

Chapter 4

Study on Direct Pattern Method of Low-k Hydrogen Silsesquioxane (HSQ) Using Electron Beam Lithography Technology

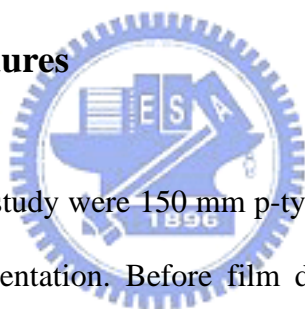
4.1 Introduction

As integrated circuit dimensions continue to shrink into sub-100 nm nanoscale fields, the interconnect RC delay will be increased and becomes a serious issue of performance [82]. The crosstalk and power dissipation both also increase with the escalating parasitic RC delay. In order to overcome this problem, there is a trend to integrate low dielectric constant (low-k) [108-111] materials with copper wiring to form damascene structure in multilevel interconnect. It is necessary to simplify the fabrication procedures for interconnect architecture, especially etch-stop-layer, photoresist stripping, dry-etching processes for damascene interconnect structure. In addition, the complexity of dielectric pattern in traditional procedures of damascene manufacture is a critical issue for semiconductor industries (as shown in Fig. 4-1). Furthermore, it is worthily noticed that low-k materials are easily degraded during photoresist stripping processes [112-113]. Direct patterning of low-k dielectrics using electron-beam (e-beam) lithography is one of promising choices to reduce process steps and avoid the damage from photoresist stripping during Cu damascene manufacture [114]. This e-beam lithography process flow is shown in Fig. 4-2. It was found that several low-k dielectric materials are sensitive to e-beam exposure. One of them, hydrogen silsesquioxane (HSQ) [115] was used as a negative tone electron beam resist [116], since HSQ did not only show high resolution with sensitivity

comparable to poly(methyl methacrylate) (PMMA) but also a very low edge roughness [117]. For the e-beam resist applications, HSQ layers are always stripped after finishing pattern transfer. Thereby, previous studies of HSQ as an e-beam resist have not considered the effect of e-beam processing on dielectric properties. However, for inter-metal dielectric applications, low-k electrical characteristics such as leakage current and dielectric constant should be carefully taken into consideration [118-119].

In this study, we will discuss the leakage current and dielectric properties of e-beam exposed HSQ after various treatments required for e-beam direct patterning technology. In addition, pattern images of 60 nm line-width will be demonstrated to examine the practicability of e-beam direct patterning technology.

4.2 Experimental procedures



The substrates used in this study were 150 mm p-type ($11-25 \Omega\text{-cm}$) single crystal silicon wafers with (100) orientation. Before film deposition, they were boiled in $\text{H}_2\text{SO}_4+\text{H}_2\text{O}_2$ at 120°C for 20 minutes to remove particles on surface and followed by a 100:1 HF dip to remove the native oxide on surface. HSQ resins diluted in methylisobutyl ketone (MIBK) were spun on Si wafers at 2000 rpm for 20 sec to form 400-nm-thick films. After baking at 150°C on a hot plate for 1 min, e-beam exposure was carried out overall on as-baked HSQ films with doses ranging from 100 to 700 $\mu\text{C}/\text{cm}^2$ by use of a Leica Weprint200 stepper. 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 HSQ lines, as-baked HSQ films were irradiated with e-beam according to desire pattern layout. After e-beam exposure, the resulted wafers were developed in an aqueous solution containing 2.38 % tetramethylammonium hydroxide (TMAH) for 1 min and

rinsed in deionized water for 1 min until the desirable pattern was completed. Simultaneously, we observed the exposed pattern by scanning electron microscope (SEM) image to demonstrate the feasibility of e-beam direct patterning on HSQ films. Moreover, furnace annealing at 300 ~ 350 °C for 60 min was finally performed to remove residual organic solvent and to enhance the dielectric properties of e-beam exposed HSQ films. In addition, control samples were also manufactured, according to a typical commercial recipe, by prebaking as-spun HSQ films at 150 °C, 200 °C, and 300 °C for 1 min, and followed by thermal curing in a furnace at 400 °C for 1 hr. The chemical structures of all aforementioned samples were characterized by Fourier transform infrared (FTIR Bio-Red QS300) spectroscopy. Electrical measurements were conducted on metal insulator semiconductor (MIS) capacitors. The dielectric constant measurements were conducted using a Keithley Model 82 CV meter. The area of the gate electrode was 0.00503 cm² for C-V analysis. The leakage current (I-V) characteristics were measured using a HP4156 electrical meter. Material analysis using thermal desorption spectroscopy (TDS) was also carried out upon heating samples from room temperature to 600 °C at a heating rate of 20 °C/s in vacuum (10⁻⁵ Pa). In the TDS analysis, M/e (mass-to-charge ratio) =18 peak attributed to H₂O was monitored.

4.3 Results and discussions

Figure 4-3 presents the FTIR spectra of HSQ film before and after a series baking and curing processes. The functional groups of HSQ films in FTIR spectra are described as follows. The Si-H stretching bond is at near 2250 cm⁻¹. This Si-H bond makes the surface hydrophobic and prevents the moisture absorption. Besides, Si-O stretching cage-like bond is at 1132 cm⁻¹, Si-O stretching network-like bond is at 1072

cm^{-1} , Si-O bending cage-like bond is at 863 cm^{-1} , and Si-O bending network-like bond is at 830 cm^{-1} . The FTIR spectra of HSQ are almost the same during a series baking steps. However, after a $400 \text{ }^\circ\text{C}$ curing process, a significant change will be observed in chemical structure of HSQ film. It was found that the signal of Si-O stretching network-like peak grows at the expense of the intensity of Si-O stretching cage-like peak. Also, the intensity of the absorption at 2250 cm^{-1} with respect to Si-H stretching mode is decreased. The results indicate that the Si-H bond of HSQ film would be broken after $400 \text{ }^\circ\text{C}$ curing. Therefore, the structure of HSQ film changes from cage-like structure to a 3D network structure by breakage of Si-O cage-like and Si-H bonds. The cage-like and network-like structures of HSQ are shown in Fig. 4-4. In order to realize the direct patterning of HSQ film by e-beam exposure, the dielectric relations between HSQ films and e-beam irradiation were firstly investigated to determine the optimized doses used in HSQ films. Figure 4-5 shows the FTIR spectra of HSQ films with different doses of E-beam exposure. In the furnace-cured HSQ, Si-O bending cage-like peak (863 cm^{-1}), Si-O stretching modes (cage-like at near 1132 cm^{-1} , network-like at near 1072 cm^{-1}), and Si-H stretching mode (near 2250 cm^{-1}) are observed. The Si-H group makes the surface hydrophobic and prevents moisture uptake. The low dielectric properties of HSQ film can be achieved if the density of Si-H bonding is maintained at a high level [120]. After e-beam exposure, the peak of Si-O stretching vibration and that of bending vibration significantly change. E-beam exposure provides the as-baked HSQ film energy to be cross-linked and transfer the HSQ from cage-like structure to network-like one. It clearly shows 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. In addition, the intensity of Si-H stretching mode is slightly decreased with increasing e-beam exposure doses. This indicates the structure of the HSQ film changes from the

cage-like to a stable three-dimensional network structure via the breakage of Si-O cage-like and Si-H bonds, and subsequently forming Si-O-Si network. However, an excess of Si-H bonding breakdown will lead to the generation of dangling bonds in HSQ film, resulting in degraded dielectric properties [121-122]. Figure 4-6 shows the leakage current of e-beam exposed HSQ films at different doses. It is observed that the leakage current of e-beam exposed HSQ film with e-beam dosage from 100 $\mu\text{C}/\text{cm}^2$ to 600 $\mu\text{C}/\text{cm}^2$ have the similar values close to that of furnace cured one. Meanwhile, the leakage current of e-beam exposed HSQ with a dose of 400 $\mu\text{C}/\text{cm}^2$ is lower than others. While the exposure dosage exceeds 700 $\mu\text{C}/\text{cm}^2$, the leakage current density of e-beam exposed HSQ will increase one order of magnitude than that of furnace-cured one. The dielectric constant of e-beam as-exposed HSQ films at different doses is shown in Fig. 4-7. The results reveal that the dielectric constant of e-beam as-exposed films with e-beam doses between 100 $\mu\text{C}/\text{cm}^2$ and 600 $\mu\text{C}/\text{cm}^2$ is larger than that of furnace-cured one. Especially, the dielectric constant of e-beam exposed HSQ will increase significantly, as the dose exceeds 700 $\mu\text{C}/\text{cm}^2$. According to aforementioned electrical analyses, the dielectric loss is inferred to be due to the destruction of Si-H functional groups and the adsorption of polarized components in HSQ films after the e-beam exposed dose over than 400 $\mu\text{C}/\text{cm}^2$. The inference can be verified by the FTIR spectra shown in Fig. 4-5. The intensity of Si-H bonds was found to be smaller than that of furnace-cured HSQ as the e-beam dosage exposed from 400 to 700 $\mu\text{C}/\text{cm}^2$. This implies that the e-beam dosage cannot be too high to obtain the required dielectric properties of low-k HSQ. In this work, the optimum e-beam exposure dosage was obtained with a dose of 400 $\mu\text{C}/\text{cm}^2$.

In order to verify the feasibility of e-beam direct patterning on HSQ films, we perform the e-beam exposure according to desired pattern layout with the optimum dose of 400 $\mu\text{C}/\text{cm}^2$. In some cases, it was found that portions of dense line patterns

were collapsed after development processes in an aqueous solution of 2.38 % TMAH, rinsed with water, and dried in a nitrogen blow, as shown in Fig. 4-8. The most likely scenario is that the development process is overtime so that the dense lines become finer. It reduces the sustaining force between patterned HSQ film and Si substrate. Moreover, a capillary force is produced from the surface tension of the rinse solution remaining in the spaces between pattern lines [123]. If the capillary force is larger than the sustaining force during drying process, the pattern collapses will arise after development process (as illustrated in Fig. 4-9). For such a reason, with careful control of drying processes, the image of line patterns with line width of 60 nm can be obtained in our work, as shown in Fig. 4-10. According to the above results, the coverage of HSQ films exposed by e-beam can be cross-linked, while the others without e-beam exposure will be dissolvable in the TMAH aqueous solution and forming trench patterns. Therefore, it demonstrated the feasibility of e-beam direct patterning on HSQ films.

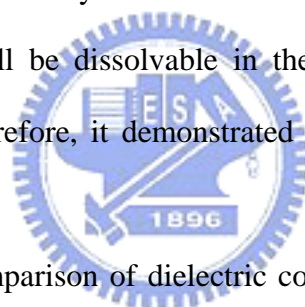


Figure 4-11 shows the comparison of dielectric constant of e-beam exposed HSQ for various treatments during e-beam direct patterning process. The dielectric constant of HSQ after e-beam exposed and TMAH developed processes was higher than that of furnace-cured one. This implies the TMAH development process would remain some polarized component (such as moisture) within the e-beam exposed HSQ. However, it can be removed by thermal annealing process. Therefore, the dielectric constant can be recovered to similar state as that of furnace-cured one after thermal annealing processes. Figure 4-12 reveals the leakage current of HSQ films cured by e-beam irradiation in comparison with furnace thermally cured one. It is found that the leakage current of e-beam exposed HSQ after TMAH development solution followed by thermal annealing processes was superior to that of furnace-cured one. This phenomenon could be attributed to the fact that furnace curing above 375 °C

leads to Si-H bonds being broken [120-121], generating dangling bonds in the HSQ films. These dangling bonds are electrically trap centers and prone to moisture uptake, easily forming leaky paths in HSQ film. As compared to furnace curing process, electron beam curing uses high-energy electrons rather than heat, to initiate polymerization and cross-linking reactions in the silicate base polymer. Then, the thermal annealing process below 350 °C can be conducted to eliminate the residual polarized solvent in HSQ after TMAH development process. The e-beam exposure technology thereby enhances specific physical and chemical properties, minimizing the formation of dangling bonds. TDS analysis shown in Fig. 4-13 surely confirms our inference that higher moisture content is monitored in the furnace-cured HSQ than that in e-beam exposed HSQ film after TMAH development and thermal annealing processes. Therefore, the furnace-cured HSQ exhibits inferior dielectric characteristics to that of the e-beam cured HSQ technology due to relatively high moisture adsorption.



4.4 Conclusion

In this chapter, we have performed e-beam lithography technique to direct pattern the low-k HSQ film. The smallest size of 60 nm has been demonstrated in this work. Such technique does not need the use of photoresist; therefore, it effectively avoids the damage from O₂ plasma ashing and stripping. The dielectric constant of e-beam exposed HSQ film after TMAH development can be recovered to that of furnace-cured one, due to the remove of polarized component after thermal annealing process. In addition, the e-beam exposed HSQ film with thermal annealing can exhibit superior insulating properties to that of the furnace-cured one. It is attributed to minimizing the break of Si-H bonds and moisture uptake. Therefore, the electrical

properties of e-beam direct patterned HSQ can be recovered by post-exposure furnace annealing. It is believed that the technique can be incorporated into next generation of interconnect systems as the devices shrink into nano-scale regimes.

