Chapter 6

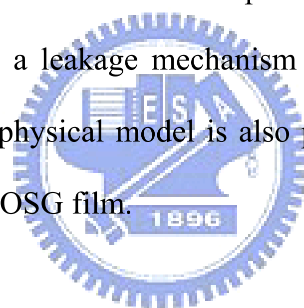
Exploration of the Effect of Electron Beam Curing on Organic Ultra Low-k Porous Organosilicate Glass (POSG) Material

6.1 Introduction

It has become apparent that utilizing low dielectric constant (low-k) materials as interlayer dielectric (ILD) for multilevel interconnect can effectively reduce resistance-capacitance (RC) delay and power consumption [141-145]. According to the ITRS roadmap of 2003 [124], it is necessary to reduce the dielectric constant of the ILD layers below 2.4 as the device dimension shrinks into sub-65 nm nanoscale fields. In addition to employ lower polarizability materials to decrease dielectric constant of the ILD layers, introducing nanoscale pores into the dielectrics is an effective approach to achieve ultra low-k demand [146-150]. Among various porous low-k materials, porous organosilicate glasses (POSG) are promising candidates for ILD application [151-152]. For further improving the chip performance, it is also a trend to integrate low-k materials with copper wiring to form damascene structure in multilevel interconnect [153-154]. Besides, it is required to simplify the fabrication procedures for interconnect architecture, especially etch-stop-layer, photoresist stripping, dry-etching process for damascene interconnect structure. However, porous low-k materials have been reported to be easily degraded during photoresist stripping processes due to their large internal surfaces [155-156]. Direct curing of low-k dielectrics using electron-beam (e-beam) exposure to form specific pattern is one of promising choices to reduce process steps and avoid the damage from photoresist

stripping during Cu damascene manufacture. This process flow for forming single damascene pattern is shown in Fig. 6-1. Dual damascene structure also can be simply fabricated by twice POSG deposition/ e-beam exposure processes for sequentially forming via and line patterns, which is like the illustration in Fig 1-9 of chapter 1.

In this work, we investigate the effect of e-beam exposure on a porous organosilicate glasses (k=2.2), which is manufactured by Chemat Technology Inc. and is based on a methyl-silsesquioxane matrix, except that it contains CH_n (n=1-2) bridging the siloxane networks (-Si-O-Si-). The material and the electrical analyses are performed to obtain the e-beam exposure dosage. Also, the SEM images will be observed to examine the practicability of using e-beam direct curing process. In addition, we also investigate the effect of development on the dielectric properties of POSG film in detail. Finally, a leakage mechanism of e-beam exposed POSG was studied in this chapter and a physical model is also proposed to explain the leakage behavior of e-beam exposed POSG film.



6.2 Experimental procedures

The substrates used in this study were 150 mm p-type (11-25 Ω-cm) single crystal silicon wafers with (100) orientation. The precursor solution of the porous organosilicate glass (POSG) diluted with methylisobutylketone (MIBK) were spun on Si wafers at the first-stage spin rate of 450 rpm for 4 s and the second 3000 rpm for 30 s, respectively. As-spun wafers were baked at 100 ^{o}C on a hot plate for 1 min. The resulting wafers were exposed blanketly by a Leica Weprint200 e-beam stepper with doses ranging from 2 uC/cm^2 to 820 uC /cm^2. The e-beam energy was 40 KeV with beam size 20 nm. The exposure doses of e-beam irradiation could be determined according to material and electrical analyses. As for the pattern formation of POSG,

as-baked samples were exposed with e-beam according to desire pattern layout. After e-beam irradiation, the resulted wafers were developed in a mixed solution containing 2.38 wt% tetramethylammonium hydroxide (TMAH) and methanol with the ratio of 1: 8 and rinsed in deionized water until the desirable pattern was completed. Furthermore, a furnace annealing process (at 400 ^oC, 30 min) was performed on the e-beam exposed wafers to enhance dielectric properties of e-beam exposed porous OSG films. In addition, the control samples were also manufactured, according to a typical forming recipe, by transferring the as-spun wafers to a quartz furnace and heated from room temperature to 400 ^oC at a ramping rate of 20 ^oC/min. After that, it is followed by thermal curing process at 400 ^oC for 1 h under nitrogen atmosphere. In order to investigate the of PR stripping during conventional manufacturing process, the O_2 plasma treatment was applied on some of as-cured PPSZ films in plasma-enhance chemical vapor deposition (PECVD) chamber. The O_2 plasma was operated with an rf power density of 1.13 (W/cm^2) at a pressure of 300 mtorr. The refractive index and thickness of the above-mentioned POSG films were measured with an n&k analyzer. Infrared spectrometry was performed from 4000 to 400 cm^{-1} using a Fourier transform infrared (FTIR Bio-Rad QS300) spectrometer calibrated to an unprocessed wafer, for determining the chemical structures of all aforementioned samples. Electrical measurements were performed on metal insulator semiconductor (MIS) capacitors, which are constructed on e-beam exposed and O_2 plasma-treated blanket POSG films through shadow mask. Dielectric constant measurements were conducted using a Keithley Model 82 CV analyzer. The area of gate electrode was 0.00503 cm^2 for C-V analysis. The leakage current (I-V) characteristics of dielectric were measured using a HP4156 electrical meter. Moreover, the I-V properties of dielectric were measured at various temperatures to explore the leakage behaviors of e-beam exposed POSG films. Finally, the scanning electron microscope (SEM) image

was conducted to examine the final pattern of e-beam cured POSG films after development process.

6.3 Results and discussions

Figure 6-2 presents the FTIR spectra of as-spun POSG after a series of bake and furnace curing steps. It was found that the peak intensity of the Si-OH + H2O (near at 3400 cm-1) decrease after a series of baking process at furnace due to the gelation reaction of Si-OH groups. The Si-OH groups in each methyl silicone resins easily react with another Si-OH group in another methyl silicone resins during gelation. As a result, many methyl silicone resins can condense each other so that the POSG structure can form a crosslink matrix network material. After subjected to the furnace curing on furnace at 400 ^{o}C for 30 min, the porogen in POSG will be eliminated to form a porous methylsilsesquioxane-like (MSQ-like) low-k material (as illustrated in Fig. 6-3). As for the sake of exploring the impact of PR stripping on POSG, the FTIR spectra of POSG film after subject to O_2 plasma ashing for 30 to 90 sec are shown in Fig. 6-4. It was found that the intensities of Si-OH + H2O signals increased as the O_2 plasma was applied to as-cured POSG. Moreover, the intensities of Si-C (781, 1273cm^{-1}) and C-H (2980 cm^{-1}) bonds are decreased dramatically. This means that the oxygen radical can diffuse deeply into porous inner structure of POSG film and attack a large amount of Si-C and C-H bonds of as-cured POSG film. This will result in a lot of dangling bonds and defects left in the film. Moreover, the dangling bond will easily absorb moisture and form Si-OH bond as exposed to the environment. The POSG film having excellent low-k properties is due to the higher Si-C and C-H functional groups. Therefore, the dielectric characteristic will be degraded as the functional group was destroyed after O2 plasma treatment. Figure 6-5 shows the electrical properties of

POSG after O_2 plasma ashing for 30 to 90 sec. It was found that the leakage current increased with the increase of O_2 plasma treatment time. In addition, the dielectric constant of O_2 plasma treated POSG were also increased. This result is consistent with the FTIR data in Fig. 6-4. In order to overcome these limitations, the e-beam direct patterning method is proposed to fabricate the damascene structure.

Firstly, a strategy based on material and electrical analyses should be proposed to determine the doses of e-beam curing on POSG film for direct patterning technology. Therefore, the effect of e-beam curing on the quality of POSG film through material and electrical analyses was investigated in this study. Figure 6-6 shows the refractive index varieties of POSG films with different e-beam exposed dosage from 2 uC/cm^2 to 810 uC/cm^2. The minimum refractive index is indicated from the figure to be present between 2 uC/cm^2 and 100 uC/cm^2. In addition, it was found that the region of POSG film without e-beam exposure can not be removed entirely during the development process used in this study as the e-beam dosage exceed 100 uC/cm^2. This phenomenon is attributed to the proximity effect of e-beam exposure. Clearly, the findings revealed that the dosage of e-beam exposure can not exceed 100 uC/cm^2. Figure 6-7 reveals the remained thickness of the e-beam exposed POSG films with different dosage after development process. It was appeared that 70 % thickness of the post-developed POSG films can be detained as the dosage exceeds 6 uC/cm^2. This implies that the threshold dosage of POSG material is about 6 uC/cm^2, which is similar to some commercial e-beam negative resist (e.g. SAL-601) [157]. As described above, the possible dosage range of e-beam curing on porous OSG films can be decided between 6uC/cm^2 and 100 uC/cm^2. Therefore, the dielectric reactions between POSG films and e-beam exposure were investigated to determine the optimized doses used on POSG films among the above dosage range. Figure 6-8 shows the FTIR spectra of POSG films with different doses of e-beam exposure. In

the furnace-cured POSG, Si-O stretching modes (cage-like at near 1144 cm^{-1}, network-like at near 1049 cm^{-1}), Si-C stretching peaks (at 781, 1273 cm^{-1}), and C-H peak (2980 cm^{-1}) are appeared in the FTIR spectra. After e-beam exposure, the peaks of Si-O stretching vibration significantly change. E-beam exposure provides the as-baked POSG film energy to be cross-linked and transfer the POSG film from cage-like structure to network-like one. It clearly reveals the intensity of Si-O network mode grows at the expense of the intensity of Si-O cage-like mode with increasing e-beam exposure doses. This indicates the structure of the POSG film changes from the cage-like to a stable three-dimentional network structure via the breakage of Si-O cage-like and subsequently forming Si-O-Si network.

The leakage current density and dielectric constant of e-beam exposed POSG films were also evaluated so as to satisfy the requirement of inter-metal dielectric applications. The leakage current densities of e-beam exposed at different doses were presented in Fig. 6-9. It is observed that the leakage current of all e-beam exposed POSG films are larger than that of furnace-cured one. Nevertheless, the leakage current of e-beam exposed POSG film with a dose of 8 uC/cm^2 has the lowest value. While the exposure dosage reaches 16 uC/cm^2, the leakage current of e-beam exposed POSG film will increase one order of magnitude than that of furnace-cured one at 1 MV/cm electric field. Figure 6-10 shows the dielectric constant of e-beam exposed POSG films at different doses. The results indicate that the dielectric constant of e-beam exposed films with all different doses is larger than that of furnace-cured one. According to aforementioned electrical analyses, the dielectric loss is inferred to be due to the formation of dangling bond owing to e-beam exposure and the adsorption of polarized components such as moisture in POSG films after the e-beam exposed dose over than 16 uC/cm^2. The inference can be demonstrated from the FTIR spectra in Fig. 6-8. The intensity of Si-OH and moisture bonds around 3400 cm^{-1} will increase

as the dosage exceeds 16 uC/cm^2. This implies that the e-beam dosage cannot be too high to obtain the required dielectric properties of ultra low-k POSG. In this work, the optimum e-beam exposure dosage can be obtained within a range of 8 to 16 uC/cm^2. As a result of the electrical properties of e-beam exposed POSG films at different e-beam exposed doses are all inferior to that of standard furnace-cured ones, thus we tried transferring these wafers to a furnace for further thermal annealing. Figure 6-11 reveals the leakage current densities of e-beam exposed POSG films at different doses with an additional annealing in a furnace at 400 ^{o}C for 30 min. It is clear that the leakage current densities are all significantly reduced after thermal annealing. Especial for the e-beam exposed sample with the dose of 8 uC/cm^2, its' leakage current density is recovered close to that of the furnace-cured one. The dielectric constant of e-beam exposed POSG films at different doses with thermal annealing is also shown in Fig. 6-12. It is demonstrated that the dielectric constants of POSG films after e-beam exposure with thermal annealing in a furnace are decreased and close to the standard furnace-cured one. This indicate that even though the dielectric constants of POSG films after e-beam exposure are higher than that of the furnace-cured one, it can be recovered by additional thermal annealing process. Therefore, the results suggest that though available electrical dielectric properties of POSG film cannot be obtained directly by the e-beam curing process, the post-exposed thermal annealing process can be utilized to recover the electrical dielectric characteristics as the desirable pattern is formed by e-beam direct patterning process.

As for the e-beam direct patterning, a homemade pattern was formed by e-beam direct patterning to estimate its practicability. In this study, we used a mixed solution containing 2.38 wt% tetramethylammonium hydroxide (TMAH) and methanol with the ratio of 1: 8 to develop the pattern, and the result is shown in Fig. 6-13. Although the well contract of the pattern was not observed after development, it is clear that the

e-beam direct patterning process can be achieved on POSG films. In addition, additional study is required to perfect the patterning resolution, but it is believed that this can be fine-tuned by varying the e-beam exposure dose and developed condition. In addition, after the development process of e-beam direct patterning for POSG films, an interesting phenomenon was found in the variation of dielectric characteristics of e-beam exposed POSG films. Therefore, we further investigated the possible mechanism by material and electrical analyses. Figure 6-14 presents the FTIR spectra of POSG films with e-beam exposure and followed by development and post-thermal annealing treatments. The FTIR spectra reveal that the functional groups (such as cage-like (~1144cm^{-1}) and network-like (~1049cm^{-1}) bonds of post-developed POSG films were weaker than that of as e-beam exposed POSG films. This implies that the uncrosslinked methyl-silsesquioxane matrix in films will be carried away by developer. Besides, the intensity of network-like peak was strong than that of cage-like peak in post-developed POSG film as compared to that of as e-beam exposed POSG film. This indicates that the e-beam exposure on as-baked POSG film only partially crosslink the methyl-silsesquioxane matrix into three-dimensional network structure. Once underwent the development process, the portion of uncrosslinked mono-polymer will be dissolved by developer used in this study. However, the crosslinked network structure of e-beam exposed POSG was carried away only a little during the development process. As a result, the network-like peak signal was stronger than the cage-like peak in the FTIR spectra of e-beam exposed POSG after development process. After subjected to thermal annealing at furnace, the residual uncrosslinked mono-polymer will be crosslinked and some remained developer solvent will be desorbed. Therefore, the intensity of network-like peak was larger than that of cage-like one after thermal annealing process. The above-mentioned reaction mechanism is illustrated in Fig. 6-15. According to above

analyses, we suggest that the porosity of e-beam exposed POSG film after development and thermal annealing processes will be higher than that as-cured POSG film. This mechanism can also be approved by electrical measurement. Figure 6-16 shows the leakage current density of e-beam exposed POSG films with 8 uC /cm^2 after underwent various treatments. The leakage current of e-beam exposed POSG film after development process was larger 2 to 3 order of magnitude than that of as e-beam exposed POSG films as measured at 1 MV /cm. Nevertheless, the leakage current of as developed POSG films can be recovered to that of as-cured POSG film through thermal annealing process. This implies that a number of leakage paths were generated during the development process due to that the portion of uncrosslinked material was carried away and replaced by the development solvent. After the thermal annealing process, the residual development solvent will be desorbed and the perfect network structure of POSG will be finished. Therefore, the leakage current of as-developed POSG can be recovered to similar to that of as-cured one after thermal annealing process. Figure 6-17 shows the dielectric constant of e-beam exposed POSG films with 8 uC /cm^2 dosage after underwent various treatment. It was found that the dielectric constants of POSG after e-beam exposure and development processes are all higher than that of as-cured POSG films. However, after underwent thermal annealing process, the dielectric constant was even lower than that of as-cured one to about 1.89. This result is consistent with the FTIR analyses discussed in Fig. 6-14. Also, the leakage current behaviors of intrinsic and e-beam exposed POSG film were investigated in this chapter. Figure 6-18 shows the leakage current behavior of furnace cured POSG film as a logarithm of leakage current density versus square of electric field. The linear relation of current corresponds to either schottky emission or Poole-Frenkel (PF) emission [158]. The current density in the schottky emission can be quantified by the following equation:

$$J = A^* T^2 \exp[\frac{\beta_s E^{1/2} - \phi_s}{k_B T}] \quad (1)$$

where $\beta_s=(e^3/4\pi\varepsilon_o\varepsilon)^{1/2}$, e is the electronic charge, ε_o is the dielectric constant of free space, ε is the high frequency relative dielectric constant, A* is effective Richardson constant, T is absolute temperature, E is the applied electric field, ϕ_s is the contact potential barrier, and k_B is the Boltzman constant. And the current density of PF emission can be expressed by:

$$J = J_o \exp[\frac{\beta_{PF} E^{1/2} - \phi_{PF}}{k_B T}] \quad (2)$$

where $Jo=\sigma_o E$ is the low field current density, σ_o is the low field conductivity, $\beta_{PF}=(e^3/\pi\varepsilon_o\varepsilon)^{1/2}$, and ϕ_{PF} is the height of trap potential well. From above description, the β value depends on the dielectric constant of the material. For POSG (k~2.2), the theoretical β_s and β_{PF} are 3.7141 x 10^{-23} $Jcm^{1/2}V^{1/2}$ and 7.4282 x 10^{-23} $Jcm^{1/2}V^{1/2}$, respectively. In figure 6-18, the experimental β, extracted from the slope of the linear region (β=slope x $k_B T$), is 3.70855 x 10^{-23} $Jcm^{1/2}V^{1/2}$. In virtue of the β value is close to the β_s, the carrier conduction mechanism should be dominated by schottky emission at high field. The band diagram of schottky emission for a MIS capacitor is shown in Fig. 6-19. As for the sake of exploring the leakage behaviors of e-beam exposed POSG, we measured the leakage current density of e-beam exposed POSG film at various temperature as shown in Fig. 6-20. It was found that the leakage current density of e-beam exposed POSG film measured at 150 oC increased about two orders of magnitude than that measured at room temperature. In order to clarify the leakage behaviors, we transformed Fig. 6-20 into leakage current density versus square of electric field relation at room temperature and 150 ^oC, which is shown in Fig. 6-21 and Fig. 6-22, respectively. The results indicate that J is linearly proportional to E^2 at high field. Moreover, the phenomenon was more clearly at high temperature I-V measurement. This kind of conduction mechanism is similar to

space-charge-limited current conduction (SCLC). As considering the space-charge-limited conduction [159-160], the current density can be expressed as follows:

$$J = \frac{9\varepsilon_o \varepsilon_r \mu \theta E^2}{8d} \propto E^2 \qquad (3)$$

where μ is the free carrier mobility, εo is the permittivity of free space, εr is the relative dielectric constant of material, d is the dielectric thickness, and θ is the ratio of the free charge carriers to trapped ones. The phenomenon can be explained by the band diagram of e-beam exposed POSG MIS structure as shown in Fig. 6-23. After the as-baked POSG film was exposed with the e-beam, there are many charge trapping sites remained in as-exposed POSG film, which will result in local potential barrier height so that the free carrier mobility will be reduced. Therefore, as a large amount of free carrier electron cross the potential barrier built at the interface between metal and insulator, the SCLC carrier conduction mechanism will occur. Especially for the leakage current measured at high temperature and electric field, the SCLC carrier conduction behavior will be more obviously. This is the reason of why that the leakage current density of e-beam exposed POSG measured at 150 oC has the more linear fitting than that measured at room temperature.

6.4 Conclusion

In this chapter, the e-beam direct curing process for ultra low-k POSG as inter-metal dielectric (IMD) has been investigated in detail. The novel direct patterning technology on the POSG can avoid the damage during conventional photoresist removal process. The material analysis shows the e-beam curing can provide POSG films energy to make the cage-like bonds of POSG partially transfer to

network bonds. And the possible doses of e-beam exposure on POSG film is within the range of 8 uC /cm^2 to 16 uC /cm^2, which is satisfied the requirement of e-beam lithography technology. Then the part of POSG films without e-beam cured can be developed using the mixed solvent of 2.38 wt% tetra-methyl ammonium hydroxide (TMAH) and methanol. However, the electrical properties of e-beam exposed POSG films have a large change after development and post thermal annealing process. The experimental results reveal that the porosity of e-beam exposed POSG will be reduced after development and thermal annealing process. This will result in the lower dielectric constant of POSG film to about 1.89. In addition, the leakage current behaviors of POSG films will be transformed from schottky emission into space-charge-limited current conduction mechanism after e-beam exposure process. As for the perfect pattern resolution, an additional study is required to perfect the pattern resolution, but it is believed that this can be fined tuned by varying the e-beam exposure dose and develop condition.