Chapter 5

Study on the Feasibility of Electro-Beam Direct Patterning on Low-k MSZ for Interconnection Applications

5.1 Introduction

With integrated circuit dimensions continue to shrink into ultra large integrated circuit (ULSI) regimes, the interconnect RC delay becomes a serious problem [124]. In order to reduce the RC delay of IC, there is a trend towards using low dielectric constant (low-k) materials and copper wiring to replace the traditional SiO_2 and Al in interconnect technology. Among the candidates for low-k materials [125-131], spin-on-glass (SOG) materials have been one of promising candidates to be used as interlayer dielectrics in multilevel interconnections because they are easily applied and have relatively low process costs. One of the most potential SOG materials is Methylsilsesquiazane (MSZ) an organic low-k dielectric with reasonable mechanical hardness and exceptional thermal and dimensional stability (in excess of 550 ℃) [132-135]. In order to integrate copper and low-k materials into multilevel interconnections. The damascene process is presently the only option. However, the etching issues and photoresist stripping are critical during the damascene process [136-138]. The etching process governs the pattern transfer and becomes more difficult as the pattern becomes much smaller. Also, the photoresist stripping process has been demonstrated to have the ability to damage the low-k dielectrics with O_2-based plasma gases [139-140].

The direct pattering with electron beam (e-beam) exposure on low-k will solve the above problems and it will be a useful tool in next generation lithography as the device dimension get into the 32 nm technology node [124]. The advantage of direct patterning is that it can effectively avoid some issues encountered during Cu damascene process. Using direct patterning technology, the parts of film exposed to e-beam will be cured. The other parts are dissolved in a suitable solvent used for developing the light exposed photoresist in industries.

In this work, we will discuss the material and the electrical dielectric properties of e-beam exposed MSZ, and compare them with conventional thermal curing processes. In addition, pattern images will be observed to examine the feasibility of using e-beam direct patterning.

5.2 Experimental procedures

The substrates used in this study were 150 mm p-type (11-25 Ω-cm) single crystal silicon wafers with a (100) orientation. Before film deposition, they were boiled in $H_2SO_4+H_2O_2$ at 120 ℃ for 20 minutes to remove particles on surface. These wafers were coated with a low-k MSZ precursor solution diluted by its solvent propylene glycol monomethyl ether acetate (PGMEA) on a model 100CB spin coater. The recipe of coater was set at a spin speed of 2000 rmp for 30 sec for each sample. Then the as-spun wafers were followed by a series of thermal baking steps, sequentially on a hot plate at 150 ^{o}C and 280 ^{o}C for 3 min. The resulting wafers were then given a hydration treatment. The treatments were performed in a clean room for 48 hours. During the period of time, the precursor structure of MSZ films is transformed to MSQ-like structure through hydrolysis and condensation processes, which has been described in chapter 2. Then, it was followed that the resultant wafers (as-reacted wafers) were transferred to a Leica Weprint200 stepper to carry out a curing process.

The e-beam energy was 40 KeV with beam size of 20 nm. The doses of e-beam exposure were chosen with 100 to 800 uC/cm^2. As for the pattern formation of MSZ lines, as-reacted MSZ films were exposed with e-beam according to desire pattern layout. After e-beam exposure, the resulted wafers were developed in an aqueous solution consisting of 10 % 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 optical microscopy (OM) and scanning electron microscope (SEM) images to evaluate the feasibility of e-beam direct patterning on MSZ films. Furthermore, a furnace annealing process (at 400 ℃, 1 hour) was performed on the e-beam exposed wafers to enhance MSZ dielectric properties. On the other hand, the control samples were also fabricated according to a typical commercial recipe, by prebaking as-spun MSZ films at 150 ^{o}C and 280 ^{o}C for 3 min respectively, followed by hydration reaction in clean room, and followed by thermal curing in a furnace at 400 ^{o}C for 1 hour. After okay, Al electrodes were evaporated on the front surface of the films and backside of the substrate to complete the metal-insulator-semiconductor (MIS) device. The thickness of all MSZ films in this experiment was performed by an n&k 1200 analyzer by light interference effects in the films. Infrared spectrometry was performed from 4000 to 400 cm^{-1} using a Fourier transform infrared (FTIR) spectrometer calibrated to an unprocessed wafer, for determining the chemical structure of MSZ films after e-beam exposure. Dielectric constant measurements were conducted using a Keithley Model 82 CV analyzer. The area of gate electrode was 0.00528 cm^2 for C-V analysis. The leakage current (I-V) characteristics of dielectric were measured using a HP4156 electrical meter.

5.3 Results and discussions

Figure 5-1 presents the thickness variation of e-beam exposed MSZ films with different doses. It was found that the thickness of MSZ films was gradually decreased with the increase of e-beam exposed doses. The possible reason is that some solvent such as moisture and residual PGMEA were desorbed due to the energy of e-beam during the e-beam exposure process. Figure 5-2 shows the FTIR spectra of e-beam exposed MSZ films with different doses. After the e-beam exposure, it was found that the Si-O network bond (at near 1030 cm^{-1}) of e-beam exposed MSZ films was increased slightly in FTIR spectra. Meanwhile, the Si-OH bonds (at near 3400 cm^{-1}) decreased gradually with the increase of e-beam exposed doses. This result implies that the Si-O-Si three-dimensional network structure of MSZ film was formed in virtue of the partial curing by e-beam exposure. Moreover, the decrease of Si-OH bonds after e-beam exposure in FTIR spectra is consistent with the result of decrease of thickness after e-beam exposure. Figure 5-3 shows the leakage current of e-beam exposed MSZ film as compared to that of traditional furnace cured one. Unfortunately, the leakage current densities of e-beam exposed MSZ films are breakdown no matter what doses were applied. Moreover, the dielectric constant of e-beam exposed MSZ all can not be measured by C-V analyzer. Based on the results of electrical measurement, we deduce that the complete three-dimensional structure was not obtained by e-beam exposure. Therefore, there were many defects or leakage paths existed in the e-beam exposed MSZ films, which would cause the large leakage current. In order to enhance the dielectric properties of e-beam exposed MSZ films, we tried transferring these wafers to a furnace for further thermal annealing. Figure 5-4 shows the FTIR spectra of e-beam exposed MSZ with different doses after thermal annealing. The Si-OH groups of e-beam exposed MSZ film disappeared obviously after thermal annealing process. Furthermore, the functional groups of e-beam exposed MSZ films such as Si-O network-like peak, Si-CH_3 peak, and C-H peak etc. were all kept in high level the same as that of furnace-cured MSZ films. This indicates that the complete three-dimensional structure will be formed after thermal annealing for e-beam exposed MSZ films. The electrical properties of e-beam exposed MSZ film with different doses after thermal annealing is shown in Fig. 5-5. The leakage current of all e-beam exposed MSZ films are improved to no more one order of magnitude than that of furnace-cured MSZ one. Nevertheless, the leakage current of e-beam exposed MSZ films increased with the increase of e-beam exposed doses. This possible reason is attributed to the defect generated from the e-beam exposure. The more doses is exposed, the more defect will be generated, which can not be recovered even after the thermal annealing process. On the other hand, the dielectric constants of e-beam exposed MSZ films are similar to furnace cured MSZ films after thermal annealing process. As for the pattern formation, the transfer curve of e-beam exposed MSZ films with different doses after 10 % wt TMAH development process is shown in Fig. 5-6 to evaluate the possible dosage for e-beam direct patterning on MSZ films. The sensitivity of MSZ film for e-beam lithography was about 500 uC/ cm^2, which is defined as the threshold doses of e-beam exposure that can make 90 % thickness of e-beam exposed MSZ remain after development process. According to the results, we applied the e-beam exposed doses of 500 uC /cm^2 to as-hydrated low-k MSZ and followed by 10 % wt TMAH development to directly pattern the low-k MSZ film. As a result, the clear pattern of single line of e-beam exposed MSZ film after development can be observed by optical image in Fig. 5-7. Moreover, the cross section image of dense pattern lines of e-beam exposed MSZ film with 500 uC/ cm^2 after development is also shown in Fig. 5-8. The dimension of the pattern line is about 120 nm. Although the perfect patterning resolution is still required to improve, it is believe that this can be fine-tuned by varying the e-beam exposure doses and the development condition such as TMAH concentration, development time, and development concentration. After the pattern is finished, the electrical dielectric characteristics of MSZ can be recovered by the post-exposure furnace annealing.

5.4 Conclusion

In summary, e-beam lithography for low-k MSZ as inter-metal dielectric (IMD) has been investigated in this chapter. Materials analysis and electrical properties show e-beam exposure tends to give the as-hydrated MSZ energy to partial cross-linking the matrix material into three-dimensional structure. However, the energy of e-beam is not enough to form the perfect three-dimensional structure of MSZ and remain many defect and leakage paths in bulk MSZ. This makes both leakage current and dielectric constant of MSZ film breakdown. Nevertheless, an additional post-exposure furnace annealing can make the electrical properties of e-beam exposed MSZ recover to be similar to that of traditional furnace cured one.

In this work, the sensitivity of e-beam exposure on MSZ film was about 500 uC /cm^2. Although the pattern of e-beam exposed MSZ film can be obtained in this study, an additional study is required to perfect the patterning resolution. It is believe that the method can be incorporated into next generation of multilevel interconnect systems as the devices shrink into nano-scale regimes.