Mat. Res. Soc. Symp. Proc. Vol. 612. © 2000 Materials Research Society

# STUDY OF DRY PHOTORESIST STRIPPING PROCESSES FOR HYDROGEN SILSESQUIOXANE THIN FILMS

HUEY-CHIANG LIOU[1], JERRY DUEL[1], VICTOR FINCH[1], QINGYUAN HAN[2], PALANI SAKTHIVEL[2], AND RICKY RUFFIN[2]
[1]Semiconductor Fabrication Materials, Dow Corning Corporation, Midland, Michigan 48686-0994; [2]Fusion System Division, Semiconductor Equipment Operation, Eaton Corporation, Rockville, MD 20855-2798

## ABSTRACT

The impact of dry stripping process chemistries on the selective removal DUV photoresist (PR) in the presence of hydrogen silsesquioxane (HSQ) have been studied along with HSQ film properties in order to develop a new, effective process to minimize changes in HSQ during the PR stripping processes. The results show that oxygen-free gas mixtures, specifically $H_2/N_2$ gas mixtures, have the best combination of PR:HSQ ash selectivity and minimized changes in HSQ films. However, gas mixtures containing $CF_4$ or $O_2$ greatly reduce PR/HSQ ash selectivity. The process temperature is another parameter that strongly influences ash selectivity. While the higher ash temperature greatly enhances selectivity in oxygen-free gas mixtures, the ash selectivity is only marginally enhanced with increasing ash temperature in the presence of $O_2$. Furthermore, the k-value of HSQ suffers in the presence of $O_2$ due to the oxidization of HSQ films. The data also shows that lower pressure will help to increase ash selectivity. In this study, processes have been demonstrated, which yield a PR:HSQ selectivity greater than 150, while maintaining the dielectric constant of HSQ at 2.8.

## INTRODUCTION

As the minimum geometry of ultra large scale integrated (ULSI) devices moves toward below 0.2 μm, implementation of low k dielectric materials in the fabrication of these devices is needed to reduce the intraline capacitance between metal lines and to increase the signal propagation speed [1]. Among all available low k materials, hydrogen silsesquioxane (HSQ) has attracted attention in the semiconductor industry due to its lower dielectric constant ($k \leq 3.0$, after cure), ease of processing, excellent gap fill and excellent planarization capabilities. In addition, HSQ has been used in production for 0.35-0.5 μm devices [2]. However, one of the challenges in applying HSQ in < 0.20 μm devices is the photoresist (PR) stripping step due to possible interactions between stripping chemistries and HSQ films and, therefore, change its dielectric properties.

The general chemical composition of HSQ before curing is $(HSiO_{3/2})_n$ and a representative molecular structure is shown in Figure 1. From the infrared spectrum, it has been shown that HSQ consists of random network linkages based on the eight-corner $H_8Si_8O_{12}$ structure [3]. When thermally processed, the bonds in HSQ break and its molecular structure is rearranged/redistributed into an amorphous film with more network bonding.

It has been known that HSQ films are sensitive to the amine based PR stripper used in wet PR stripping processes and to $O_2$ used in the traditional $O_2$ downstream plasma stripping processes [4-5]. The HSQ film shrinkage after the PR stripping step can lead to via bowing and higher via resistance. Therefore, for applications in deep submicron devices, there is a need to

develop a better dry PR stripping process for HSQ without changing the HSQ film properties. In this study, the impact of gas mixture, process pressure, and process temperature for photo resist strip have been investigated.

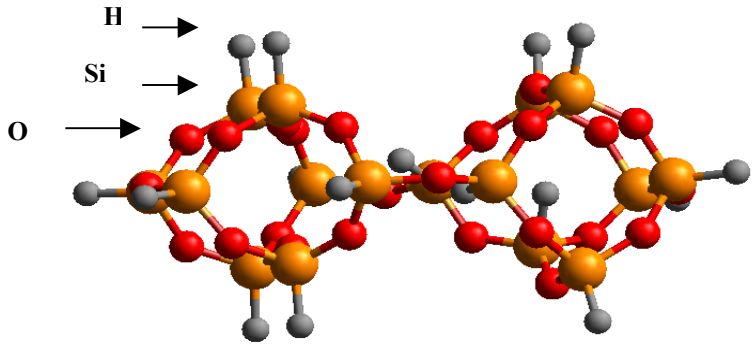


Figure 1. Simulation of HSQ molecule.

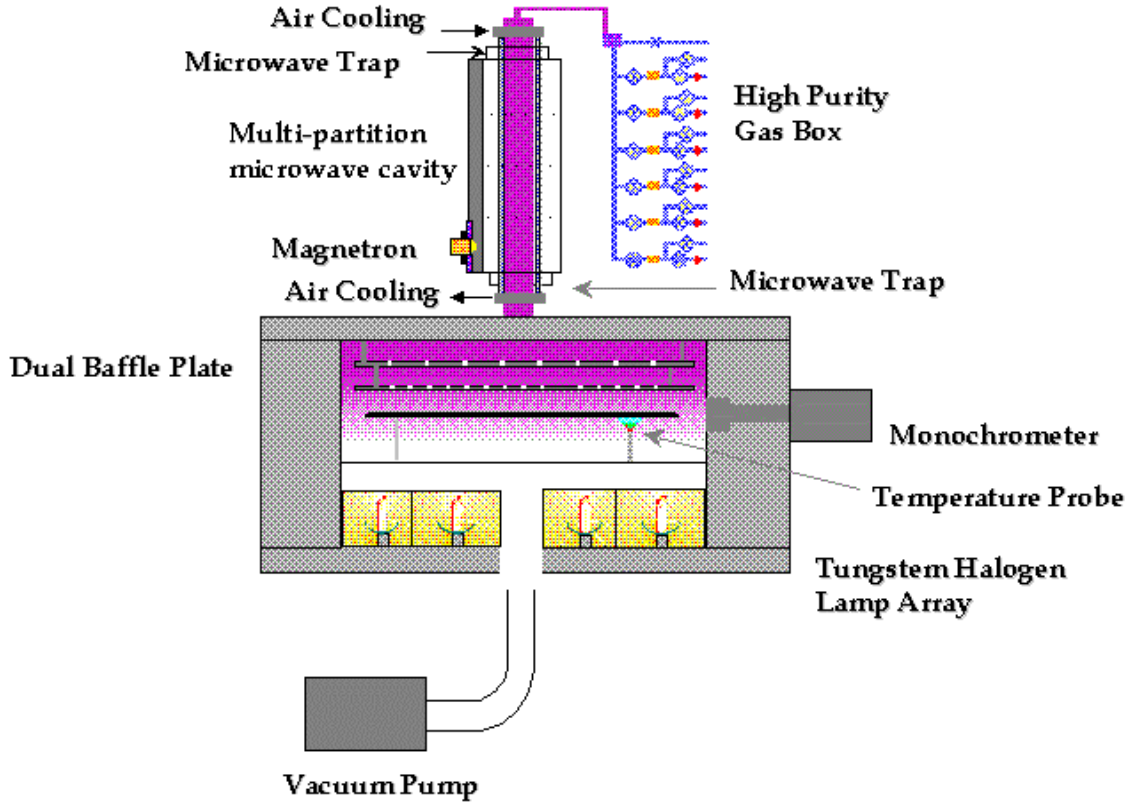


Figure 2. Fusion Gemini ES plasma Asher.

## EXPERIMENTAL

HSQ films with an approximate thickness of 4000 Å were prepared by spin-coating Dow Corning FOx®-15 solution onto Si wafers. This was followed by heating on three hot plates at 150°C, 200°C, and 350°C for one min. each. The films were then cured in a quartz furnace at different temperatures and different gas ambients as listed in Table 1. 8500Å of DUV

photoresist (PR) (Shipely, UV-6.08) were processed on a Flexfab spin-coater and baked at 120°C for one min. These PR wafers and HSQ wafers were exposed to the same plasma conditions to calculate the PR:HSQ selectivity. The ashing process was performed in a downstream microwave plasma asher (Eaton Corp, Fusion System Division, Model #Gemini ES) as shown in Figure 2. The ash conditions are listed in Table 1. Wafer #12 is the control wafer, which was not treated by ashing. The thickness and the refractive index (R.I.) of the HSQ films before and after ashing were measured by a Tyger Thin Film Analyzer. The Si-H bond density remaining in the HSQ films was measured by Transmission Fourier Transform Infrared (FTIR) spectroscopy. The dielectric constant of the HSQ films was evaluated at 1 MHz using metal-insulator-semiconductor capacitors with Al gate electrodes

Table 1. The ash conditions for HSQ and photoresist.

| Run # | Time (seconds) | Pressure (torr) | Temperature (°C) | Process Gas |
|---|---|---|---|---|
| 1 | 60 | Low | 270 | GasMix 1 |
| 2 | 60 | High | 270 | GasMix 1 |
| 3 | 60 | Low | 270 | GasMix 2 |
| 4 | 60 | Low | 200 | GasMix 2 |
| 5 | 90 | Low | 80 | GasMix 3 |
| 6 | 30 | Low | 140 | GasMix 3 |
| 7 | 30 | Low | 120 | GasMix 3 |
| 8 | 60 | Low | 100 | GasMix 3 |
| 9 | 40 | Low | 140 | GasMix 4 |
| 10 | 20 | Low | 200 | GasMix 4 |
| 11 | Same as run # 10, with 60-second pre-treatment* | | | |
| 12 | Control Wafer | | | |

GasMix 1: $H_2/N_2$
GasMix 2: $H_2/N_2/CF_4$
GasMix 3: $H_2$ rich, $H_2/N_2/CF_4/O_2$
GasMix 4: $O_2$ rich, $H_2/N_2/CF_4/O_2$
*Pretreatment under $H_2/N_2$ plasma

**Results and Discussions**

The thickness shrinkage rate and the refractive index (R.I.) of HSQ films after ashing are shown in Figures 3 and 4, respectively. In general, HSQ films ashed in GasMix 1 and GasMix 2 had relatively smaller thickness changes compared to those ashed in GasMix 3 and GasMix 4. The data shows that HSQ films ashed in $H_2/N_2$ GasMix 1 have negligible changes in thickness and R.I. compared to control wafer. The data also shows that HSQ films ashed in GasMix 3 (runs # 5-8) have larger thickness loss compared to the control. However, the R.I. of the HSQ films is lower compared to the control, which may be due to these HSQ being exposed to the $CF_4$ plasma and a reduction of the dipolar polarization through fluorine incorporation. Under the GasMix 3 condition, HSQ films were etched away by the plasma. HSQ films ashed in GasMix 4 (runs # 9-11) show slightly smaller thickness loss compare to those ashed in the GasMix 3 but show a dramatic increase in R. I. to higher than 1.4. The results suggest that ashing in $O_2$ rich GasMix 4 may oxidize the HSQ film. Apparently, $O_2$ is detrimental to the HSQ films ashed in both GasMix 3 and GasMix 4 ambients. However, it has been reported that the change of the

HSQ films in the via sidewall is expected to be much less than the blank films due to less plasma exposure and the vertical directionality of plasma components [6].

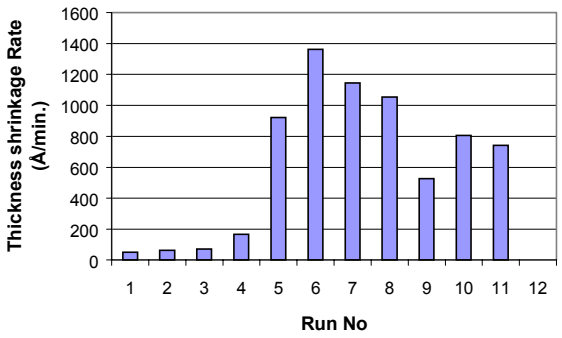


Figure 3. Thickness shrinkage rate of HSQ films under different conditions.

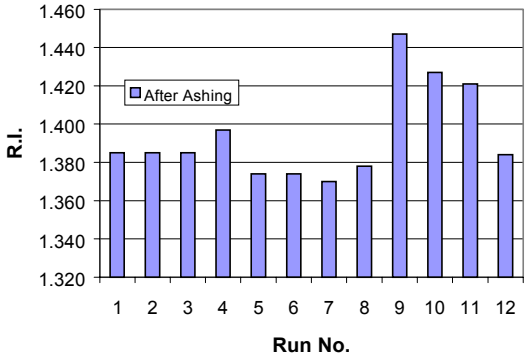


Figure 4. R.I. of HSQ films after ashing process.

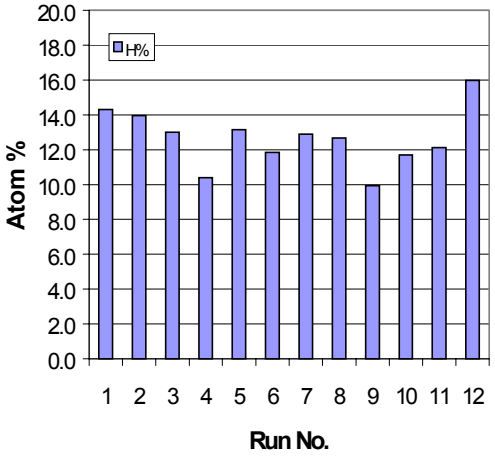


Figure 5. Atomic percent of H in HSQ films after ashing.

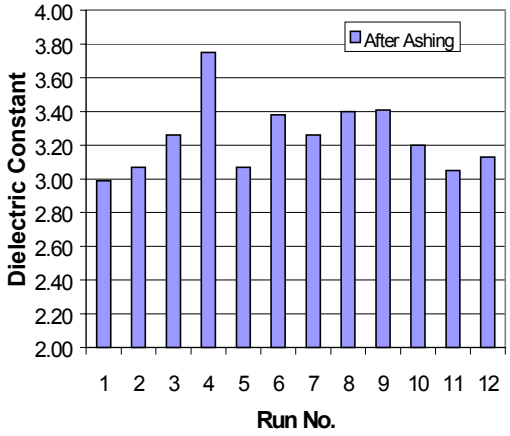


Figure 6. Dielectric constant of HSQ films after ashing.

HSQ film cured in 400°C $N_2$ ambient contains approximately 16 % H, 31% Si and 63% O atoms [3,7]. The H percentage in HSQ films after ashing is shown in Figure 5. HSQ films can lose a certain percentage of H atoms if the Si-H bonds are broken during the PR stripping process. The HSQ film processed in GasMix 1 has the lowest H loss. In general, there is less H loss if HSQ is exposed to GasMix 3 rather than in GasMix 4. This is speculated to be due to the $O_2$ rich ambient in GaxMix 4 which expedites the oxidation of HSQ films and leads to larger amount of H loss. However, there are large variations in H loss in GasMix 2, 3, and 4 depending on other process parameters.

The dielectric constant of HSQ films after ashing is shown in Figure 6. It shows that the HSQ film exposed to GasMix 1 has a lower k value than other films. It has been reported that the k value of HSQ film can be maintained when treated by $H_2$ plasma [8]. Therefore, $H_2/N_2$ GasMix will help to maintain the k value for HSQ films during ashing processes. However, the k value of HSQ films will increase due to the generation of –OH group when HSQ is treated by

$O_2$ plasma [9]. For HSQ exposed to GasMix 3, run # 5 has lower k value than other films. It indicates that a lower ash temperature should be used to maintain the k value of HSQ film if $O_2$ is present in the gas mixtures, such as GasMix 3 and 4. The k value of run # 11 also showed little change compared to the control. Since the k of HSQ can be stabilized by $H_2$ plasma treatment, the k value of HSQ films with $H_2/N_2$ plasma pre-treatment remains low compared to films run without pretreatment. Run #4 has the highest k value due to large percentage of H loss in the HSQ film after ashing.

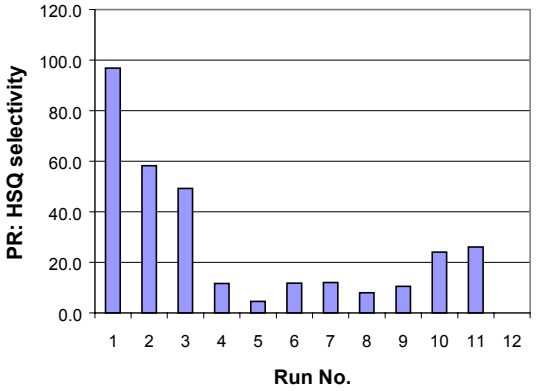


Figure 7. The PR:HSQ ash selectivity.

The PR: HSQ ash selectivity is shown in Figure 7. Among all the GasMix ambients used in the ashing processes, $H_2/N_2$ GasMix 1 shows ash selectivity close to 100:1 with minimal impact on the film thickness, R.I., and k value. Comparing the PR:HSQ ash selectivity between run # 1 and run #3, shows that adding $CF_4$ into the $H_2/N_2$ mixtures will reduce the ash selectivity. All HSQ film treated in GasMix 3 and GasMix 4 have ash selectivity less than 30, which can not be used in production. HSQ films treated in GasMix 3 have more film etched than in GasMix 4. However, there was more oxidization of HSQ films treated in GasMix 4.

The impact of pressure during ash on HSQ can be observed in runs #1 and #2. Lower ash pressure leads to slightly lower H loss and K for HSQ films but much larger PR/HSQ selectivity. This is mostly due to the enhanced PR strip rate at lower pressures.

The impact of ash temperature for GasMix 2 can be observed from runs #3 and #4. There is more HSQ thickness loss when using a lower ash temperature. It has been reported that the etch rate of PR increases with temperature [8]. With higher loss of H, the R.I. of run # 4 is larger than run #3. In addition, the dielectric constant of run # 4 is 0.5 higher than run # 3. The PR:HSQ ash selectivity is higher for run #3, which has higher ash temperature.

However, the HSQ thickness shrinkage rate increases with increasing the ash temperature in an $O_2$ environment. The H% loss also increases with increasing the ash temperature and the dielectric constant of HSQ films follows the same trend. In this case, the PR:HSQ selectivity is very low and it shows that higher temperature has slightly higher selectivity. The same phenomena were observed on tests # 9 and #10. Higher ash temperature will lead to larger loss of HSQ films and H %, which results in a higher dielectric constant.

One interesting finding is that a 60-second $H_2/N_2$ pretreatment will slightly improve the resistance of HSQ in an $O_2$ plasma environment and the PR/HSQ selectivity also increases. It is

consistent with Liu's results on HSQ that $H_2/N_2$ plasma treatment can enhance the resistance of HSQ to $O_2$ plasma processes [7].

Finally, optimization of the recipes using GasMix 1 and GasMix 2 for HSQ has been explored. The results shows that the PR:HSQ selectivity is greater than 150 while the k value of HSQ remained less than 2.9 as listed in Table 2.

Table 2 Optimized ash processes for HSQ films

| GasMix | Pressure | Ash Time | HSQ loss | R.I. | SiH remaining | K | PR/HSQ selectivity |
|---|---|---|---|---|---|---|---|
| 1 | Low | 30 sec. | < 30 Å | 1.376 | > 72 % | 2.8 | > 150 |
| 2 | Low | 30 sec. | < 50Å | 1.376 | > 72 % | 2.8 | > 150 |

## SUMMARY

The impact of gas mixture, process pressure, and process temperature on PR strip over HSQ films has been investigated in this study. The results show that the $H_2/N_2$ gas mixtures have better PR:HSQ ash selectivity with less changes in HSQ films compared to other gas mixtures. In addition, adding $CF_4$ to the $H_2/N_2$ gas mixtures can reduce the PR:HSQ ash selectivity. Gas mixtures containing $O_2$ react with the SiH bonds of the HSQ films and greatly reduce PR:HSQ ash selectivity. The ash temperature has strong impact on the ash selectivity. It is found that higher ashing temperature enhances the ashing selectivity in gas mixtures without the presence of $O_2$, while maintaining the k value. On the other hand, a slight enhancement in selectivity was observed by increasing the ashing temperature in $O_2$ gas mixtures but it compromises the k value, due to the oxidization of HSQ films. The data also shows that lower ash pressure will help to increase the ash selectivity. Finally, optimized processes have been demonstrated to have a PR:HSQ selectivity greater than 150 while the k of HSQ is less than 2.9.

## REFERENCES

1. The National Technology Roadmap for Semiconductors, Semiconductor Industry Association, San Jose, CA, 1997.
2. S. P. Jeng, K. Taylor, T, Seha, M. Chang, J. Fattaruso, and R. Havemann, Proceedings of VLSI symposium, Kyoto, Japan, 1995, pp. 15-21.
3. M. Loboda, C. M. Grove, R. F. Schneider, J. Electrochem. Soc., **145**, 1998, p. 2861.
4. H. Meynen, R. Uttecht, T. Gao, M. V. Hove, S. Vanhaelemeersch, and K Maex, Proceeding of 3rd Int. Symp. on low and high dielectric constant materials, San Diego, CA, May 5, 1998.
5. D. Louis, E. Lajoinie, F. Pires, W. M. Lee, and D. Holmes, Microelectronic Engineering, 41/42, 1998, p. 415-418.
6. T. Gao, B. Coenegrachts, J .Waeterloos, G. Beyer, M. Meynen, M. Van Hove, and K. Maex, Proceedings of 2nd IITC, San Francisco, CA, 1998, P. 53.
7. H. C. Liou, E. Dehate, J. Duel, and F. Dall, submitted to The Journal of Electrochemical Society.
8. P. T. Liu, T. C. Chang, S. M. Sze, F. M. Pan, Y. J. Mei, W. F. Wu, M. S. Tsai, B. T. Dai, C. Y. Chang, F. Y. Shih, and D. H. Huang, Thin Solid Films, 332, 1998, pp. 345-350.
9. P. Gillespie, R. Mohondro, M. A. Jones, W. L. Krisa, and T. Romig, Semiconductor International, July 1997, p. 161.