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# Highly reliable chemical–mechanical polishing process for organic low-$k$ methylsilsesquioxane

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In this work, chemical–mechanical polishing (CMP) of the organic polymer, methylsilsesquioxane (MSQ), has been investigated. For conventional silicate-based slurry, the CMP removal rate of MSQ is low and many scratches are formed at the surface. Moreover, the dielectric properties of a post-CMP MSQ film are degraded in comparison to the as-cured MSQ. We have proposed a reliable process for the CMP of MSQ which includes a slurry of additive and a post-CMP $NH_3$ plasma treatment. Experimental results show that the modified slurry provides a high polishing rate and uniform surface topography. In addition, the $NH_3$ plasma process can form a thin nitrogen-containing layer on the post-CMP MSQ surface, which enhances the resistance to moisture absorption and copper diffusion.  [DOI: 10.1116/1.1385684]

## I. INTRODUCTION

As devices continuously scale down, interconnect delay becomes the performance barrier for high-speed conduction. Insulating dielectrics with low permittivity (low-$k$)[1–3] have been popularly applied to multilevel interconnect architecture reducing signal propagation time delay, cross talk, and power consumption issues. In general, organic polymers are known to exhibit lower dielectric constants than inorganic oxides and nitrides, and may be considered as candidates for intermetal dielectric (IMD) in the ultralarge scale integrated circuit era.[4,5] However, polymer dielectrics still have several process integration issues that must be addressed prior to implementation. The biggest concern for low-$k$ polymer applications is the ''poisoned-via'' issue.[6] An etchback step is commonly performed to solve this issue. By removing the low-$k$ films from where the vias will subsequently be formed, the possibility of moisture outgassing from the low-$k$ dielectrics is effectively prevented.[7] Therefore, surface planarization after etchback processing is a key technology during the manufacturing of multilevel interconnects. The chemical–mechanical planarization (CMP) process is satisfactory to achieve global topography planarization. Due to the hydrophobic surface of organic low-$k$ polymers, CMP is a difficult process. Many deep scratches are formed on the organic surface when these dielectrics are polished mechanically.[8–11] These defects are harmful for the performance of the device, so care must be taken not to damage the polymer IMD during the polishing of the low-$k$ film.

In this work, we will present a reliable CMP process for organic low-$k$ methylsilsesquioxane (MSQ). Methylsilsesquioxane having the general formula $(CH_3SiO_{1.5})_{2n}$, $n = 2, 3$, etc. belongs to the polymeric family of silicones.[12] The silicones are polymers containing an inorganic backbone of alternating silicon and oxygen atoms with organic groups attached to silicon. MSQ, which exhibits a relatively low dielectric constant ($k = 2.6$–$2.8$) as compared to $SiO_2$ ($k = 4.0$), is intrinsically hydrophobic, and has reasonable mechanical hardness, and possesses exceptional thermal and dimensional stability.[13–15] For these reasons, MSQ represents an excellent candidate for applications on the multilevel interconnect architecture as IMD.

The polishing of MSQ film with conventional silica-based slurry is discussed in this study. Additionally, tetramethylammonium hydroxide (TMAH) was added to a conventional silica-based slurry and its effect on the polish rate was investigated. This study has employed material analyses and electrical measurements to characterize the post-CMP MSQ. Finally, a $NH_3$ plasma technique was implemented and characterized as a post-CMP treatment for the processing of low-$k$ MSQ.

## II. EXPERIMENT

The precursor for the films evaluated in this study was X418, a commercially available solution of methyl silsesquioxane in ethanol, $n$-butanol, propylene, glycol methyl ether acetate manufactured by Allied Signal Corporation. MSQ films were prepared by spin-coating X418 solution onto 6 in. $p$-type (25 $\Omega$ cm) single crystal silicon wafers with (100) orientation. Spin speed was 3000 rpm and the spinning time was 20 s, which gave a MSQ thickness about 500 nm. Then, the wafers were baked sequentially on a hot plate at 180 °C for 2 min and 250 °C for 1 min. The resulting wafers were cured in furnace at 400 °C for 30 min under nitrogen ambi-

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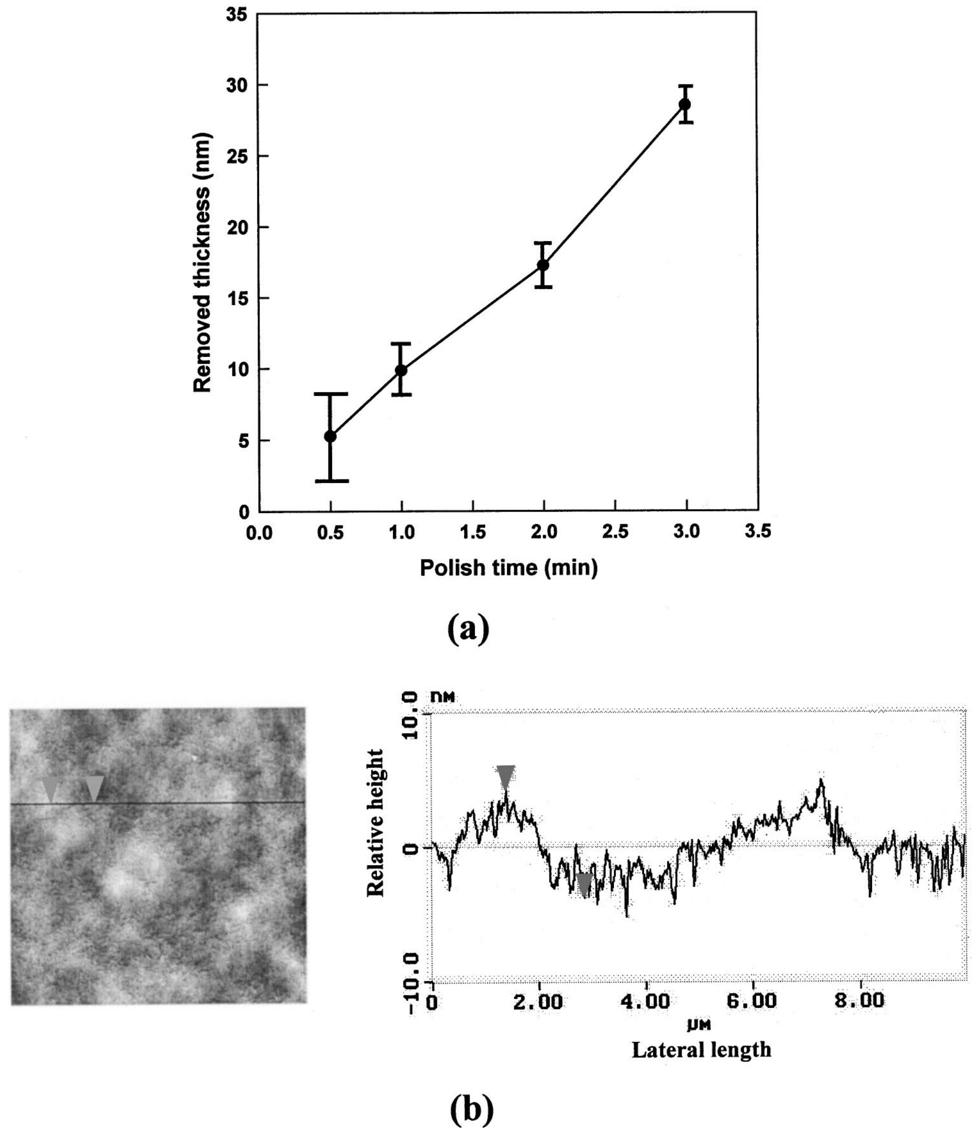


FIG. 1. (a) Variation in the removed thickness of CMP MSQ vs polish time. A large variation in the film thickness of MSQ is observed. (b) Top view (left) and surface line scanning profile (right) by AFM measurement for the surface of polished MSQ with silicate-based SS-25 slurry only. A poor surface topography is observed. The *Ra* within an image area of 100 $\mu m^2$ is 1.32 nm.

ent. It was followed that as-cured MSQ films were processed through CMP. The CMP experiment was carrier out on an IPEC/Westech 372M CMP processor consisting of a Rodel IC 1400 pad on the primary polishing platen, a Rodel Politex Regular™ embossed pad on the final buffing platen, a carrier to hold wafers against the pad, and a Rodel R200-T3 carrier film to provide buffer between the carrier and the wafer. 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, 30 wt % solid content, *p*H 10.4, mean particle size 110 nm, named CABOT SS-25™ slurry. Since low-*k* MSQ is one group of siloxane-based SOG films, the slurry used in this work was SS-25 slurry diluted 1:1 with deionized water. In parallel, work was developed to increase the CMP removal rate and uniformity of MSQ in silica-based slurry by adding 0.1–0.2 M TMAH aqueous solution to commercial SS-25 slurry. The resultant solution *p*H is in the range of 11–12. The optimum polishing parameters, such as down force, back pressure, platen and carrier rotation speeds, and slurry flow rate, were set to be 3 psi, 2 psi, 50 rpm, 60 rpm, 150 ml/min, respectively. The thickness and refractive index of all the blanket films before and after CMP polishing were measured using an *n* and *k* 1200 Analyzer, with 12 points measured.

Subsequently, the polished wafers were transferred to plasma enhanced chemical vapor deposition chamber for the $NH_3$ plasma posttreatment. The $NH_3$ plasma was operated at a pressure of 300 mTorr and with a $NH_3$ gas flow rate of 700 sccm. A rf power of 200 W, which established the $NH_3$ plasma, was applied to the upper electrode and the wafers were placed on the bottom by a grounded electrode, which can be rotated for improving uniformity, at a substrate temperature of 300 °C. The structural properties of the MSQ

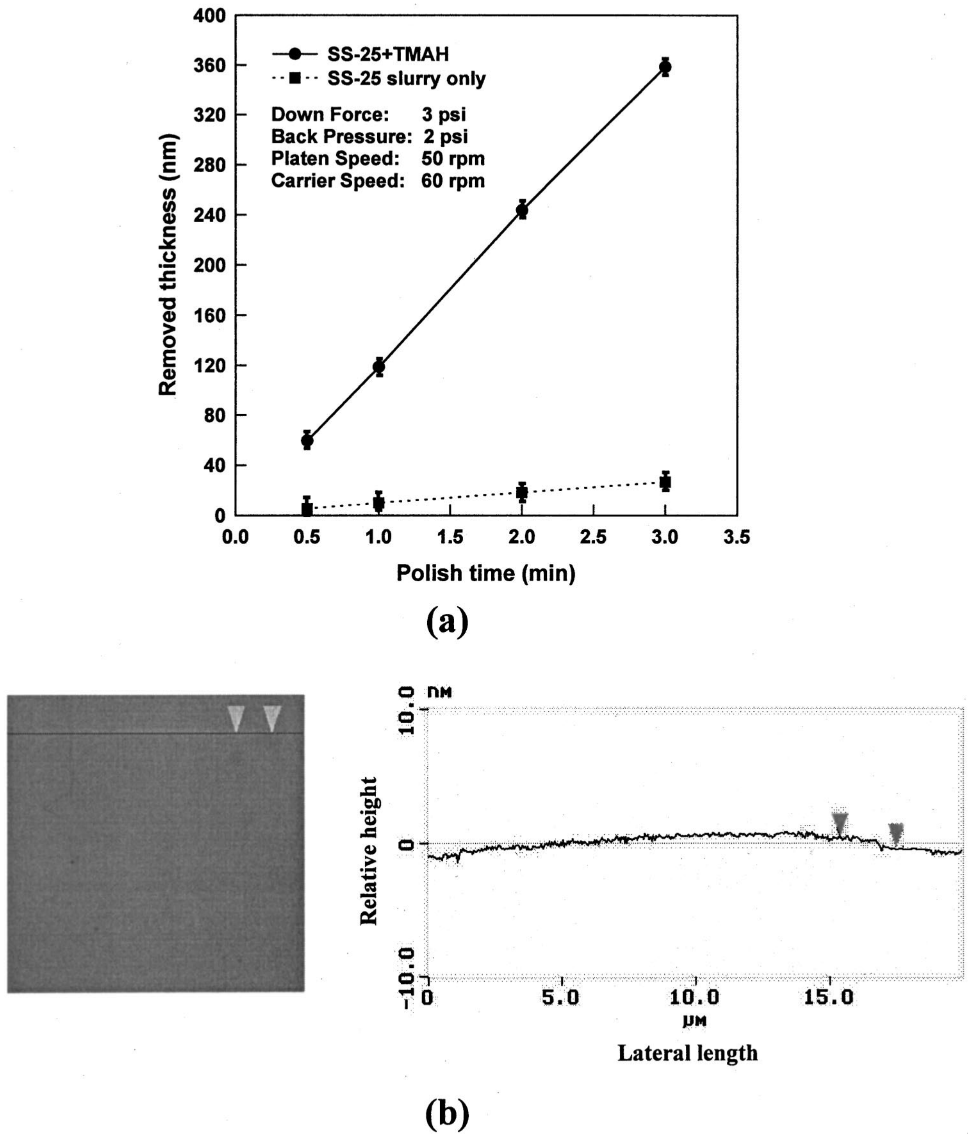


FIG. 2. (a) Removed thickness of CMP MSQ with and without additive TMAH for the same polishing parameters of CMP process. The removal rate is 1200 and 100 Å/min, respectively. (b) Top view (left) and surface line scanning profile (right) by AFM measurement for the surface of polished MSQ with TMAH-added slurry. The surface topography of polished MSQ film is smooth. The *Ra* within an image area of 100 $\mu m^2$ is 0.235 nm.

films were studied using Fourier transform infrared absorption spectra (FTIR). The surface morphologies of the polished films were investigated by atomic force microscopy (AFM) with a scan area 100 $\mu m^2$. Material analysis such as thermal desorption system spectrometer (TDS) was carried out to monitor the desorbed moisture from the post-CMP MSQ films during a high temperature process. Electrical characterizations of post-CMP MSQ films were performed on the metal–insulation–semiconductor capacitors with metallic aluminum deposition as top electrode. Leakage current–voltage and capacitance–voltage characteristics were also used to analyze the leakage current behavior and measure dielectric constant of post-CMP MSQ film, respectively. For all electrical measurements, 21 dies were measured on per wafer and 50 pieces of wafers in total.

## III. RESULTS AND DISCUSSION

For the initial experiments, the CMP process was implemented with commercial silica-based slurry SS-25™ since the MSQ is one of the silicon-based low-*k* materials. Figure 1(a) illustrates the variation of removed thickness versus polish time. The results show that the polishing rate of CMP organic MSQ is rather low (about 100 Å/min). In addition, a large variation in the film thickness of MSQ is observed. AFM images were used for further observation of the resultant topography after CMP, as shown in Fig. 1(b). The mean surface roughness (*Ra*) within an image area of 100 $\mu m^2$ is even up to 1.32 nm as compared to 0.154 nm of pre-CMP surface. This difficulty in polishing is also consistent with Forester *et al.*[11] which presents that the organic content in the dielectric films will inhibit the hydration reaction during

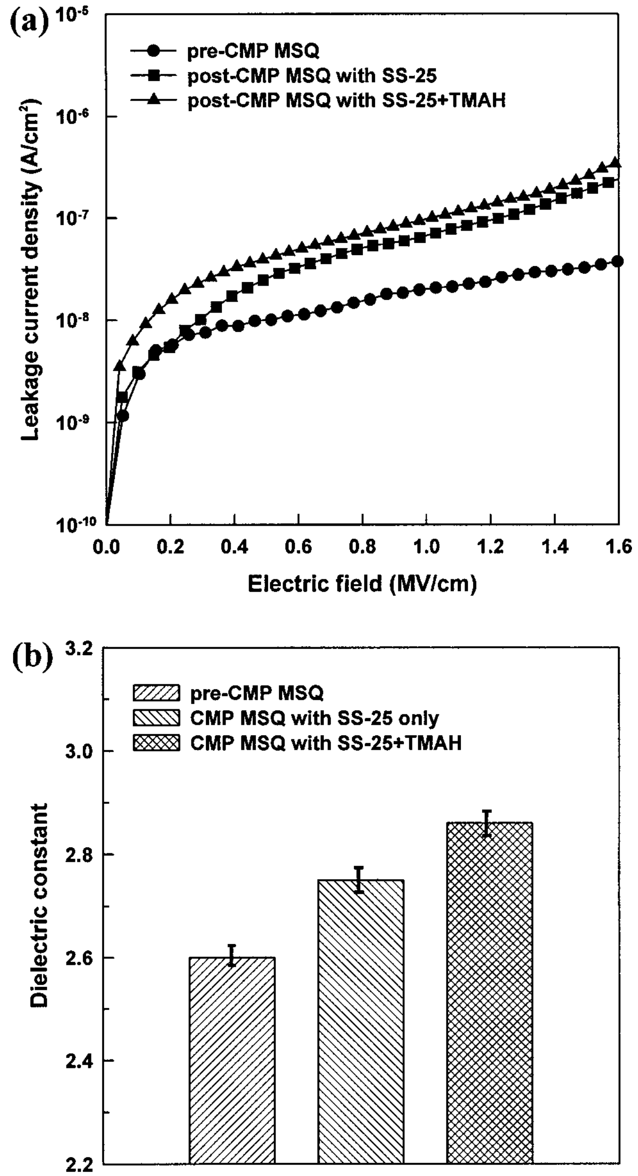


FIG. 3. Dielectric properties of MSQ polished with and without additive TMAH. (a) Leakage current density of post-CMP MSQ as a function of electric field. (b) Dielectric constant of post-CMP MSQ films. Both the leakage current and dielectric constant of post-CMP MSQ are higher than that of pre-CMP MSQ.

CMP. Thus, the polishing of polymers can be regarded as a chemical reaction limited process rather than mechanically limited. In order to increase the polishing rate, the chemical surfactant TMAH which can improve the MSQ surface wettability is mixed with SS-25™ as the modified slurry in this study. Figure 2(a) shows the removed thickness of CMP MSQ with and without additive TMAH for the same polishing parameters. A higher MSQ removal rate (about 1200 Å/min) is observed for the SS-25™ slurry mixing with additive TMAH. The surface line scanning profile of polished MSQ with TMAH-added slurry is shown in Fig. 2(b). Compared to the polished surface with SS-25™ slurry only, the surface roughness of post-CMP MSQ with TMAH is significantly decreased to 0.235 nm. This implies a more uniform dissolution and removal is occurring on the surface of organic MSQ. In this work the surfactant TMAH which has both hydrophilic and hydrophobic groups in its molecular components, can reduce the surface energy between abrasive and the hydrophobic MSQ. In addition, the ammonium hydroxide ion pairs will absorb on the organic MSQ surface resulting in the increased $p$H locally (from 10.4 to 11) on the surface than KOH ions do in the SS-25 slurry. This will facilitate the hydrolysis reactions of MSQ in a more basic environment. Both the improvement in MSQ surface wettability and the increase in dissolution constant of hydroxide ions are the necessary factors to improve the CMP MSQ. The hydration reaction scheme has been proposed in a previous article.[16] Therefore, in aqueous solution the modified slurry (SS-25™ + TMAH) is capable of dissolving the organic content uniformly and initiating hydration reactions to breaking the Si–O bonds in the MSQ films. 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 MSQ backbone. With an enhanced hydration reaction and the assistance of the proceeding mechanical event, a high removal rate of CMP MSQ can be obtained as compared to SS-25™ slurry only.

Furthermore, we investigate the electrical characteristics of the post-CMP MSQ film to evaluate the influence of the CMP process on low-$k$ properties. Figures 3(a) and 3(b) show the leakage current and dielectric constant of MSQ after the CMP process with and without TMAH-added slurry. The leakage current densities of both cases of post-CMP MSQ are increased as much as one order of magnitude higher than that of pre-CMP MSQ. The dielectric constant of post-CMP MSQ is also increased from an as-cured value of 2.6–2.86. In addition, we observe that both the leakage current and dielectric constant of post-CMP MSQ with TMAH-added slurry are slightly increased when compared to the case of CMP MSQ without the TMAH additive. FTIR spectra show that the peak intensity of the Si–C bond and the C–H bond of post-CMP MSQ is reduced in comparison with that of pre-CMP MSQ, as shown in Fig. 4. The destruction of organic functional bonds from kinematic mechanical abrasion and chemical reaction leads to dielectric deterioration and inevitably results in the increased leakage current and dielectric constant. This is especially true for the enhanced hydrolysis reaction of MSQ with the addition of TMAH which is responsible for even more degradations in electrical characteristics. This delitescent effect will offset partial advantage of using additive TMAH.

To alleviate the electrical degradation, an $NH_3$ plasma treatment was applied upon the post-CMP MSQ. Figures 5(a) and 5(b) show the leakage current density and dielectric constant of post-CMP MSQ treated with $NH_3$ plasma treatment for 3–9 min. These results show that both the leakage current and dielectric constant of post-CMP MSQ decrease and approach the pre-CMP values, with the increase in $NH_3$ plasma treatment within 9 min. In this work, a $NH_3$-plasma treatment within 10 min is an appropriate condition, or more nitridation would raise the dielectric constant of the MSQ

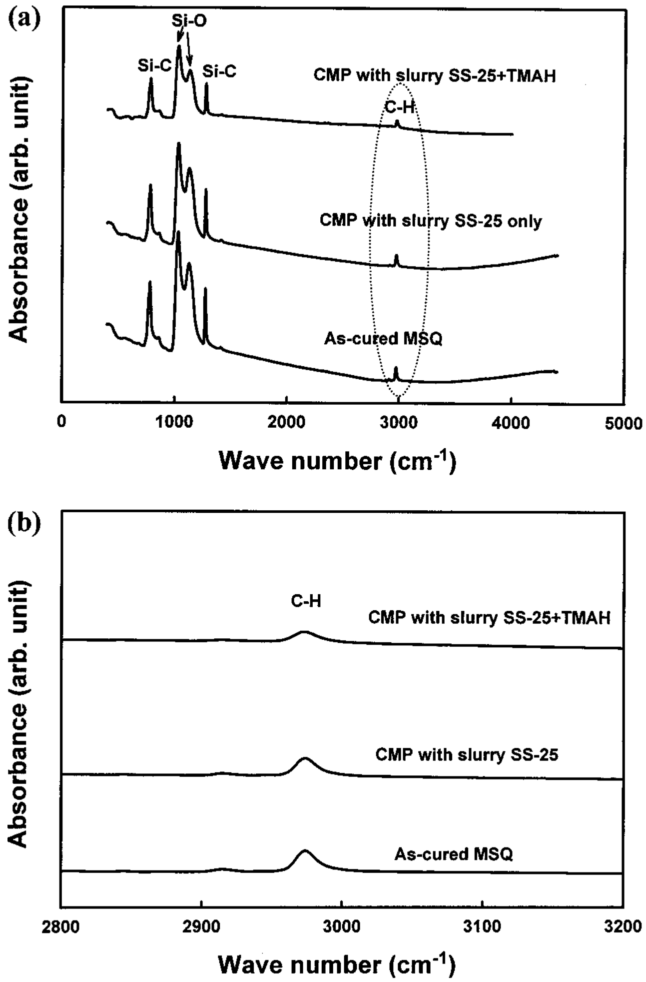


FIG. 4. (a) FTIR spectra of low-*k* MSQ film before and after CMP process. (b) An enlargement of the 2800–3200 $cm^{-1}$ region for (a). The destruction of function groups (Si–C and C–H bonds) appear after CMP MSQ.

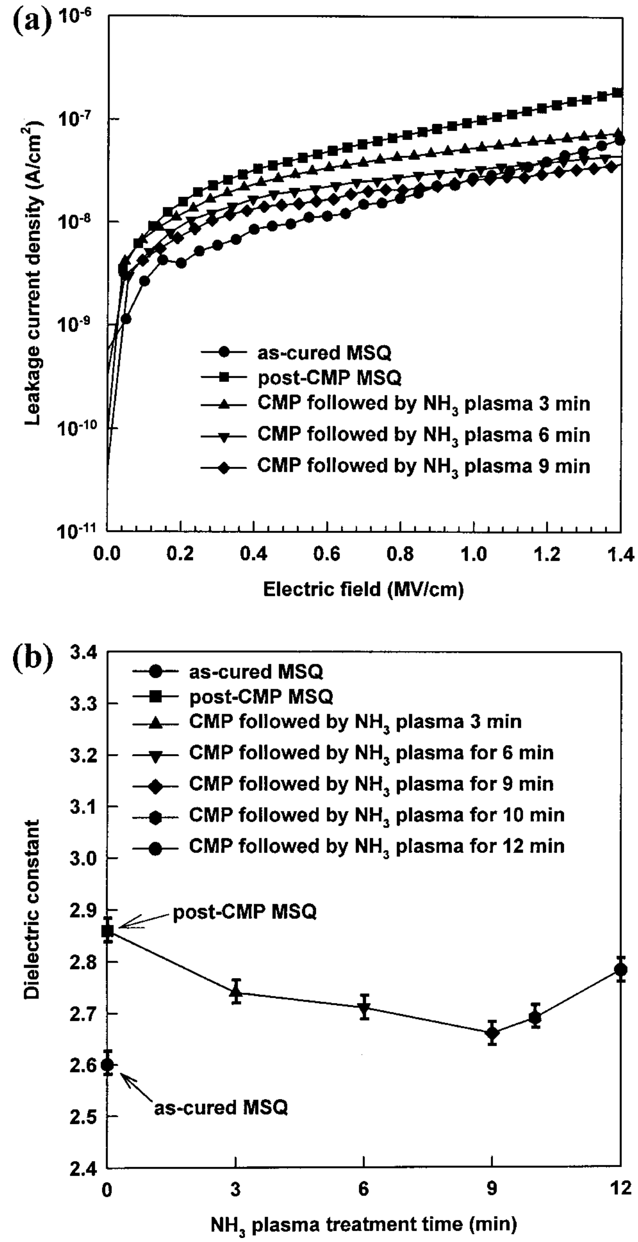


FIG. 5. (a) Leakage current density of post-CMP MSQ with $NH_3$-plasma treatment as a function of electric field. (b) Dielectric constant of post-CMP MSQ with $NH_3$-plasma treatment as a function of treatment time. Both the leakage current and dielectric constant decrease and approach the pre-CMP values. An $NH_3$-plasma treatment within 10 min is an appropriate condition, or more nitridation will raise the dielectric constant of MSQ film gradually.

film gradually. These significant improvements in electrical characteristics of post-CMP MSQ can be interpreted by material analyses. X-ray photoelectron spectroscopy (XPS) analysis confirms the modification of the MSQ surface. Figures 6(a) and 6(b) show XPS diagrams of the post-CMP MSQ film before and after $NH_3$ plasma treatment. Compared to Fig. 6(a), it is found that a significant signal of nitrogen appears at about 400 eV in Fig. 6(b). This means that the nitrogen atoms are shallowly doped in the MSQ. Jeong *et al.* demonstrated that the SiON phase is formed in the MSQ surface after $NH_3$ treatment.[17] In order to realize the SiON barrier against moisture uptake, TDS analysis was performed for further investigation. Figure 7 shows the temperature dependence of moisture desorption from post-CMP MSQ film with and without $NH_3$ plasma treatment. The moisture content in $NH_3$-plasma treated MSQ is lower than that of untreated post-CMP MSQ. The inert passivation layer formed by $NH_3$-plasma treatment effectively prevents moisture absorption in post-CMP MSQ. The leakage current and dielectric constant of post-CMP MSQ are thereby decreased due to the reduction in polar moisture uptake.[18,19] Additionally, $NH_3$-plasma treatment can block copper penetration in post-CMP MSQ. Secondary ion mass spectroscopy (SIMS) analysis was carried out to observe the distribution of copper element after removing the Cu electrode from the thermally stressed Cu/MSQ/Si capacitors. Figure 8 shows SIMS depth profile of copper in post-CMP MSQ with and without $NH_3$-plasma treatment after being subjected to a thermal stress of 500 °C for 30 min under nitrogen ambient. The SIMS profile shows copper penetrates and piles up on the interface between the untreated MSQ film and the Si substrate under thermal stressing. This is a serious problem since the existence of copper in dielectrics leads to reliability

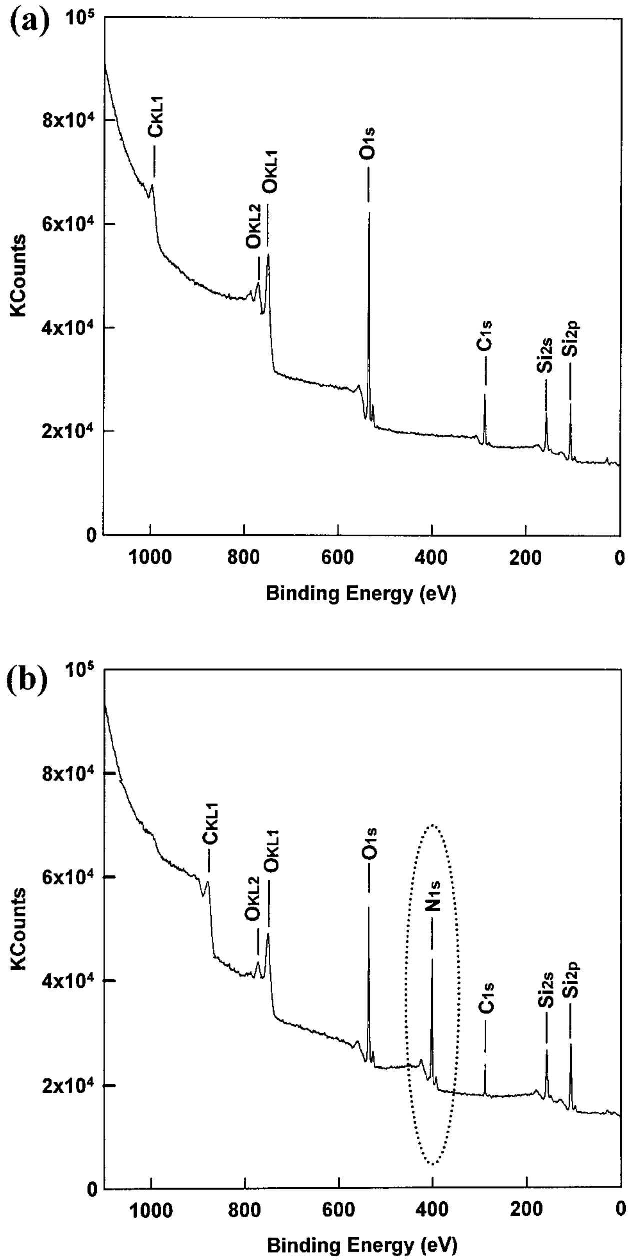


FIG. 6. (a) Full XPS profile of as-deposited MSQ surface. (b) Full XPS profile of $NH_3$-plasma treated MSQ surface, showing the presence of element N.

issues.[20,21] By contrast, the profile of copper has a relatively shallow distribution which rapidly tails off in the $NH_3$-plasma treated MSQ film due to the presence of nitrogen. Therefore, the $NH_3$-plasma treatment also effectively enhances the resistance of the post-CMP MSQ to copper penetration.

## IV. CONCLUSIONS

The existence of the methyl group in a dielectric film will largely reduce the CMP removal rate and make CMP difficult to achieve a uniform polish across the wafer when using conventional oxide CMP slurry. This work has reported an efficient CMP process for organic low-*k* MSQ as an inter-

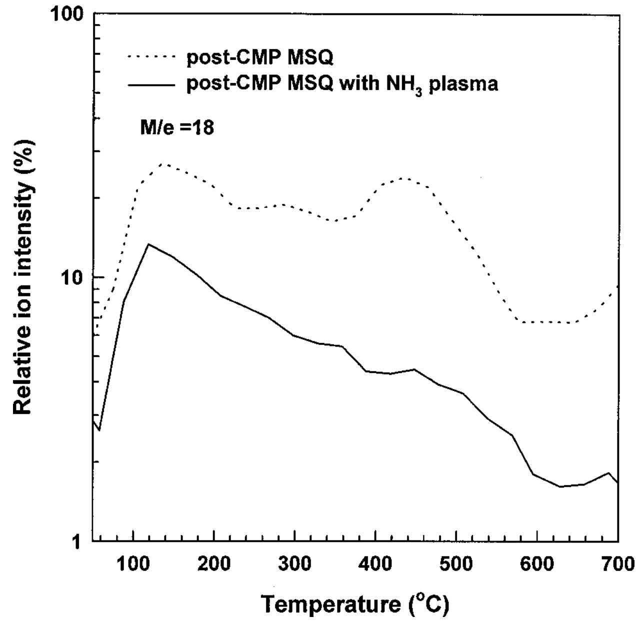


FIG. 7. Temperature dependence of moisture desorption from post-CMP MSQ films with and without $NH_3$-plasma treatment. The moisture content in $NH_3$-plasma treated MSQ is lower than that of untreated post-CMP MSQ.

metal dielectric material. The commercial SS-25™ silica-based slurry combined with the additive TMAH can accelerate the polish rate of organic MSQ film. Since the addition of TMAH is quite capable in converting the hydrophobic MSQ surface into a more hydrophilic condition, the removal rate of low-*k* MSQ is promoted from approximately 100–to 1200 Å/min. In addition, the application of a $NH_3$-plasma post-

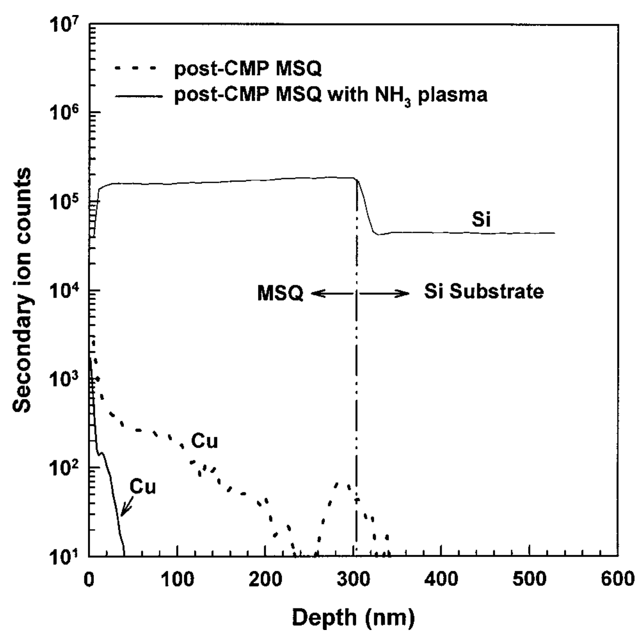


FIG. 8. SIMS depth profiles of copper in post-CMP MSQ film with and without $NH_3$-plasma treatment after being subjected to a thermal stress of 500 °C for 30 min under nitrogen ambient. A relatively shallow copper distribution is observed in $NH_3$-plasma treated MSQ in comparison to untreated MSQ.

CMP treatment will restore the dielectric degradation due to the mechanical abrasion and chemical etching reaction during the CMP process. XPS spectrum has shown the presence of nitrogen on the surface of an $NH_3$-plasma treated post-CMP MSQ. The presence of nitrogen effectively prevents the post-CMP MSQ from moisture uptake and copper diffusion which have been confirmed by TDS and SIMS analysis, respectively.

## ACKNOWLEDGMENTS

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[1] *International Technology Roadmap for Semiconductors* (Semiconductor Industry Association, San Jose, CA, 1997).
[2] T. Nakano and K. Tokunaga, J. Electrochem. Soc. **142**, 1303 (1995).
[3] P. T. Liu, T. C. Chang, Y. L. Yang, Y. F. Cheng, J. K. Lee, F. Y. Shih, E. Tsai, G. Chen, and S. M. Sze, J. Electrochem. Soc. **147**, 1186 (2000).
[4] A. K. Stamper, V. McGahay, and J. P. Hummel, Proceedings of the 3rd International Dielectrics for ULSI Multilevel Interconnection Conference, DUMIC, Santa Clara, CA, 10–11 February 1997, p. 13.
[5] M. Morgen, J. H. Zhao, M. Hay, T. Cho, and P. S. Ho, Mater. Res. Soc. Symp. Proc. **565**, 69 (1999).
[6] J. Wataerloos, H. Meynen, B. Coenegrachts, and L. Van den hove, No. 97-ISMIC-222D, Proceedings of the 3rd International Dielectrics for ULSI Multilevel Interconnection Conference, Santa Clara, CA, 18–20 June 1996, p. 52.
[7] L. Forester, S. B. Kim, D. K. Choi, J. H. Ko, J. C. Kim, M. Ross, W. R. Livesay, and J. J. Yang, Proceedings of the 2nd International Dielectrics for ULSI Multilevel Interconnection Conference, Santa Clara, CA, 18–20 June 1996, p. 119.
[8] Y. Homma, T. Furusawa, H. Moroshima, and H. Sato, Solid-State Electron. **41**, 1005 (1997).
[9] T. Hara, T. Tomisawa, T. Kurosu, and T. K. Doy, J. Electrochem. Soc. **146**, 2333 (1999).
[10] C. L. Borst, R. J. Gutmann, and W. N. Gill, Proceedings of the 16th International VLSI Multilevel Interconnection Conference, Santa Clara, CA, 7–9 September 1999, p. 207.
[11] L. Forester, D. K. Choi, R. Hosseini, J. Lee, B. Tredinnic, K. Holland, and T. Cale, Proceedings of the 12th International VLSI Multilevel Interconnection Conference, Tampa, FL, 27–29 June 1995, p. 482.
[12] N. H. Hendricks, Mater. Res. Soc. Symp. Proc. **443**, 3 (1997).
[13] C. T. Chua, G. Sarkar, and X. Hu, J. Electrochem. Soc. **145**, 4007 (1998).
[14] P. T. Liu, T. C. Chang, Y. S. Mor, and S. M. Sze, Jpn. J. Appl. Phys. **38**, 3482 (1999).
[15] A. T. Kohl, R. Mimna, R. Shick, L. Rhodes, Z. L. Wang, and P. A. Kohl, Electrochem. Solid-State Lett. **2**, 77 (1999).
[16] 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).
[17] H. D. Jeong, H. S. Park, H. J. Shin, B. J. Kim, H. K. Kang, and M. Y. Lee, Proceedings of the 1999 International Interconnect Technology Conference, San Francisco, CA, 24–26 May 1999, p. 190.
[18] A. L. S. Loke, J. T. Wetzel, J. J. Stankus, M. S. Angyal, B. K. Mowry, and S. S. Wong, IEEE Electron Device Lett. **19**, 177 (1998).
[19] R. A. Swalin, *Thermodynamics of Solids* (Wiley, New York, 1972), p. 302.
[20] G. Raghavan, C. Chiang, P. B. Anders, S. M. Tzeng, R. Villasol, G. Bai, M. Bohr, and D. B. Fraser, Thin Solid Films **168**, 262 (1995).
[21] A. L. S. Loke, J. T. Wetzel, P. H. Townsend, T. Tanabe, R. N. Vrtis, M. P. Zussman, D. Kumar, C. Ryu, and S. S. Wong, IEEE Electron Device Lett. **46**, 2178 (1999).