Improvement of Post-Chemical Mechanical Planarization Characteristics on Organic Low *k* Methylsilsesquioxane as Intermetal Dielectric

Po-Tsun Liu,[a,*] Ting-Chang Chang,[a,b,,z] Ming-Chih Huang,[c] Ya-Liang Yang,[a] Yi-Shian Mor,[c]**
M. S. Tsai,[a,] H. Chung,[d] J. Hou,[d] and Simon-M. Sze [a,c]**

[a]*National Nano Device Laboratory, HsinChu 300, Taiwan*
[b]*Department of Physics, National Sun Yat-Sen University, Taiwan*
[c]*Department of Electronics Engineering and Institute of Electronics, National Chiao Tung University, Taiwan*
[d]*Allied Signal Incorporated, Taiwan*

This work has investigated the electrical and material characteristics of post-chemical mechanical planarization (CMP) methyl-silsesquioxane (MSQ). Experimental results have shown that the dielectric properties of low *k* MSQ deteriorate after the CMP process. However, by applying H_2-plasma post-treatment, the degraded characteristics can be restored to a similar state as that of a pre-CMP MSQ film. Material and electrical analyses were performed to elucidate the detailed mechanisms of H_2-plasma treatment on post-CMP MSQ. H_2-plasma treatment provides active hydrogen radicals to passivate the dangling bonds exposed in the MSQ after the CMP process. The hydrogen-rich passivation layer is hydrophobic and effectively prevents further moisture uptake. Therefore, a degradation-free CMP process can be achieved employing H_2-plasma treatment.
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As integrated circuit dimensions continue to shrink, interconnect resistance $\times$ capacitance (RC) delay becomes an increasingly serious problem. Fabrication of interconnect structures using copper wiring and low permittivity (low *k*) material to replace the traditional Al and SiO_2 interconnect technology is in high demand.[1,2] Among various low *k* materials, the organosilicates offer many properties of silica (SiO_2) such as hardness and thermal and dimensional stability. Methylsilsesquioxane (MSQ) represents an important member of this family. It exhibits a relatively low *k* value (*k* = 2.6-2.8), is intrinsically hydrophobic, and shows reasonable mechanical hardness and exceptional thermal stability (in excess of 450°C).[3-5] For these reasons, MSQ represents an excellent candidate as an intermetal dielectric (IMD) for the multilevel interconnect architecture. However, there still are several issues when implementing MSQ into process integration. The greatest concern for low *k* polymer application is the "poisoned-via" issue.[6] Consequently, the etchback process has been extensively performed to avoid the problem of "poisoned-via." Surface planarization is a key technology during the manufacture of multilevel interconnects. The chemical mechanical planarization (CMP) process is satisfactory for the requirement of global topography planarization and etchback technology.[7,8] An advantage of CMP spin-on-glass (SOG) films is that it is easy to control the final IMD thickness, because by capping oxides of different thicknesses after polishing SOG one can reach the target IMD thickness.[9] In the development of CMP low *k* dielectrics,[10-12] Forester *et al.* found that the polish rate of alkyl siloxane-based SOG was lower than that of plasma-enhanced chemical vapor deposition (PECVD) oxide or thermal oxide using conventional silica-based slurry only.[12] The polish rate of alkyl siloxane-based SOG is dependent on the organic content when using conventional oxide slurries. A higher Si-R/Si-O ratio in the SOG films induces a lower hydration reaction rate, leading to a lower polish rate. Several reports[13,14] indicated that the use of new alkaline cerium oxide-based slurry and the introduction of additives[15] can greatly improve the removal rate for organic spin-on materials. However, much experimental data is needed to qualify such new consumables before adopting them into production. In addition, CMP includes kinetic mechanical abrasion and chemical etching reactions; it can cause destructive changes in the characteristics of the low *k* material. Therefore, the investigation of post-CMP characteristics such as electrical performance and desorption of con-

stitution water should be emphasized much more for optimum CMP of low *k* materials.

In this work, we have presented the characteristics of organic low *k* MSQ after the CMP process. The polishing of MSQ with conventional silica-based slurry is discussed first. Instead of developing new chemical slurries, tetramethylammonium hydroxide (TMAH) was added to commonly used silica-based slurries. In addition, its effects on the polish process were investigated comprehensively. Finally, an H_2-plasma technique was implemented as a post-treatment for the CMP of low *k* MSQ.

Experimental

Unpatterned silicon wafers were coated with a single layer of MSQ film, and baked sequentially on a hot plate at 180°C for 2 min and at 250°C for 1 min. The resulting wafers were furnace cured at 400°C for 30 min. The CMP process was applied to the as-cured MSQ film. The CMP experiment was carried out on an IPEC/Westech 372M CMP processor. The wafer was mounted on a template assembly for a single 6 in. wafer during the polishing experiment. The most commonly used slurry for SiO_2 polishing is silica with potassium hydroxide (KOH) aqueous solution, called CABOT SS-25 slurry. Since low *k* MSQ is one group of siloxane-based SOG films, in our work, SS-25 slurry was thereby used for the MSQ polishing. In parallel, work was developed to increase the CMP removal rate and uniformity of MSQ in silica-based slurry. The addition of 0.1-0.2 M TMAH aqueous solution to commercial SS-25 slurry causes an increase in the CMP removal rate. The polishing parameters, such as down force, back pressure, platen and carrier rotation speeds, and slurry flow rate, were set to be 3-9 psi, 2-9 psi, 50-80 rpm, 60-80 rpm, and 150 mL/min, respectively. The thickness and refractive index of all samples before and after CMP polishing were measured using an n&k 1200 analyzer by means of light interference effects in MSQ film.

Subsequently, the polished wafers were transferred to a PECVD chamber for H_2-plasma post-treatment. The H_2-plasma was operated at a pressure of 300 mTorr and with a hydrogen gas flow rate of 300 standard cubic centimeters per minute. A radio frequency power of 110 W, which established the hydrogen plasma, was applied to the upper electrode, and the wafers were placed on the bottom by the grounded electrode, which can be rotated for improving uniformity, at a substrate temperature up to 300°C. The structural properties of the MSQ films were studied using Fourier transform infrared spectroscopy (FTIRS). The surface morphologies of the polished films were investigated by atomic force microscopy (AFM). Thermal de-

sorption spectroscopy (TDS) was carried out to monitor the desorbed elements from post-CMP MSQ films during the high temperature process. Electrical characterizations of post-CMP MSQ films were performed on the metal-insulator-semiconductor (MIS) capacitor with metallic aluminum deposition as the top electrode. Leakage current-voltage and capacitance-voltage characteristics were also used to analyze the leakage current behavior and measure the dielectric constants of post-CMP MSQ films, respectively.

Results and Discussion

First, the CMP of organic MSQ using commercial silica-based slurry SS-25 is discussed. Figure 1 illustrates the variation of removed thickness *vs.* polish time. The CMP removal rate of MSQ with 22% organic content is about 100 Å/min. A large fluctuation in the film thickness of MSQ is also observed. This indicates that the polishing rate of organic MSQ with commonly used oxide slurries is rather low, which thereby leads to poor surface topography and nonuniform film thickness. Generally, an increase in the down force and platen speed can enhance the hydration reaction of Si–O bonds and accelerate CMP removal rate. However, in our case, the polishing rate of the organic MSQ film still remains low due to high chemical durability, even by increasing the down force and platen speed of CMP, as shown in Fig. 2. It can be regarded as a chemical-reaction-limited rather than a mechanical-reaction-limited process. This result is also consistent with the result of Forester *et al.*[12] that organic content in low *k* films inhibits the hydration reaction during the CMP process.

It is well known that only if both chemical and mechanical actions work simultaneously can a successful CMP process be achieved. To increase the polishing rate, TMAH was added to SS-25 slurry to enhance the hydration reaction between abrasive and organic components in the MSQ film. The resultant solution pH is in the range of 11-12, higher than that of SS-25 slurry alone (about 10.2-10.4). Figure 3 shows the removed thickness of CMP MSQ with and without TMAH additive, at the same polishing parameters. A higher CMP removal rate (about 1200 Å/min) is observed at the slurry with higher pH, which suggests that a more basic environment enhances the chemical alteration of the MSQ surface. In addition, the thickness fluctuation in the case of polishing MSQ using TMAH additive is slight compared to the CMP of MSQ with SS-25 slurry only. This
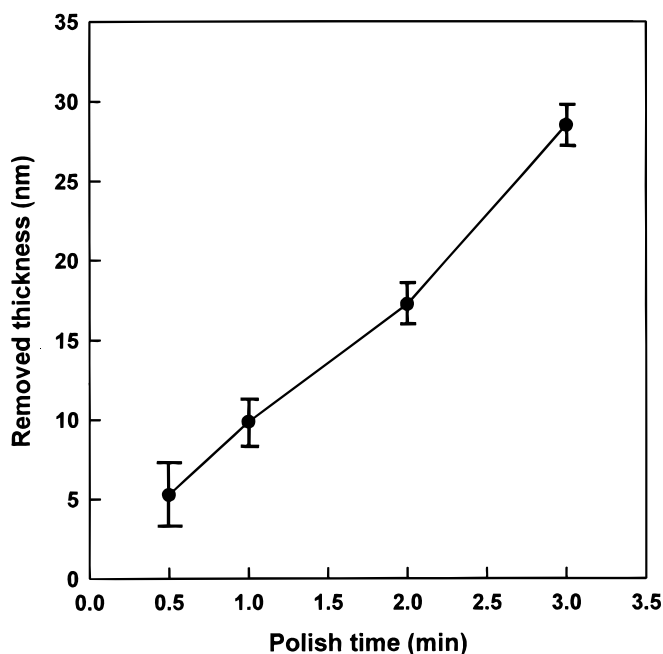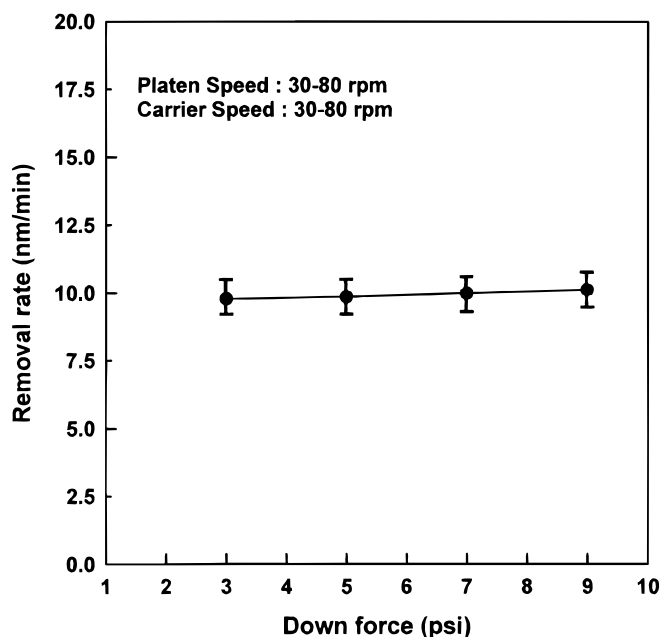
Figure 2. The relationship of CMP MSQ removal rate and down force.

is consistent with AFM observation. Figures 4a and b show the surface roughness of MSQ after the CMP process with and without TMAH additive, respectively. The surface roughness of polishing MSQ with TMAH additive is significantly less than that of CMP MSQ with SS-25 slurry only, implying a more uniform dissolution and removal occurring on the surface of organic MSQ. This CMP mechanism is simply described as follows. TMAH is a kind of surfactant that has both hydrophilic and hydrophobic groups in its molecular components. In aqueous solution, the ammonium hydroxide ion pairs adsorb on the hydrophobic MSQ surface, which results in the pH increasing locally on the surface. The hydration reaction between MSQ and TMAH is illustrated further in Fig. 5.[15] The addition of TMAH surfactant into SS-25 slurry is capable of initiating hydration reactions to break the siloxane bonds (*i.e.*, Si–O–Si net-
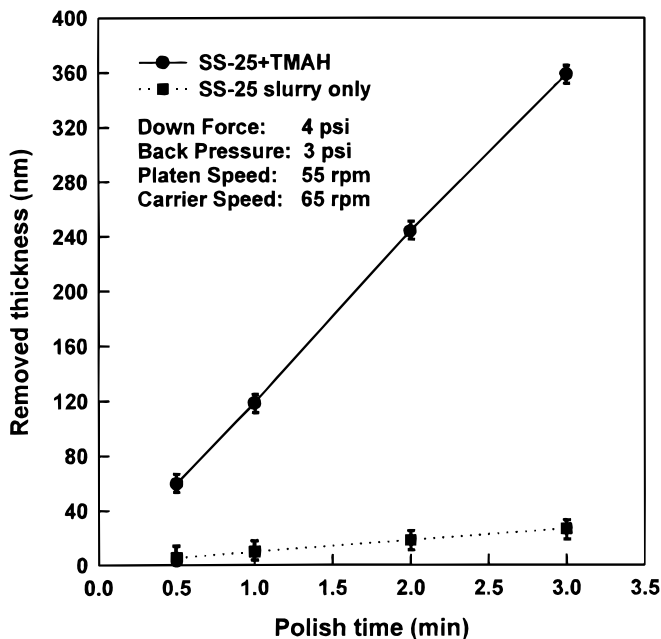
Figure 1. The variation in the removed thickness of CMP MSQ *vs.* polish time.

Figure 3. The removed thickness of CMP MSQ with and without TMAH additive at the same polishing parameters.

(a)

Image Rq = 0.490 nm
Image Ra = 0.396 nm

X 5.000 µm/div
Z 20.000 nm/div

(b)

Image Rq = 1.651 nm
Image Ra = 1.321 nm
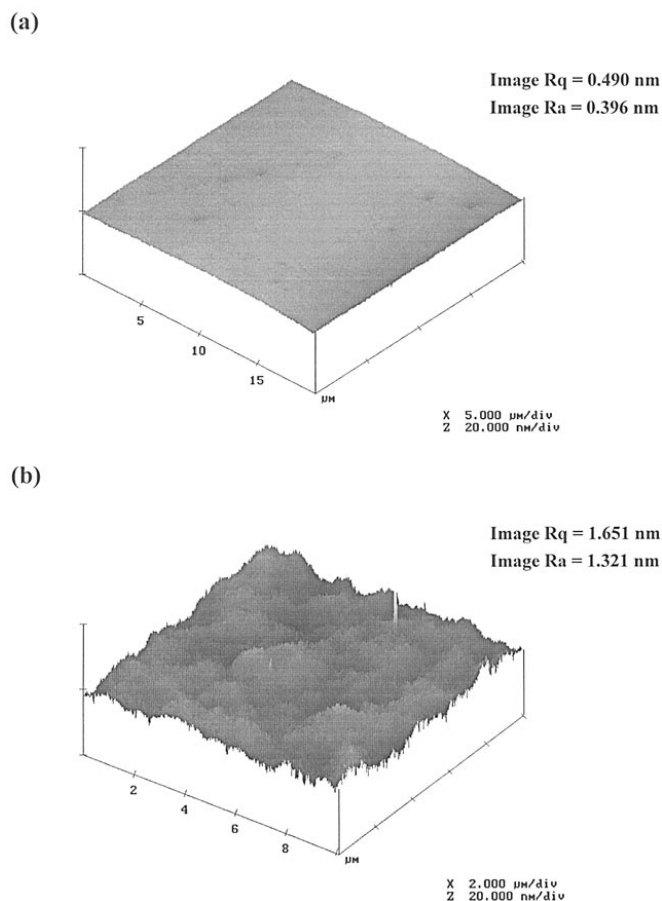
X 2.000 µm/div
Z 20.000 nm/div

Figure 4. AFM micrograph of polished MSQ surface. (a) CMP process with silicate-based SS-25 slurry and TMAH additive; (b) CMP process with silicate-based SS-25 slurry only.

work) in MSQ and helps slurry particles bond with MSQ through TMAH. Meanwhile, the mechanical force during the CMP process provides another energy to enhance moving the slurry particles away, which is associated with the breakdown of the backbone of MSQ. With the enhanced hydration reaction and the assistance of the proceeding mechanical event, a high-speed CMP removal rate of organic MSQ can be obtained.

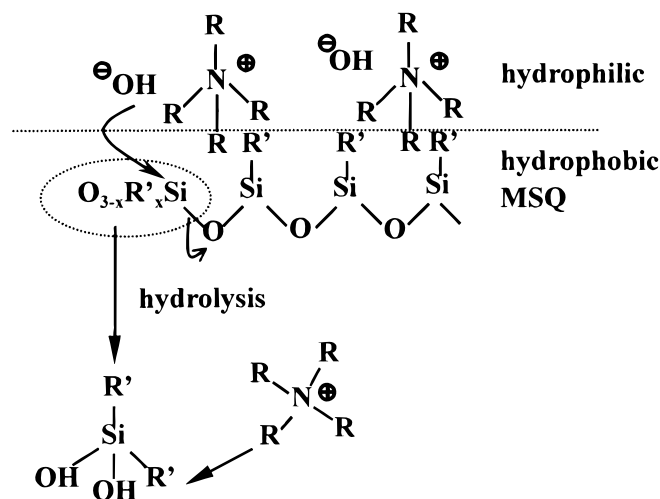Furthermore, the electrical characteristics of post-CMP MSQ were investigated to evaluate the impact of the CMP process on MSQ. Figures 6a and b show the leakage current and dielectric constant of MSQ after the CMP process with and without TMAH-containing slurry. The electrical properties of post-CMP MSQ are all degraded whether the MSQ films are polished with TMAH additive or not. The leakage current of post-CMP MSQ increased as much as one order of magnitude from that of pre-CMP MSQ. The dielectric constant of post-CMP MSQ increased from the as-cured value of 2.6 to 2.86 as well, as shown in Fig. 6b. In addition, both the leakage current and dielectric constant of post-CMP MSQ with TMAH-containing slurry increased slightly over that of CMP MSQ without TMAH additive. These degradations on electrical characteristics are due to damages from kinetic mechanical abrasion and slurry chemicals during the CMP process. The enhanced hydrolysis reaction of MSQ due to the addition of TMAH should be especially responsible for more degradation in electrical characteristics. This also offsets the partial advantage of using TMAH additive.
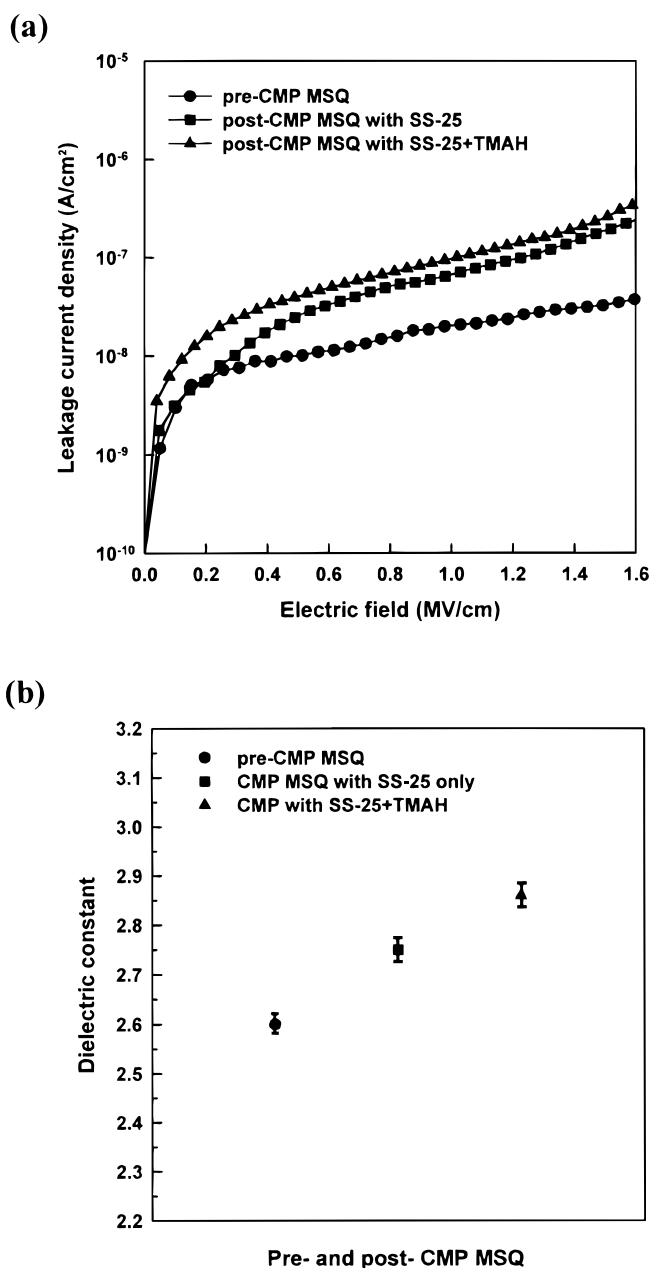
(a)

- pre-CMP MSQ
- post-CMP MSQ with SS-25
- post-CMP MSQ with SS-25+TMAH

Leakage current density (A/cm²)

Electric field (MV/cm)

(b)

- pre-CMP MSQ
- CMP MSQ with SS-25 only
- CMP with SS-25+TMAH

Dielectric constant

Pre- and post- CMP MSQ

Figure 5. The hydration reaction between organic MSQ and TMAH solution.

Figure 6. Dielectric properties of MSQ polished with and without additive TMAH. (a) Leakage current density of post-CMP MSQ films as a function of electric field; (b) dielectric constant of post-CMP MSQ films.

To address the issues for electrical degradations, we applied H_2-plasma post-treatment on post-CMP MSQ. Figures 7a and b show the leakage current density and dielectric constant of post-CMP MSQ treated with H_2-plasma for 3-9 min. Both the leakage current and dielectric constant of post-CMP MSQ obviously decrease and approach a state similar to that of pre-CMP, with increasing H_2-plasma treatment time. This indicates that the electrical degradations of low k dielectrics are effectively restored using H_2-plasma post-treatment. These significant improvements in the electrical characteristics of post-CMP MSQ can be interpreted by material analyses. Figure 8a shows FTIR spectra of post-CMP MSQ before and after H_2-plasma treatment. An enlargement of the 2400-2100 cm^{-1} region for Fig. 8a is shown in Fig. 8b. From Fig. 8a, it is first found that the intensities of the Si–C bond peak and C–H bond peak are slightly reduced in comparison with those of pre-CMP MSQ. Meanwhile, no

other bonds generate except the reduction of function groups. The destruction of functional bonds from mechanical abrasion and slurry chemicals during the CMP process leaves many dangling bonds in post-CMP MSQ. These dangling bonds are unstable sites in dielectrics, which tend to react with moisture at ambience and inevitably lead to increased leakage current and dielectric constant. This is also consistent with the electrical performance, as mentioned above. In contrast, the peak of Si–H bonds appears gradually, and the intensity increases with increasing H_2-plasma treatment time, as shown in Fig. 8b. The appearance of Si–H bonds is confirmed from H_2-plasma post-treatment. By applying H_2-plasma treatments, many active hydrogen radicals are generated and effectively passivate the dangling bonds either on the surface or in the bulk.[16] It is thought that a porous MSQ structure is helpful for the diffusion of hydrogen atoms with small volume. Consequently, the bulk signal of the Si–H peak is detected by FTIR. Since the formation of hydrogen-rich pas-
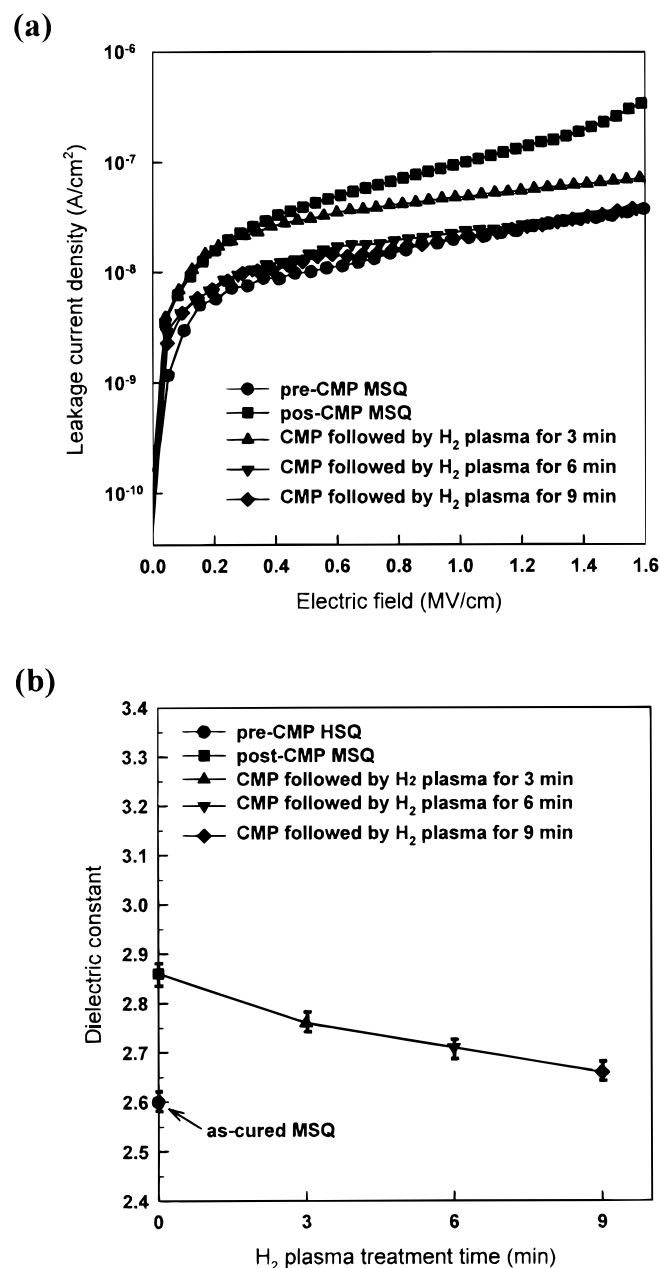

(a)

(b)

Figure 7. Dielectric properties of post-CMP MSQ films with H_2-plasma post-treatment. (a) Leakage current density of H_2-plasma-treated MSQ films as a function of electric field; (b) dielectric constant of H_2-plasma-treated MSQ films as a function of H_2-plasma treatment time.
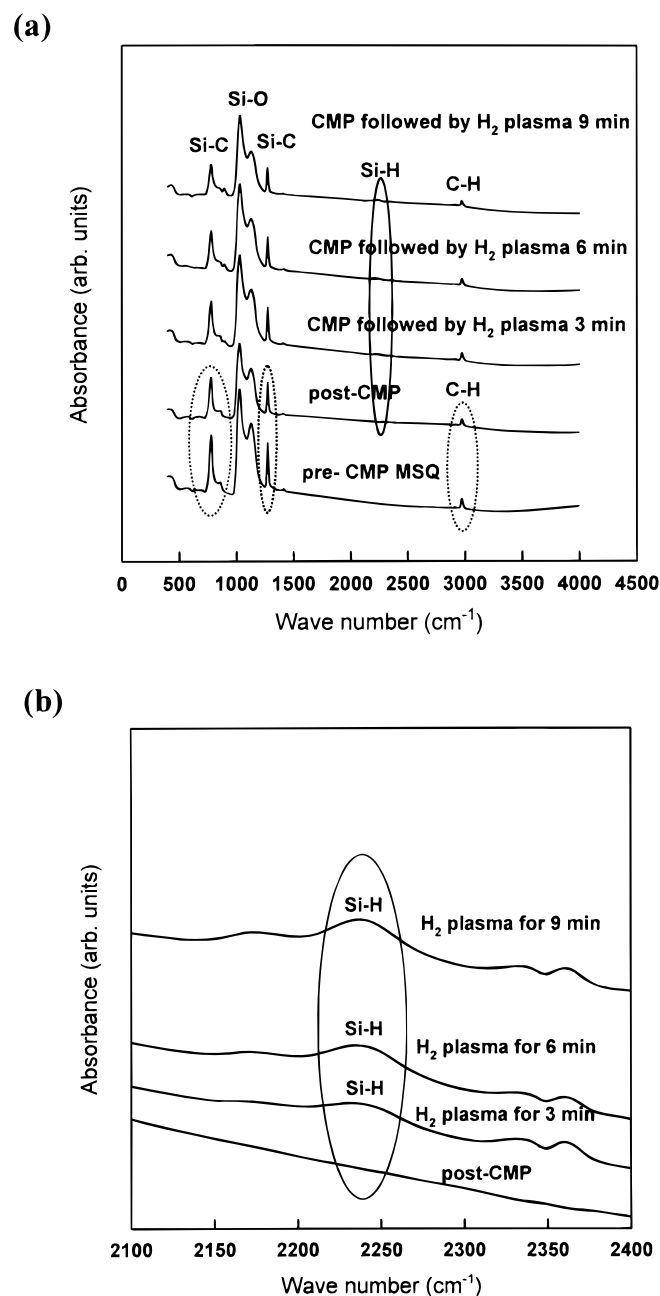

(a)

(b)

Figure 8. (a) FTIR spectra of post-CMP MSQ films with H_2-plasma treatment; (b) an enlargement of 2400-2100 cm^{-1} region.
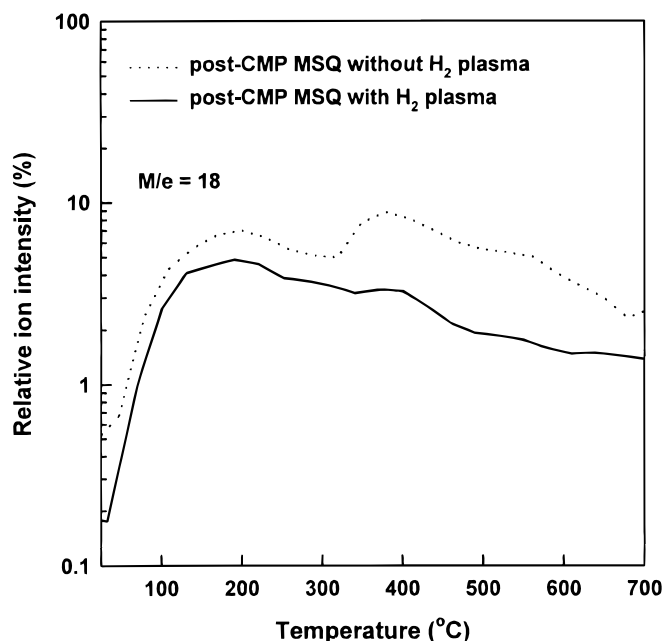
Figure 9. Temperature dependence of moisture desorption from post-CMP MSQ films.

sivation makes post-CMP MSQ surfaces hydrophobic,[17,18] the probability of moisture absorption is effectively reduced. TDS analysis can confirm the above inference. Figure 9 shows the temperature dependence of moisture desorption from post-CMP MSQ with and without H_2-plasma-treatment. The moisture content from H_2-plasma treated MSQ is lower than that of MSQ without H_2-plasma treatment. This indicates that the H_2-plasma treatment effectively forms a passivation layer to prevent moisture absorption in the MSQ film. The leakage current and dielectric constant of post-CMP MSQ are thereby decreased due to the reduction of polar water molecules.

Conclusions

Alkyl content in dielectrics greatly reduces CMP removal rate, and it is difficult to achieve uniform polishing across the wafer when using commercial silica-based slurries. We have reported an efficient CMP process for organic low *k* MSQ as IMD material. Instead of developing new slurries, the commonly used SS-25 slurry associated with TMAH surfactant can accelerate the polish rate of organic MSQ. The CMP removal rate of organic MSQ is promoted from approximately 100 to 1200 Å/min since TMAH can enhance the hydration reaction between slurry and MSQ films. However, dielectric degradation occurs after the CMP process due to mechanical abrasion and chemical hydrolysis reaction. We applied H_2-plasma post-treatment to passivate dangling bonds in post-CMP MSQ. The formation of a Si·H-containing passivation layer prevents post-CMP MSQ from moisture absorption. Therefore, the degraded properties

of post-CMP MSQ can be significantly restored employing a hydrogen plasma technique.

References

1. L. Peters, *Semiconduct. Int.*, 64 (Sept 1998).
2. *International Technology Roadmap for Semiconductors*, Semiconductor Industry Association, San Jose, CA (1999).
3. W. Volksen, R. D. Miller, J. L. Hedrick, C. J. Hawker, J. F. Remenar, P. Furuta, C. Nguyen, D. Y. Yoon, and M. Toney, No. 99-IMIC-109, in *Proceedings of the 16th International VLSI Multilevel Interconnection Conference (VMIC)*, p. 407, Santa Clara, CA, Sept 7-9, 1999.
4. P. A. Kohl, Q. Zhao, K. Patel, D. Schmidt, S. A. Bidstrup-Allen, R. Shick, and S. Jayaraman, in *Dielectric Material Integration for Microelectronics,* W. D. Brown, S. S. Ang, M. Loboda, B. Sammaki, R. Singh, and H. S. Rathore, Editors, PV 98-3, p. 169, The Electrochemical Society Proceedings Series, Pennington, NJ (1998).
5. C. T. Chua, G. Sarkar, and X. Hu, *J. Electrochem. Soc.*, **145**, 4007 (1998).
6. J. Wataerloos, H. Meynen, B. Coenegrachts, T. Gao, J. Grillaert, and L. Van den hove, No. 97-ISMIC-222D, in *Proceedings of the 3rd International Dielectrics for ULSI Multilevel Interconnection Conference*, DUMIC, p. 310, Santa Clara, CA, Feb 10-11, 1997.
7. L. J. Chen, S. C. Tseng, S. C. Chang, and C. M. Wang, No. 97-ISMIC-107, in *Proceedings of the 14th International VLSI Multilevel Interconnection Conference (VMIC)*, p. 125, Santa Clara, CA (1997).
8. J. M. Neirynck, R. J. Gutmann, and S. P. Murarka, *J. Electrochem. Soc.*, **146**, 1602 (1999).
9. H. G. Chiu, C. Wu, H. B. Lu, and J. T. Lin, No. 98-IMIC-300P, in *Proceedings of the Third International Chemical Mechanical Polish (CMP) for VLSI/ULSI Multilevel Interconnection Conference*, CMP-MIC, p. 328, Santa Clara, CA, Feb 19-20, 1998.
10. T. Hara, T. Tomisawa, T. Kurosu, and T. K. Doy, *J. Electrochem. Soc.*, **146**, 2333 (1999).
11. C. L. Borst, R. J. Gutmann, W. N. Gill, No. 99-IMIC-109, in *Proceedings of the 16th International VLSI Multilevel Interconnection Conference (VMIC)*, p. 207, Santa Clara, CA, Sept 7-9, 1999.
12. L. Forester, D. K. Choi, R. Hosseini, J. Lee, B. Tredinnic, K. Holland, and T. Cale, No. 95-IMIC-104, in *Proceedings of the 12th International VLSI Multilevel Interconnection Conference (VMIC)*, p. 482, Tampa, FL, June 27-29, 1995.
13. Y. Homma, T. Furusawa, K. Kusukawa, and M. Nagasawa, No. 96-ISMIC-100P, in *Proceedings of the First International Chemical Mechanical Polish (CMP) for VLSI/ULSI Multilevel Interconnection Conference*, CMP-MIC, p. 67, Santa Clara, CA, Feb 22-23, 1996.
14. B. Trednnick, J. Lee, K. Holland, and T. Bibby, No. 96-ISMIC-100P, in *Proceedings of the First International Chemical Mechanical Polish (CMP) for VLSI/ULSI Multilevel Interconnection Conference*, CMP-MIC, p. 107, Santa Clara, CA, Feb 22-23, 1996.
15. Y. L. Wang, C. Liu, S. T. Chang, M. S. Tsai, M. S. Feng, and W. T. Tseng, *Thin Solid Films*, **308-309**, 550 (1997).
16. P. T. Liu, T. C. Chang, Y. L. Yang, Y. F. Cheng, F. Y. Shih, J. K. Lee, E. Tsai, and S. M. Sze, *Jpn. J. Appl. Phys.*, **38**, 6247 (1999).
17. D. Thomas, G. Smith, and L. Nguyen, No. 97-ISMIC-222D, in *Proceedings of the 3rd International Dielectrics for ULSI Multilevel Interconnection Conference*, DUMIC, p. 361, Santa Clara, CA, Feb 10-11, 1997.
18. V. M. Gahay, A. Acovic, B. Agarwala, G. Endicott, D. Nguyen, M. Shapiro, and S. Yankee, No. 96-ISMIC-106, in *Proceedings of the 13th International VLSI Multilevel Interconnection Conference (VMIC)*, p. 116, Santa Clara, CA, Feb 10-11, 1996.