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Effects of H_2 plasma treatment on low dielectric constant methylsilsesquioxane

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The quality of organic low-*k* methylsilsesquioxane (MSQ) film is degraded by the damage of oxygen plasma and hygroscopic behavior during photoresist stripping. In addition, the interaction between MSQ and copper is worth investigating. In this work, we have studied the H_2 plasma treatment to improve the quality and enhance the copper penetration resistance of MSQ. Experimental results show the leakage current of MSQ decreases as the H_2 plasma treatment time is increased. The dielectric constant of treated samples also remains constant (~2.7). In addition, the copper diffusion resistance of MSQ film is significantly promoted. The H_2 plasma treatment can provide additional hydrogen to passivate the inner structure of porous MSQ film as well as reduce the probability of moisture uptake and interaction with Cu atoms. Therefore, the low-*k* dielectric properties of MSQ are significantly enhanced by H_2 plasma treatment. © *1999 American Vacuum Society.* [S0734-211X(99)05105-7]

I. INTRODUCTION

As the critical dimension of integrated circuits is scaled down, the linewidth and spacings between metal interconnects are made smaller. Circuit speed is limited by *RC* delays associated with the metal interconnect system[1] and not the transistor delay.

In search for a better performance metallization system, copper is a prime candidate because of its low resistivity (1.67 $\mu\Omega$ cm for bulk) and high electromigration resistance. In addition, interlayer dielectric films with lower dielectric constant *k* have been proposed to reduce the coupling capacitance between metal lines. These interlayer dielectric films can be either organic or inorganic materials, and can be deposited by either chemical vapor deposition (CVD) or spin-on glass (SOG) techniques.[2,3] SOG materials have been widely used as an interlayer dielectric in multilevel interconnect architectures because of their process simplification (lower cost) and good local planarization capabilities. Inorganic SOGs such as hydrogen silsesquioxane (HSQ), aerogels, and xerogels (which have hydrophobic pores) have been developed by introducing the Si–H group and by film formation through controlled gelation. Most of the Si–H groups in HSQ tend to decompose into Si–OH groups due to moisture absorption and thermal cycling at temperatures exceeding 400 °C.[4] Much research has been done on these issues with HSQ films.[5,6] The aerogel films have a dielectric constant of 1.3–2.0,[7] and the xerogel films have a dielectric constant of 1.3–2.5.[8] These dielectric films show very low dielectric constants due to the high porosity of the internal structure. Nevertheless, these materials easily absorb moisture that increases the dielectric constant. It seems that the procedure of film formation has limited applicability at present. An organic SOG, methylsesquioxane (MSQ) (Allied Signal Advanced Microelectronic Materials), which has a dielectric constant of ~2.7, is one of the most promising materials for intermetal applications. It has been developed by increasing the number of the Si–methyl group which causes the film density to decrease[9] and to lower film polarization resulting in a low *k*. The methylsilsesquioxane polymer ($CH_3SiO_{1.5}$) exhibits good adhesion to silicon, CVD oxide, and aluminum. Furthermore, MSQ provides superior flow and excellent gap fill capability down to small gaps of 0.06 μm.[10] Similar to other organic low *k* materials, however, the quality of MSQ film is degraded by the damage from oxygen plasma and hygroscopic behavior during photoresist stripping.[11] This instability is one of the major problems in using MSQ as a low-*k* material. Moreover, it is necessary to evaluate the interaction between MSQ and copper in order to integrate the low-*k* and copper interconnect system successfully.

In this work, we have studied how the H_2 plasma post-treatment can improve the quality of MSQ film. In addition, the effects of O_2 plasma ashing and copper penetration were

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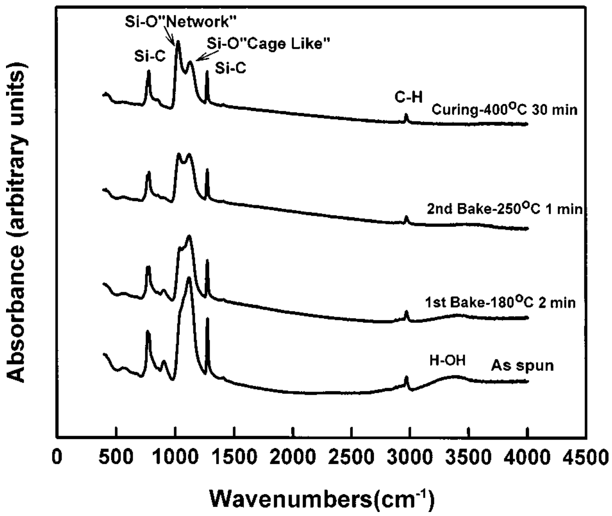

FIG. 1. FTIR spectra of MSQ before and after a series of bake and curing steps.

investigated to understand the impact of integrated processes on the dielectric quality. Dielectric properties of MSQ film were evaluated by electrical characterization as well as chemical composition analyses.

II. EXPERIMENT

The unpatterned silicon wafers were coated with a single layer of MSQ film, and baked sequentially on the hot plate at 180 °C for 2 min and 250 °C for 1 min. The resulting wafers were followed by furnace curing at 400 °C for 30 min. For each condition, film stress, shrinkage, refractive index, and Fourier-transform infrared (FTIR) absorption measurements were carried out. In this experiment, two types of samples were prepared. Sample STD was the as-cured MSQ film. Samples A3, A6, and A9 were the as-cured MSQ films with H_2 plasma post-treatment for 3, 6, and 9 min, respectively. All of the samples were annealed at a temperature range of 400–550 °C to investigate the thermal stability of the MSQ film. In addition, the O_2 plasma treatment was done on all the samples to investigate the impact to the MSQ film during the photoresist stripping. A plasma enhanced CVD chamber was used for various plasma treatments. Each of plasmas was operated at a pressure of 300 mTorr with a rf power of 200 W. The flow rate for each of these gases was 300 sccm, and the temperature of the chamber was kept at 300 °C. It was followed by sputtering aluminum and copper onto all the samples as the top electrode for metal–insulator–semiconductor capacitors, respectively. Cu–electrode samples were annealed at temperatures over a range of 400–500 °C for 30 min to evaluate the effect of copper penetration. A Keithley model 82 capacitance–voltage (C-V) meter was used to measure the dielectric constants of MSQ films. The capacitors were measured at 1 MHZ with an ac bias for high frequency $C-V$ curves. Leakage current–voltage characteristics of MSQ were measured by an HP4145B semiconductor parameter analyzer.

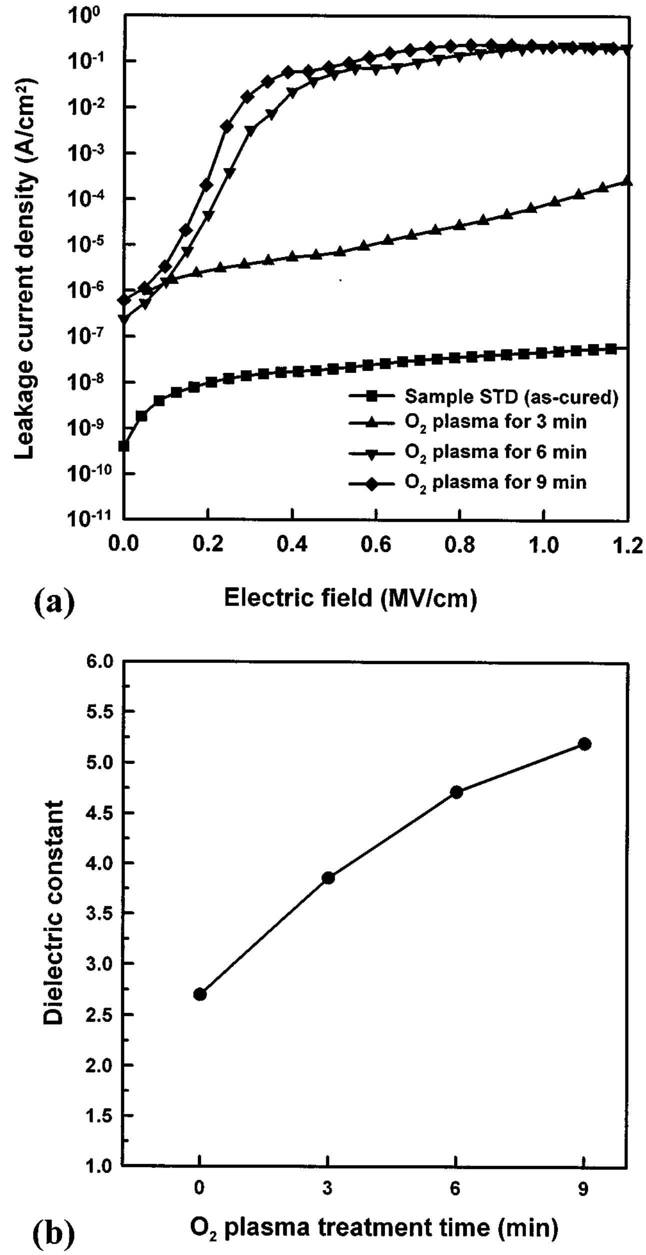

FIG. 2. (a) Leakage current density of sample STD after the O_2 plasma treatment for 3–9 min. (b) Dielectric constant of samples STD with O_2 plasma treatment as a function of the treatment time.

III. RESULTS AND DISCUSSION

Figure 1 shows the FTIR spectra of MSQ before and after a series of baking and curing steps. After 180 and 250 °C baking, H–OH peak intensities were reduced due to evaporation of the solvent. The intensity of the Si–O peak signal is decreased and the Si–O–Si peak intensity is increased. After 400 °C curing, the peak signal of the H–OH bonds was totally removed and a sharp Si–O–Si peak significantly appeared. It is evident that a large amount of Si–O bonds are crosslinking into Si–O–Si bonds, forming a more porous network structure.

In the integrated processes, the photoresist stripping was implemented conventionally by utilizing O_2 plasma ashing to

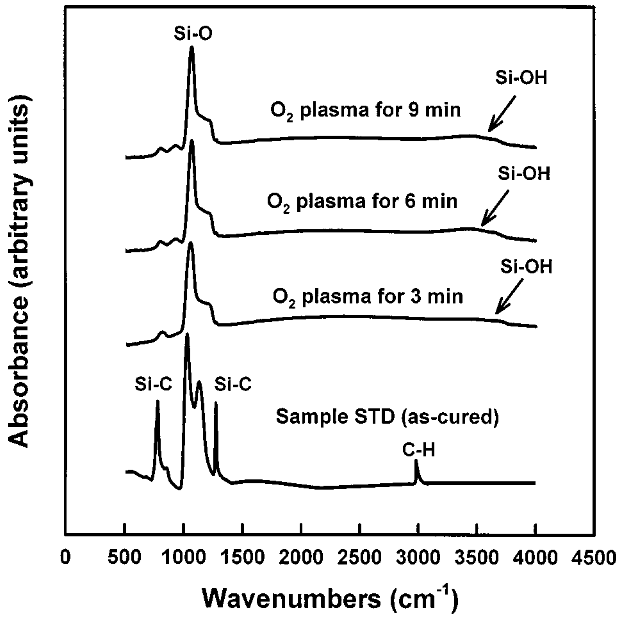

FIG. 3. FTIR spectra of samples STD after O_2 plasma treatment for 3–9 min.

remove organic elements. The impact of O_2 plasma on the quality of MSQ film is significant. Figure 2(a) shows the leakage current density of sample STD after the O_2 plasma treatment at 300 °C for 3–9 min. The leakage current increases with increasing duration of the O_2 plasma treatment. In addition, the dielectric constant of MSQ increases as O_2 plasma time is increased, as shown in Fig. 2(b). These results are due to conversion of the Si–CH_3 bonds into Si–OH bonds when O_2 plasma is applied to MSQ. Exposure to the O_2 plasma causes a significant amount of the Si–CH_3 bonds to break, leaving several dangling bonds in the film. Some of those dangling bonds form Si–O bonds and others convert into Si–OH bonds. Therefore, the film absorbs moisture quickly leading to the increased leakage current and high dielectric constant. These results are consistent with Fig. 3,

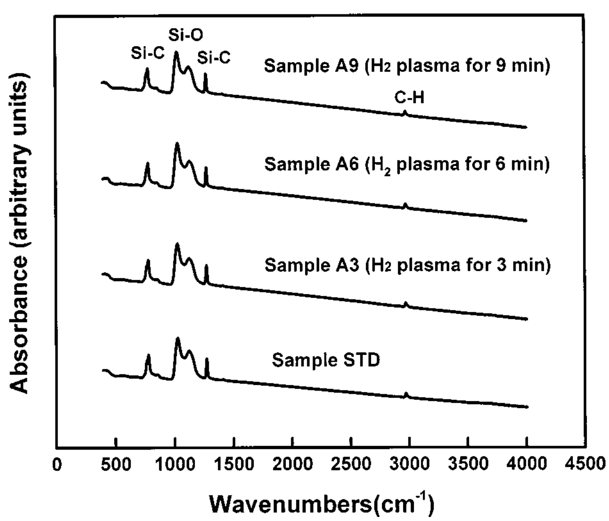

FIG. 4. FTIR spectra of samples STD, A3, A6, and A9.

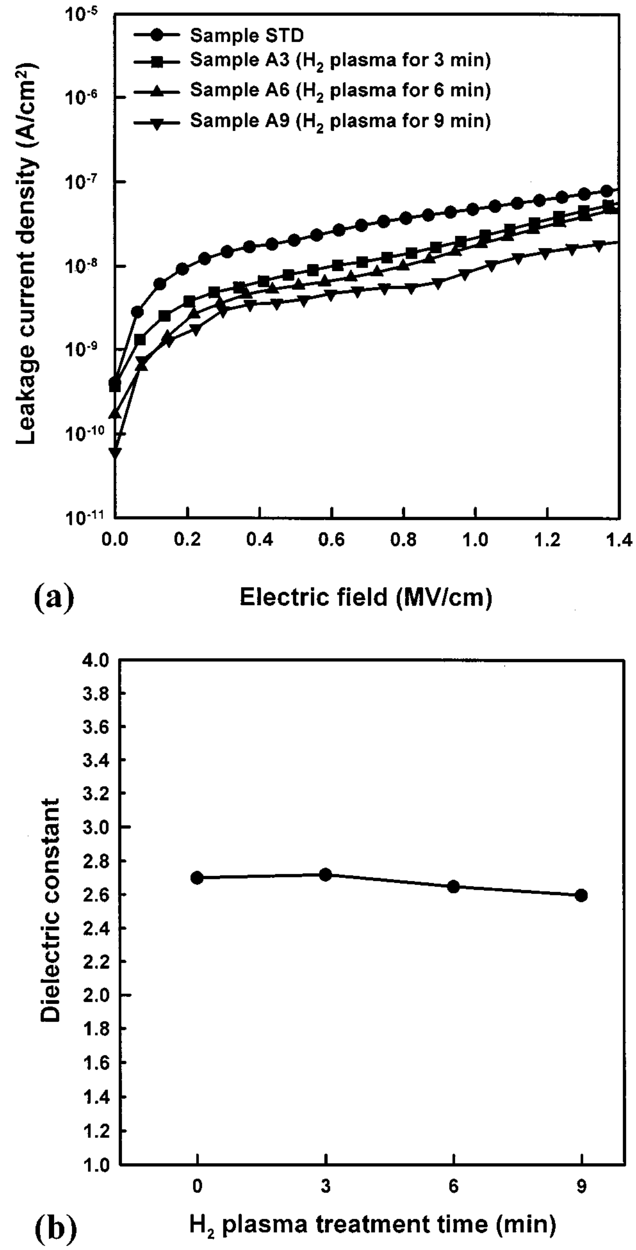

FIG. 5. (a) Leakage current densities of samples STD, A3, A6, and A9. (b) Dielectric constant of MSQ as a function of the H_2 plasma treatment time.

which shows the FTIR spectra of sample STD with O_2 plasma treatments. In these spectra, the intensity of the Si–C bond signal is decreased dramatically and the intensity of the Si–OH bond signal is increased when the MSQ was treated by O_2 plasma. This indicates that oxygen radicals deeply diffuse into the porous inner structure of the MSQ film to break the Si–C bonds in the MSQ film. The increase of the Si–OH bond signal has two possible causes. One is that when the O_2 plasma breaks Si–CH_3 bonds, MSQ absorbs oxygen radicals to convert Si–CH_3 bonds into Si–OH bonds. The other is that the defect sites (or dangling bonds in MSQ) absorb water immediately when the sample is exposed to the environment. As a result, the MSQ becomes unstable after O_2 plasma treatment. Both the leakage current and dielectric

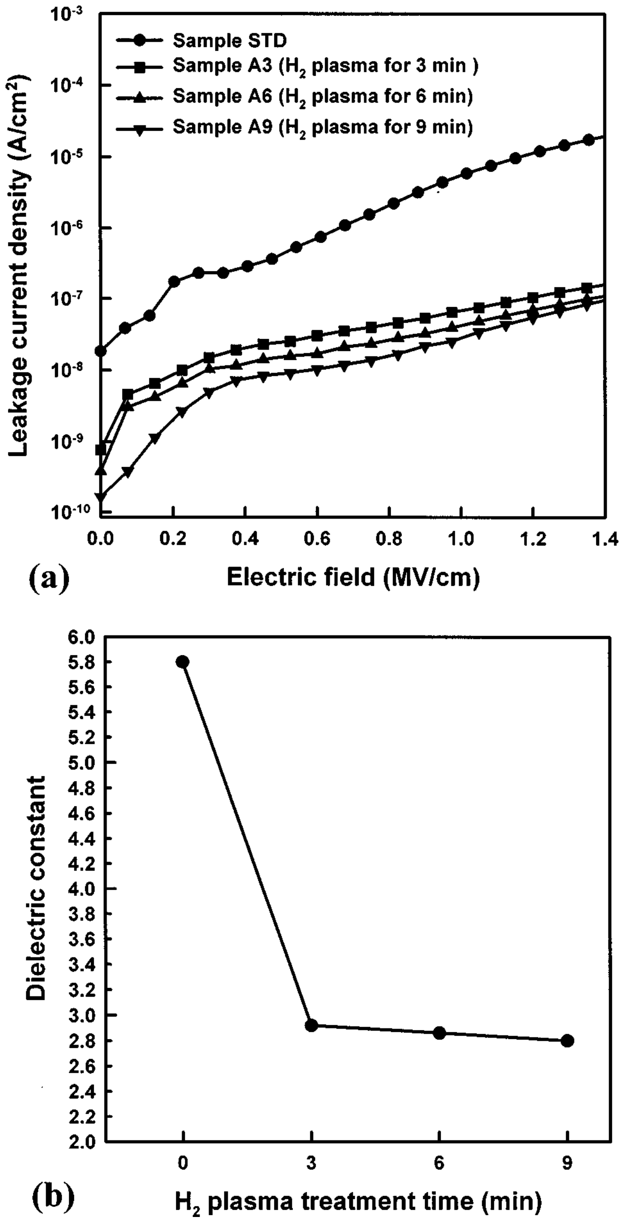

FIG. 6. (a) Leakage current densities of samples STD, A3, A6, and A9 after annealing at 550 °C for 30 min. (b) Dielectric constants of samples STD, A3, A6, and A9 after annealing at 550 °C for 30 min.

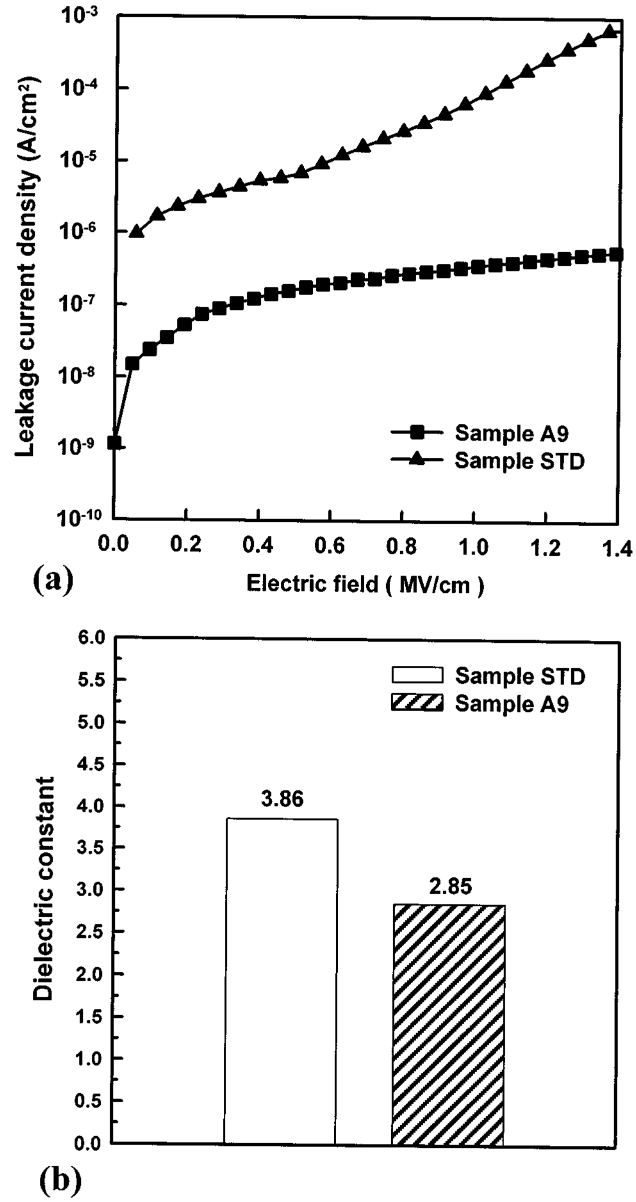

FIG. 7. (a) Leakage current densities of samples STD and A9 after O_2 plasma treatment for 3 min. (b) Dielectric constants of samples STD and A9 after O_2 plasma treatment for 3 min.

constant of MSQ increase due to moisture absorption and dangling bond formation.

Figure 4 shows the FTIR spectra of the MSQ film treated by H_2 plasma for 3–9 min. In comparison with as-cured film, no significant change can be observed in the treated MSQ films. The intensity of both Si–C and C–H bonds is maintained at their high levels and the signal for Si–OH bonds is not observed. The leakage current density of samples STD, A3, A6, and sample A9 is shown in Fig. 5(a). The leakage current density of MSQ film decreases as the H_2 plasma treatment time is increased. The temperature of the H_2 plasma treatment is 300 °C, which is less than the curing temperature of 400 °C. As a result, we conclude that the dominant effect on leakage current reduction of the MSQ is hydrogen post-treatment. The temperature effect is not as important a factor as the hydrogen plasma treatment. Figure 5(b) shows the dielectric constant of MSQ as a function of the H_2 plasma treatment time. A slight reduction of dielectric constant is observed from the as-cured value of 2.7. This result indicates that the H_2 plasma treatment can provide a stable low dielectric constant for MSQ. Figure 6 shows both the leakage current densities and dielectric constants of samples STD, A3, A6, and A9 after annealing at 550 °C for 30 min. The leakage current of MSQ film decreases with the increasing time of H_2 plasma treatment. In addition, the dielectric constant of MSQ film without H_2 plasma treatment becomes very high (about 5.8) after annealing at 550 °C for 30 min. However, the dielectric constant of the MSQ film with H_2 plasma treatment remains very low. Therefore, it

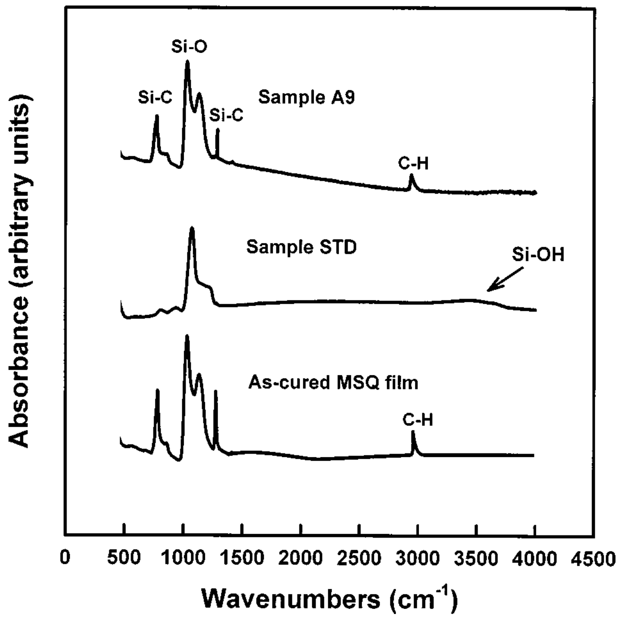

FIG. 8. FTIR spectra of samples STD and A9 after O_2 plasma treatment for 3 min.

clearly shows that the H_2 plasma treatment enhances the thermal stability of the MSQ film.

To study the resistance of MSQ film to O_2 plasma attack using H_2 plasma treatment, the O_2 plasma treatment is performed for samples STD and A9. Figure 7 shows both the leakage current densities and dielectric constants of samples STD and A9, which were treated by O_2 plasma for 3 min. Both the leakage current and dielectric constant of sample A9 are much lower than that of sample STD. Figure 8 shows the FTIR spectra of samples STD and A9 with O_2 plasma treatment for 3 min. The Si–C and C–H bonds dramatically decrease while the Si–OH bond appears in the spectrum of sample STD after O_2 plasma treatment. However, the Si–C and C–H bonds of sample A9 still remain at a high level after exposure to O_2 plasma. Moreover, Si–OH and H–OH bonds do not appear in the FTIR of sample A9. The experimental results show that the oxygen plasma attack resistance of MSQ film can be enhanced by H_2 plasma treatment.

Finally, the interaction between MSQ and copper was investigated by the electrical characteristic measurement. Figure 9 shows both the leakage current densities and dielectric constants of various post-treated samples with Cu gate at 500 °C annealing temperature. From Fig. 9(a), the leakage current of sample STD with the Cu gate is larger than that of sample STD with Al gate. This indicates that the degradation of dielectric quality is due to copper penetration through MSQ film. However, this issue can also be addressed by H_2 plasma treatment. The leakage current of H_2 plasma treated samples with Cu gate is decreased with increasing duration of H_2 plasma treatment on MSQ. Similar improvement is also observed in the dielectric constant reduction of treated MSQ films, as shown in Fig. 9(b).

We propose that the role of the hydrogen radical in stabilizing the MSQ is to passivate the inner structure of the porous MSQ. The porous structure of MSQ formed during the curing process results in the low dielectric constant. However, distortion of the bonding structure of the MSQ film during curing results in dangling bonds in the MSQ film. In the case of MSQ deposition without a capping oxide layer, the exposed surface area is very large. If the surface is not covered, most of those dangling bonds in the MSQ film will remain exposed. Dangling bonds can then react easily with moisture to form –OH bonds. This will result in an increased dielectric constant and leakage current. In addition, the dangling bonds can enhance the probability of reaction with Cu atoms resulting in increased probability of copper penetration through MSQ films. The hydrogen plasma can provide

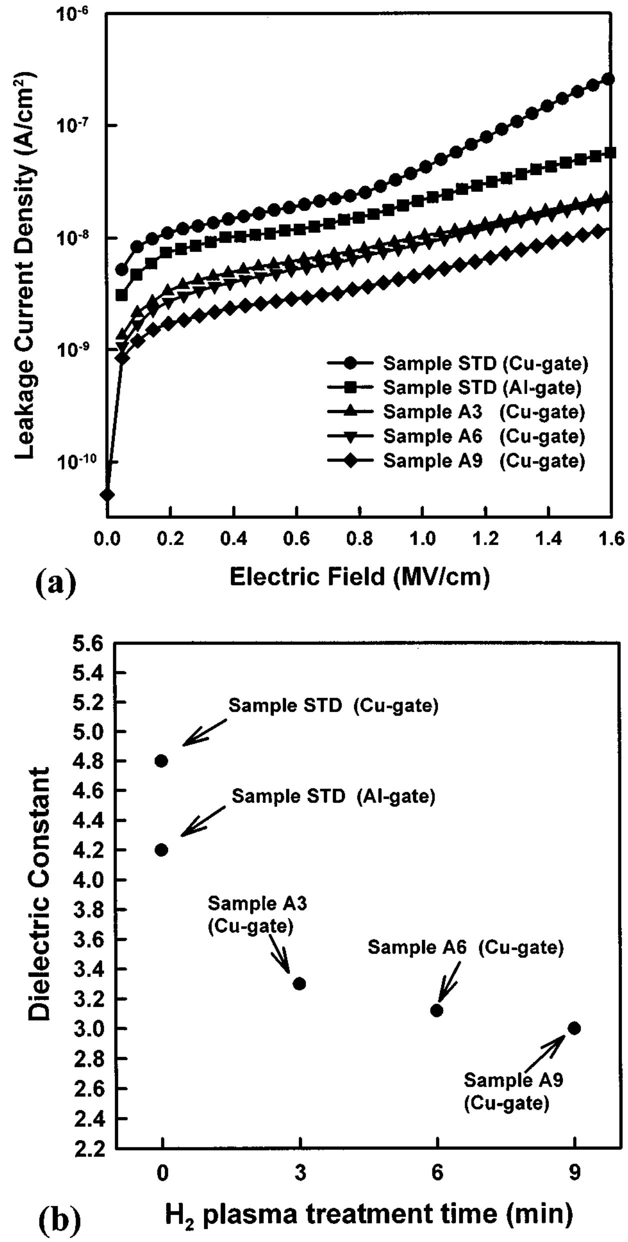

FIG. 9. (a) Leakage current density of various H_2 plasma treated samples with Cu gate after annealing at 500 °C for 30 min. (b) Dielectric constant of various H_2 plasma treated samples with Cu gate after annealing at 500 °C for 30 min.

hydrogen radicals to protect and cover the dangling bonds of the porous MSQ films to prevent the MSQ film from being damaged by oxygen during removing the photoresist and from copper diffusion through MSQ.

IV. CONCLUSIONS

In this work, the effects of H_2 plasma treatment on MSQ films have been investigated. The H_2 plasma treatment provides additional hydrogen to passivate the inner structure of porous MSQ film, and reduces the probability of moisture uptake. FTIR spectra are consistent with this inference. It is found that Si–OH bonds do not appear when MSQ film with H_2 plasma treatment was exposed to O_2 plasma. In addition, copper diffusion into MSQ films can be reduced by H_2 plasma treatment. The leakage current of H_2 plasma treated samples with Cu gate is lower than that without hydrogen plasma treatment. Therefore, H_2 plasma treatment is an effective method to improve the dielectric properties and copper penetration resistance of low-*k* MSQ films.

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