, the polishing process, which removes excess copper or TaN on damascene structures and maintains a flat surface for building-up multilevel interconnects scheme [100-101] is crucial in industrial communities. In other words, Cu or TaN CMP should be an inevitable step for Cu damascene interconnection [102-103]. In addition, in order to made the ultra porous low-k materials be able to use as a pre-metal dielectric (PMD), the CMP of porous low-k using commercial SS-25 slurry should be investigated for future. Although there have been a lot of studies focused on the planariability and topography of multilevel interconnection after CMP process [104-107], little attention has been given to investigate the dielectric properties of low-k materials afte CMP process, especially for the influence of CMP slurries. In this chapter, an ultra low-k material (k~2.2), which is Porous-Polysilazane (PPSZ) available form Clariant Inc in Japan, is used to investigate if it would be compatible with CMP process during Cu damascene interconnect manufacture through electrical and material analyses. Moreover, the O_2 plasma pre-treatment for improvement of polishing rate on PPSZ was also studied in this chapter. This study in this chapter will lead to a better understanding of the application of PPSZ materials in interconnect system of ICs.

3.2 Experimental procedures

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, they were boiled in H_2SO_4+H_2O_2 solution and heated to 120 ^oC for 20 minutes to remove particles on the surfaces. These wafers were spin-coated with ultra low-k Porous-Polysilazane (PPSZ) solution at a spin speed of 2000 rpm for 30 seconds on a model 100CB spin coater. Then, it was followed by baking steps, sequentially on hot-plates at 150 ^oC and 280 ^oC for 3 min. The coated wafers were then followed a hydration treatment. They were left in cleanroom for 48 hours. For the polymer-structure to be transformed to porous methyl-silsesquioxane through hydrolysis and condensation process as shown in the following [89-90]:

Hydrolysis,

$$\equiv \text{Si-}\underset{\text{H}}{\text{N}}\text{-Si} \equiv + H_2O \longrightarrow \equiv \text{Si-}NH_2 \equiv + \text{HO-Si} \equiv$$

$$\equiv \text{Si-}NH_2 + H_2O \longrightarrow \equiv \text{Si-OH} + NH_3$$

Condensation,

$$\equiv \text{Si-OH} + \text{HO-Si} \equiv \longrightarrow \equiv \text{Si-O-Si} \equiv + H_2O$$

Afterward, the resulted wafers were cured in a quartz furnace at 400 ^{o}C for 30 min under N_2 ambient. The porogen (organic polymer) will be evaporated after furnace curing process and the final PPSZ films (called as-cured PPSZ, also marked as Sample STD) were formed with a thickness of 400 nm (the final structure is shown in fig. 3-1). The thickness of the deposited PPSZ film was measured by n&k 1200 analyzer. Consider the case of measuring a broad-band reflectance spectrum, R(λ), of a single film deposited on an opaque substrate. The reflectance spectrum is defined as the ratio of the reflected intensity over the incident intensity of light. Moreover, the theoretical reflectance is composed with several parameters such as refractive index (n), extinction coefficient (k), thickness (d) and so on. By comparing the resultant equation for theoretical reflectance with the actual measurement of broad-band reflectance, the required parameters such as thickness can be determined. After film formation, the thermal annealing was performed on the as-cured PPSZ films to evaluate the thermal stability of PPSZ film. Also, the thermal stress of Cu/PPSZ/Si MIS capacitor was carried out to evaluate the thermal stability of PPSZ film with Cu electrode. Besides, the electrical reliability of PPSZ films with Cu electrode was conducted by bias-temperature stress (BTS) in this study.

In order to investigate the compatibility of CMP and ultra low-k PPSZ films for interconnection, the CMP process was applied to the as-cured PPSZ films. 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, there were three types of slurries implemented separately to investigate influence on the characteristics of ultra low-k PPSZ films after CMP polishing. One was the typical slurry of polishing Cu metal provided from National Nano Device Laboratory, which was used to estimate the influence on low-k PPSZ films after CMP process. This slurry consisted of 2 vol% HNO_3, 5×10-2 citric acid, and 3 wt% Al_2O_3 (0.1 μm), which was marked as Cu slurry. Its pH value is 0.56. On the other hand, we used one type of colloidal silicate slurry (marked as TaN slurry), which included 10wt% colloidal silica and 10 vol% H_2O_2 in DI water liquid. Its pH value is 8.5. The last one is commercial COBATTM SS-25 slurry which is used to polish SiO_2 traditionally. In addition, the polishing parameters, such as pad, down force, back pressure, platen and carrier rotation speeds, and slurry flow rate are settled the same as table 2-2 for these three slurries. In addition, the proposed O_2 plasma pre-treatment method for improving the polishing rate of low-k material in chapter 2 was also investigated in this chapter by material and electrical analyses. Oxygen plasma was generated in a plasma enhanced chemical vapor deposition chamber at a pressure of 400 mtorr with a radio frequency power of 300 W for 30 sec. The flow rate of oxygen gas was 500 sccm. The wafers which were subjected to O_2 plasma treatment were labeled as "Sample O" and the wafers which underwent O_2 plasma treatment and followed by CMP process were called as "Sample C". The thickness of all of the films before and after CMP polishing were measured using a n&k 1200 analyzer by means of light interference effects in PPSZ film. The structure properties of the PPSZ films were studied using Fourier Transform Infrared Spectroscopy (FTIR). The surface morphologies of the polished films were investigated by Atomic Force Microscopy (AFM). The auger depth profile analyses were conducted to evaluate the effectiveness of O_2 plasma treatment for PPSZ films. Electrical characteristics of all PPSZ films were performed on the Metal-Insulator-Semiconductor (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 measure the dielectric constants of all PPSZ films, respectively. During the operation of Integrated Circuits (IC), it works at higher temperature and bias than that at off state. In this situation, the copper may drift into the dielectric more easily. Therefore, high bias and temperature stress (BTS) was performed to evaluate the reliability under IC operation condition. In this work, BTS was performed by applying an electric field at 2 MV/cm on the MIS capacitors at 150^{o}C for 1000 seconds. Before BTS testing, the leakage current of PPSZ films was measured at room temperature and 150 ^{o}C. After BTS testing, the leakage current was measured again at 150^{o}C and room temperature sequentially.

3.3 Results and discussions

Figure 3-2 shows the FTIR spectra of PPSZ film during formation. In the as-baked PPSZ film, Si-N bonds (at near 950 cm^{-1} and 1172 cm^{-1}), Si-CH_3 bonds (at near 1258 cm^{-1}), porogen polymer bonds (at near 1730 cm^{-1}) and C-H bonds (at near 2956 cm^{-1}) were observed in FTIR spectra. After 10 hrs hydration, it was that the intensity of Si-N bonds was decreased, while the Si-O network-like peaks and Si-OH groups grew gradually due to hydrolysis process. This implies that the hydrolysis and condensation processes took place simultaneously. During the region of 10 to 48 hrs, the consecutive poly condensation process resulted in a network-like structure throughout the bulk MSZ film. And the porogen polymer was distributed uniformly within the bulk network-like MSZ. After furnace curing process, the porogen polymer will be eliminated and the standard PPSZ film was obtained. This procedure is important for the formation of an ultra low-k porous dielectric (k<2.2). The internal stress variation of PPSZ during thermal cycle is shown in Fig. 3-3. The internal stress of PPSZ is tensile stress. As the temperature was risen, the tensile stress was decreased. This means that the expansion coefficient of PPSZ film is larger than that of Si substrate. Also, the reversible curve can prove that the dielectric properties were not changed during the thermal cycle. The thermal stability of PPSZ is good up to about 550 ^{o}C, which can be evidenced by no obvious change on Si-CH_3 as well as C-H groups in the FTIR spectra of PPSZ after thermal annealing at 550 ^{o}C for 30 min, as shown in Fig. 3-4. In Fig. 3-5 (a) and (b), the leakage current and dielectric constant of PPSZ films with various annealing temperature even up to 550 ^{o}C were all kept in the acceptable level of low-k PPSZ. This coincides with our FTIR spectra analyses in Fig. 3-4. Figure 3-5 shows the temperature dependence of thermal stress for PPSZ film with Cu electrode. It was found that the leakage current slightly increased with the increase of annealing temperature. The result can be inferred that the Cu element would penetrate into the PPSZ film and degrade the electrical properties during thermal annealing process. Fortunately, the effect of Cu diffusion into PPSZ film is not serious for the application of PPSZ film into Cu interconnection. Leakage current density of PPSZ films before and after BTS test at 190 ^{o}C and 2 MV/cm for 1000 sec is shown in Fig. 3-7. It was found that the leakage current of PPSZ was not increased distinctly even under the serious BTS condition. This means that the reliability of PPSZ with Cu electrode is appropriate for general IC operation. During the measurement of leakage current of PPSZ, an interesting phenomenon was found in this study. In Fig. 3-8, the I-V curves were measured with MIS capacitors biased at accumulation mode and repeatedly swept from 0 to -100 V. It was found that the leakage current is decreased with the sweeping times and finally approached saturation without decrease. It shows that there might be some charge trapping sites within the insulator. Moreover, the electron would be trapped by these trapping sites to form a local field and retard the other injected electron from electrode. Therefore, the leakage current will be decreased as the sweeping times are raised.

On the aspect of integration of Cu and low-k material, the compatibility of CMP and low-k materials would be a big challenge for Cu damascene interconnection. In order to obtain global planarization of multilevel interconnection and desirable pattern, the detection of end point of metal CMP must be concerned in the Cu damascene process. On the one hand, it was found that the removal rate of ultra low-k PPSZ film with TaN slurry is 17 nm/min, which is lower than that of TaN metal (68.1 nm/min) with same slurry. On the other hand, the removal rate of ultra low-k PPSZ with Cu slurry is only 3 nm/min, which is much lower than that of Cu with this slurry. The results indicated that the removal rate of copper or TaN with respect to PPSZ was high and could reduce the loss of PPSZ film during metal CMP and make the detection of end point more easily. In addition, the dielectric integrity and surface topography of ultra low-k PPSZ films after metal CMP process has to be remained at acceptable region to meet requires of multilevel interconnection. AFM images of PPSZ surface after CMP process with TaN and Cu slurries are shown in the Fig. 3-9 (a) and (b), respectively. It indicated that there were smooth PPSZ surface after CMP polishing no matter with TaN or Cu slurries, the roughness (Ra) of PPSZ films were about 0.189 and 0.253nm after TaN and Cu slurries polishing, respectively. This result indicated that the planarization surface can be obtained for PPSZ films after TaN or Cu CMP process. In addition, the effect of CMP process on PPSZ films with commercial SS-25 slurry for the PMD application was investigated in this chapter. Figure 3-10 shows the AFM surface image of polished PPSZ with SS-25 slurry. It was found that the roughness of PPSZ after CMP with SS-25 slurry is about 0.286 nm, which is acceptable for the planarization of PPSZ films. The FTIR spectra of post-CMP PPSZ with the foregoing slurries are given in Fig. 3-11. It is revealed that the Si-C and C-H bonds intensity of polished PPSZ films were still remanded high level after CMP process. This provides evidence that the chemical structure of PPSZ film would not be damage after CMP procedure with these polished slurries. In addition, the electrical characteristics of post-CMP PPSZ must be investigated to evaluate the impact of these CMP processes used in multilevel interconnect fabrication on PPSZ films. Figures 3-12(a) and 3-12(b) show the leakage current and dielectric constant of PPSZ after the CMP process with various slurries. The leakage current of post-CMP PPSZ was similar to as-cured PPSZ film regardless of PPSZ films polished with what slurry. The dielectric constants of post-CMP PPSZ films slightly increased from 2.25 of as-cured PPSZ film to the region of 2.3 to 2.4 as well, as shown in Fig. 3-12(b). However, it still accords with the requirement of low-k materials. It appears that the electrical properties of PPSZ don't be degraded during CMP process with these slurries. Figure 3-13 reveals the tendency of moisture desorption for polished PPSZ films during the raised temperature period in temperature desorption system. The concentration of moisture desorption of PPSZ polished with these slurries was silimar to that of as-cured PPSZ film. This is believed that the film characteristics are not change after CMP process. This result is consistent with the electrical properties of PPSZ films polished by these slurries. Moreover, integrating copper and low-k materials to achieve the reduction of RC delay is gradually important. In order to investigate the reliability of low-k PPSZ with copper if satisfy requires of actually IC operation, the higher temperature I-V measurement and BTS test should be conducted to evaluate the reliability of post-CMP PPSZ with copper electrode during really operation conditions. Figure 3-14 shows the leakage current density of these post-CMP PPSZ films before and after BTS test, which was measured at high and low temperature. The leakage current densities of the post-CMP PPSZ with these slurries used in this study did not arise at all after BTS stress (versus pre-BTS stressing post-CMP PPSZ films). Even measuring the leakage current densities of the post-CMP PPSZ after BTS stress at high temperature, the leakage current densities were all similar to that of pre-BTS stressing films. This implies that the electrical reliability of PPSZ can be maintained even after CMP process during Cu metallization manufacture or dielectric planarization processes. As a result, the low-k PPSZ film after the CMP processes with foregoing slurries all get the good resistance to copper drift at high field and temperature operation conditions. According to above electrical and material analysis results, it appears that the ultra low-k PPSZ films with Cu or TaN slurries have lower removal rate than Cu or TaN and could result in planarizaton surface after metal CMP process. Moreover, the dielectric characteristics of ultra low-k PPSZ could be remained after metal CMP processes with Cu or TaN slurries. Therefore, the ultra low-k PPSZ not only could be used as a lower dielectric constant of inter-metal dielectric, but also could reduce the thickness of hard mask in the Cu dual damascene process with above-mentioned TaN and Cu slurries. However, as for the application of low-k dielectric planarization, the polishing rate of PPSZ with SS-25 slurry was not enough for IC production. Therefore, we apply the proposed method in chapter 2 to increase the polishing rate of PPSZ film. As a result, the polishing rate of PPSZ with O_2 plasma treatment was increased more twice of magnitude than that without O2 plasma treatment when using SS-25 slurry (as shown in Fig. 3-15). Moreover, the surface roughness of O_2 plasma-treated PPSZ before and after CMP process is presented in Fig. 3-16. The roughness (Ra) of PPSZ films with O_2 plasma treatment was 0.440 nm, while the Ra value of O_2 plasma-treated PPSZ after subjected to a CMP process was reduced to 0.209 nm. The results indicate that the removal rate of PPSZ can be improved by O_2 plasma treatment, even with SS-25 slurry typically used to polishing SiO_2. Figure 3-17 shows FTIR spectra of O_2 plasma-treated PPSZ films before and after CMP process. Before the CMP process, both intensities of S-OH and H_2O groups (at near 993 and 3400 cm-1) increased, while the intensities of C-H (2974 cm-1) and Si-CH3 (at near 781 and 1273 cm-1) groups decreased after underwent O_2 plasma treatment. Moreover, the peak of the Si-O bond at 1070 cm-1 was formed obviously in the O_2 plasma-treated PPSZ. However, after CMP process, the peak of Si-O bond at 1070 cm-1 disappeared clearly. These phenomena can be explained by the model described in chapter 2. Nevertheless, the effect of O_2 plasma treatment on PPSZ is more serious than that of MSZ discussed in chapter, which is due to its large exposure surface area in PPSZ film. This effect can be verified by auger depth profile analyses. Figure 3-18 (a) and (b) shows the auger depth profile of as-cured PPSZ film and followed by O_2 plasma treatment for 45 sec, respectively. It was found that that the C element distribution in O_2 plasma-treated PPSZ would approach to stable level when the sputter time arrives at about 550 sec. However, the Si substrate can be reached until the sputter time arrives at about 750 seconds. Moreover, the thickness of as-cured PPSZ film was about 400 nm measured by n&k analyzer. Therefore, we can evaluate the thickness of oxygen plasma effectively penetrated into PPSZ film by the ratio of sputter time of PPSZ films with and without O_2 plasma treatment and the thickness of the as-cured PPSZ film. As a result, the depth of the oxygen plasma penetrating into PPSZ is about 293.3 nm. However, the hydrophilic layer can be removed after the CMP process. Therefore, the Si-OH peak signal disappeared in

FTIR spectra. Based on the results of foregoing stated material analysis, we will investigate the effect of the proposed method to improve polishing rate of PPSZ film on its electrical characteristics in detail. Figure 3-19 (a) and (b) show the leakage current and dielectric constant of O_2 plasma-treated PPSZ before and after the CMP process. The electrical properties of PPSZ with O_2 plasma treatment were degraded. After the CMP process, however, the leakage current and dielectric constant of PPSZ were recovered significantly. In order to explore the leakage behaviors of PPSZ 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 2-20 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 PPSZ 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 PPSZ 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 4 to 5 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^{o}C baking temperature) decreased about 3 to 4 orders 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 PPSZ film. Figure 2-21 shows the leakage current density of sample C and sample STD measured at 25 ^{o}C (curve I, II, and IV) and 150 ^{o}C(curve III), respectively. Because the modification surface layer of O_2 plasma-treated PPSZ was polished away by the CMP process, the leakage current of sample C (curve II and IV) was close to that of as-cured PPSZ film (curve I) at 25 ^{o}C. Moreover, the leakage current of sample C (curve III) increased by 1 order of magnitude compared to that of the as-cured PPSZ film (curve I) at 150 ^{o}C. 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 due to the O_2 plasma treatment would result in the increase of leakage current of PPSZ film. However, the leakage current of O_2 plasma-treated PPSZ could be recovered after polishing the most of hydrophilic layer by CMP process. These electrical results were consistent with aforementioned FTIR and auger depth profile analyses data.

These above-mentioned results suggest that the ultra low-k PPSZ film has a lot of potential to that applied in next generation of IC manufacture.

3.4 Conclusion

The intrinsic properties of organic ultra low-k (k~2.2) PPSZ and the effect of CMP on PPSZ films with various slurries provided from national nano device laboratory were investigated in this chapter. The results reveal that the thermal stability of PPSZ can reach 550 ^{o}C at least. The electrical properties of PPSZ were not degraded under serious BTS testing. The ultra low-k PPSZ materials have low polished rate with regard to TaN or Cu metal polish in the CMP process with TaN and Cu slurries and result in detection of end point of metal polish more easily. Moreover, the electrical properties of post-CMP PPSZ films with above slurries could remain in low-k characteristics. The influence of O_2 plasma treatment for the improvement on polishing rate of PPSZ film is more effective than that of MSZ film. Moreover, after CMP process, the electrical of PPSZ film can be recovered similar to as-cured one. According to these result, the ultra low-k PPSZ films not only has good reliability with copper integration, but also is compatible with CMP process. It is believed that the integration between PPSZ and Cu has reliable potential in Cu damascene structure.