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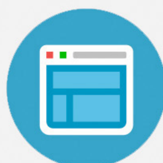
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Eliminating dielectric degradation of low-*k* organosilicate glass by trimethylchlorosilane treatment

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The interaction between low-*k* organosilicate glass (OSG) and photoresist removal is investigated. O_2 plasma ashing and chemical wet stripper are commonly performed to remove photoresist (PR) in integrated circuit fabrication. However, O_2 plasma or wet stripper will attack function groups and cause Si–OH group formation in OSG film during PR removal processing. The Si–OH groups often lead to moisture uptake and consequently dielectric degradation will occur in OSG film. Trimethylchlorosilane (TMCS) treatment can negate the damage in the OSG film after the PR removal process. In addition, chemical TMCS can react with Si–OH groups and reduces moisture uptake so that the dielectric characteristic of OSG can be maintained. Hence, TMCS treatment is a promising method for photoresist removal. © *2002 American Vacuum Society.*
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I. INTRODUCTION

As ultralarge scale integrated (ULSI) circuits are scaled down, interconnect structures with two or more metal levels have become common for the production of high-density circuits and enhance device performance. In these designs, the linewidth and spacings between metal interconnects are also made smaller. The speed-limiting factor is no longer the transistor delay, but the resistance capacitance (RC) delays associated with the metal interconnect system.[1,2]

Many low dielectric constant (low-*k*) materials are proposed in order to decrease the signal propagation delay (i.e., RC delay) for the integrated circuit application. The low-*k* dielectric layers most commonly used in interconnection structures are either spin-on glass or chemically vapor deposited films.[3–7] Spin-on materials particularly have been widely used as an interlayer dielectric in multilevel interconnect architecture because of their process simplification, low cost, and good local planarization capability. One promising low-*k* dielectric, a spin-on deposition organosilicate glass (OSG), is a strong candidate, which has a dielectric constant of 2.6.[8,9] Therefore, OSG has high promise for the future ULSI applications.

Photoresist stripping is the indispensable step in integration processing. However, the dielectric properties of the OSG films will be deteriorated after photoresist stripping.[10,11] Photoresist removal is implemented conventionally by utilizing O_2 plasma ashing and wet stripper dipping. In this work, the impact of O_2 plasma and wet stripper on the OSG film is investigated. In addition, the efficiency of trimethylchlorosilane (TMCS) treatment of the OSG film is also investigated in order to improve dielectric degradation after photoresist stripping. Furthermore, electrical measurement and material analyses have been used to evaluate the OSG characteristic.

II. EXPERIMENT

The precursor of the organosilicate glass (OSG) is one of the silica-based materials, which is stored in solution form. The solvents present are methanol (bp 65 °C), ethanol (bp 78 °C), and butanol (bp 118 °C). The OSG film $(CH_3SiO_{1.5})_n$ has been developed by increasing the number of the methyl group, which causes the hydrophobic surface and results in the lower film polarization. The spin-on deposition is performed in order to coat the OSG solution on a silicon wafer. The rotation of the spin coating was kept at 3000 rpm for 20 s. Then, the sequential bakes were on the hot plate at 180 °C for 2 min and 250 °C for 1 min, respectively. After baking, all the solvent contents (which amount to 76%) were removed, and only the methyl silicone resins are left. Finally,

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TABLE I. Types of samples after various treatments.

Sample label	Sample STD	Sample O	Sample T1	Sample S	Sample T2
Details	As-cured OSG, for comparison	OSG with O_2 plasma ashing for 1 min	Sample O with TMCS repair	OSG with wet stripper dipping at 60 °C for 10 min	Sample S with TMCS repair
Film thickness	5000 (nm)	455 (nm)	468 (nm)	580 (nm)	588 (nm)

the resulting wafers were further processed by furnace curing at 400 °C under nitrogen ambient for 30 min in order to crosslink each methyl silicone resin.

Five samples (samples STD, O, T1, S, and T2) were manufactured for this experiment. These samples are summarized in Table I. The O_2 plasma treatment was carried out in plasma enhanced chemical vapor deposition (PECVD) chamber. The O_2 plasma was operated at a pressure of 300 mTorr, and a radio frequency (rf) power of 200 W. The flow rate was 700 sccm, and the operated temperature was kept at 300 °C. In addition, the wet stripper processing was implemented by utilizing the wet stripper solution (commercial trade mark is ACT 935). The main components of the wet stripper solution were hydroxyamine (NH_2OH) and ethanolamine ($HO–C_2H_2–NH_2$). Moreover, TMCS treatment is performed under TMCS atmosphere at 60 °C for 15 min. Finally, aluminum was deposited onto all of the samples as the top electrode to complete the metal insulation semiconductor (MIS) structure.

The TMCS treatment was performed by utilizing TMCS vapor to treat samples O and S in an oven. The TMCS vapor is generated by heating the TMCS solution and the vapor is conveyed to the oven at 60 °C. Moreover, the TMCS vapor treatment is carried out at a pressure of 760 Torr.

In this study, the chemical structure of the OSG film was investigated by Fourier transform infrared spectroscopy (FTIR). FTIR measurement was performed on the Bio-Rad QS300 FTIR and the data was collected in the absorbance mode. The moisture content in OSG films was monitored by a thermal desorption system spectrometer (TDS). In the duration of the TDS analysis, samples were heated from room temperature to 600 °C at a rate of 20 °C/min in a vacuum chamber. In addition, the outgassing species were collected through the mass spectrometer. The thickness of the OSG film was measured by an n&k analyzer 1200, which can measure the reflectance spectrum of the film. By comparing the resultant equation for theoretical reflectance with the actual measurement of reflectance, the thickness of the thin film can be determined. The dielectric constant of the OSG film was measured by the Keithley Model 82 *CV* meter. The capacitance–voltage ($C-V$) characteristic was measured at 1 MHz. Finally, the current–voltage ($I-V$) characteristic was also measured by using the MIS structure to evaluate the insulating characteristic of the OSG film.

III. RESULTS

In this study, the impact of O_2 plasma ashing and wet stripper dipping on the quality of OSG film is investigated. Figures 1 and 2 show the variations of leakage current density and dielectric constant when OSG film undergoes O_2 plasma ashing and wet stripper dipping, respectively. Both the leakage current and dielectric constant increase after the OSG film undergoes either a O_2 plasma ashing or wet stripper dipping process. Figure 3 shows the FTIR spectra of OSG with O_2 plasma ashing and wet stripper dipping, respectively. The intensities of Si–OH and H_2O groups (933, $\sim$3400 cm^{-1}) increase, whereas the intensities of the C–H peak (2974 cm^{-1}) and the Si–CH_3 peaks (781, 1273 cm^{-1}) decrease when OSG film undergoes O_2 plasma ashing, as shown for sample O. However, all the functional groups of sample S are still kept up to high intensity. The decomposition of the functional groups will lead to the formation of the Si–OH groups which easily induced moisture uptake. For this reason, the TDS analysis was carried out to monitor the

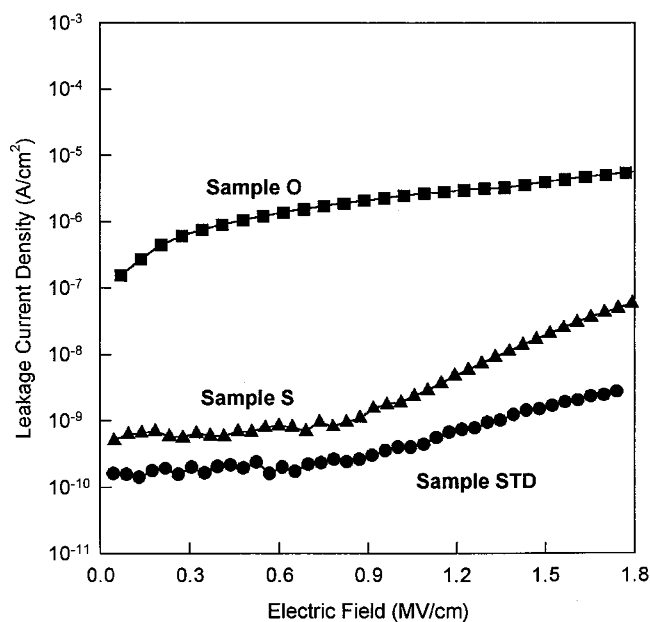

FIG. 1. Leakage current density of sample STD (as-cured OSG), sample O (OSG with O_2 plasma ashing for 1 min), and sample S (OSG with wet stripper dipping at 60 °C for 10 min).

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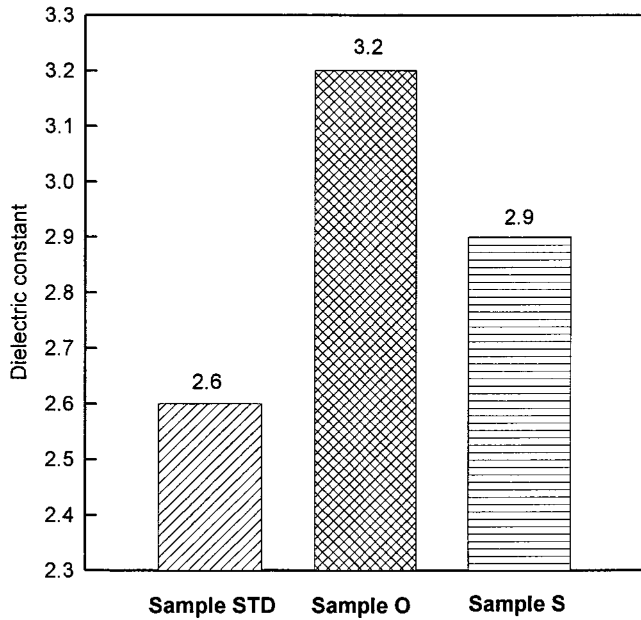


FIG. 2. Dielectric constant of sample STD (as-cured OSG), sample O (OSG with O_2 plasma ashing for 1 min), and sample S (OSG with wet stripper dipping at 60 °C for 10 min).

desorbed moisture from OSG film. The temperature dependence of moisture desorption spectra for samples STD, O, and S are shown in Fig. 4. The moisture content of the OSG film increase significantly after OSG film undergoes either O_2 plasma ashing or wet stripper dipping.

In order to overcome dielectric degradation, TMCS is provided to treat the damaged OSG film. Chemical TMCS, $(CH_3)_3Si{-}Cl$, can eliminate the Si–OH group via the reaction

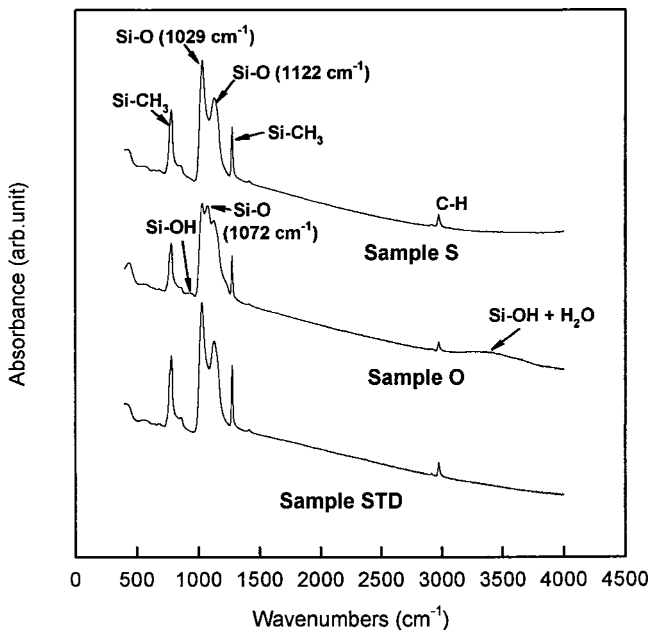


FIG. 3. FTIR spectra of sample STD (as-cured OSG), sample O (OSG with O_2 plasma ashing for 1 min), and sample S (OSG with wet stripper dipping at 60 °C for 10 min).

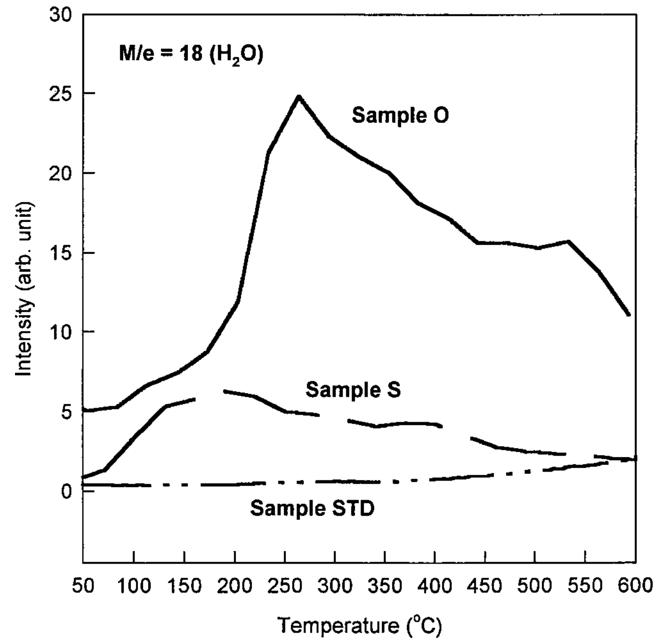
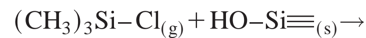


FIG. 4. Temperature dependence of moisture desorption of sample STD (as-cured OSG), sample O (OSG with O_2 plasma ashing for 1 min), and sample S (OSG with wet stripper dipping at 60 °C for 10 min).



$$(CH_3)_3Si{-}Cl_{(g)} + HO{-}Si{\equiv}_{(s)} \rightarrow (CH_3)_3{-}Si{-}O{-}Si{\equiv}_{(s)} + HCl_{(g)} . \quad (1)$$

The effectiveness of TMCS treatment to the OSG film can be proved by the material analyses and the electrical measurements. Figures 5(a) and 5(b) show the leakage current density of samples STD, O, T1, S, and T2. The leakage current density increases when sample STD undergoes O_2 plasma ashing or wet stripper dipping, as shown for samples O and S. Compared with sample T1 and sample T2, the leakage current density of samples O and S decrease after further TMCS treatment. Moreover, the dielectric constant of samples O and S are also decreased by the TMCS treatment, as shown for samples T1 and T2 (in Table II). The negation to the dielectric degradation results from the decrease content of the moisture uptake. Figures 6(a) and 6(b) show the TDS analyses of samples O, T1, S, and T2. It is found that the moisture content of samples T1 and T2 are much lower than that of samples O and S, respectively. As a result, TMCS treatment is able to not only reduce moisture uptake, but also negate dielectric degradation in the OSG film.

IV. DISCUSSIONS

In O_2 plasma ashing process, it is believed that oxygen radicals can react with a large amount of Si–CH_3 groups on OSG film, which causes the content of Si–C and C–H groups to decrease. Oxygen radicals will immediately oxidize the Si–CH_3 groups for the duration of the reaction between the O_2 plasma and Si–CH_3 groups. Hence, the oxidation will convert Si–CH_3 groups into Si–OH groups via the reaction

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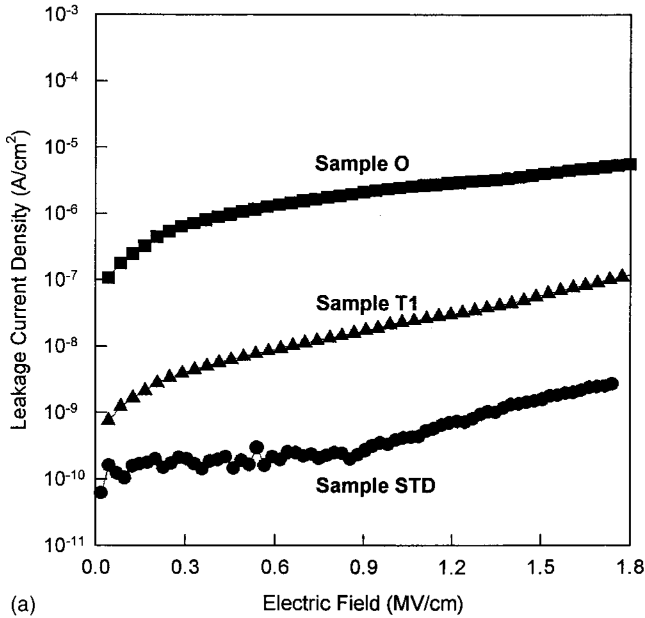


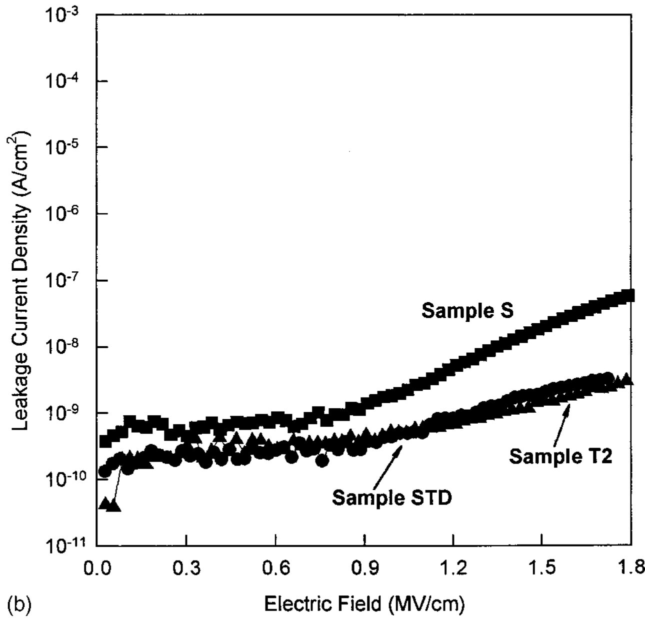
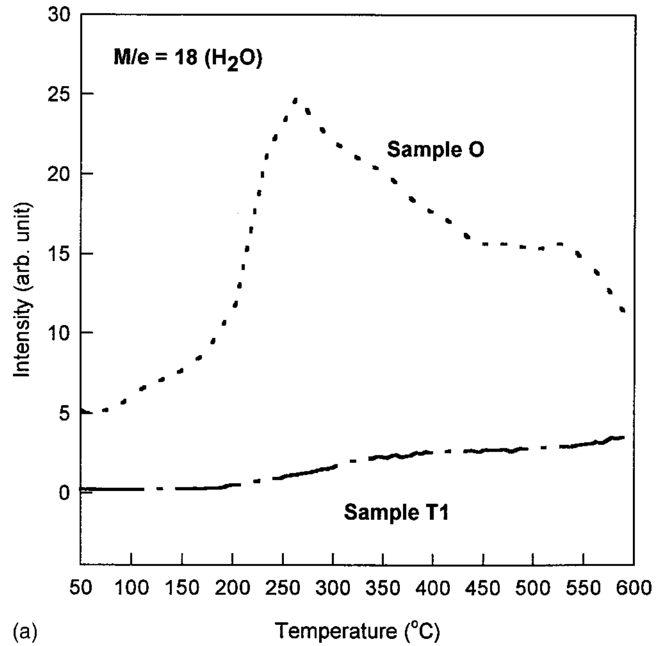


FIG. 5. (a) Leakage current density of sample STD (as-cured OSG), sample O (OSG with O_2 plasma ashing for 1 min), and sample T1 (sample O with TMCS treatment). (b) The leakage current density of sample STD (as-cured OSG), sample S (OSG with wet stripper dipping at 60 °C for 1 min), and sample T2 (sample S with TMCS treatment).



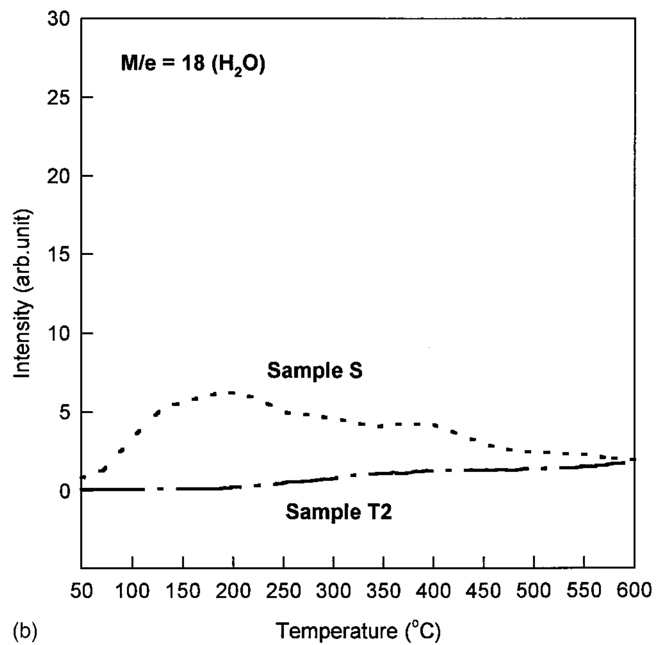


FIG. 6. (a) Temperature dependence of moisture desorption of sample O and sample T1. (b) The temperature dependence of moisture desorption of sample S and sample T2.

TABLE II. Dielectric constant of samples STD, O, T1, S, and T2.

Sample label	Sample STD	Sample O	Sample T1	Sample S	Sample T2
Details	As-cured OSG, for comparison	OSG with O_2 plasma ashing for 1 min	Sample O with TMCS repair	OSG with wet stripper dipping at 60 °C for 10 min	Sample S with TMCS repair
Dielectric constant	2.6	3.2	2.8	2.9	2.7

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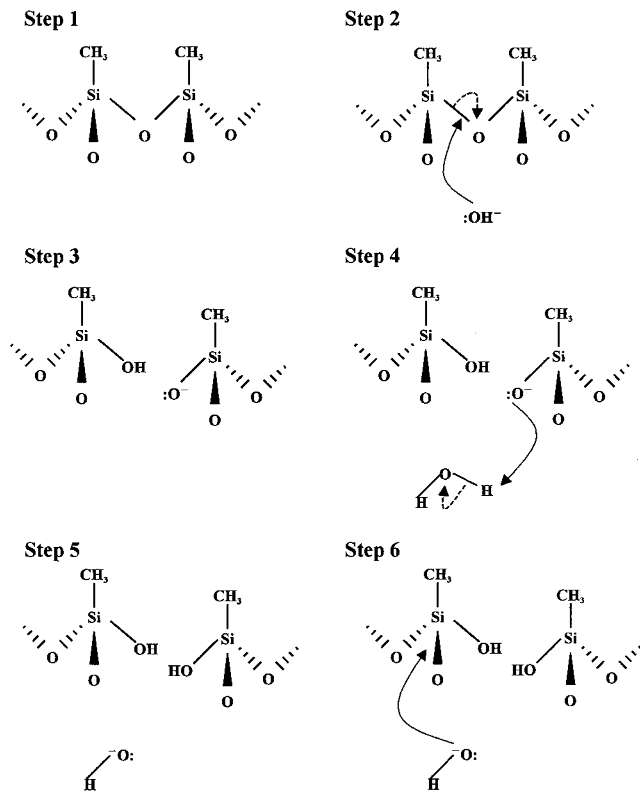
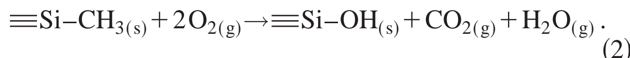
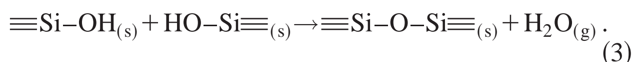


FIG. 7. Scheme of the hydrolysis mechanism on the OSG film.



$$\equiv\text{Si–CH}_{3(s)}+2\text{O}_{2(g)}\rightarrow\equiv\text{Si–OH}_{(s)}+\text{CO}_{2(g)}+\text{H}_2\text{O}_{(g)}. \quad (2)$$

Since the Si–OH group is hydrophilic, it is an easily induced moisture uptake. As a result, the intensities of the Si–OH and H_2O signals will increase after sample STD undergoes O_2 plasma ashing. In addition, a partial amount of Si–OH groups may react with each other via the reaction in the duration of O_2 plasma treatment:



$$\equiv\text{Si–OH}_{(s)}+\text{HO–Si}\equiv_{(s)}\rightarrow\equiv\text{Si–O–Si}\equiv_{(s)}+\text{H}_2\text{O}_{(g)}. \quad (3)$$

Consequently, the intensity of the absorption band (1072 cm^{-1}) is increased, which is characteristic for the Si–O–Si vibration in silica, as shown for sample O (in Fig. 3).

Moreover, the wet stripper processing is performed by utilizing the wet stripper solution (commercial trade mark is ACT 935), which contains a large amount of the high-alkalinity components [i.e., hydroxyamine (NH_2OH) and ethanolamine ($HO–C_2H_2–NH_2$)]. It is considered that the high alkalinity can lead to hydrolysis reaction to the silica film.[12,13] The OSG film belongs to the silica-based material so that the high-alkalinity content (PH = 12.6) of wet stripper solution will result in a hydrolysis reaction on the OSG surface. The hydrolysis mechanism between the OSG film and wet stripper is shown in Fig. 7. The hydroxide ions (OH^-) in the wet stripper will attack the Si–O bonds of the Si–O–Si structure at the liquid–OSG interface, which converts the Si–O bonds into Si–OH bonds. Meanwhile, this leads to the formation of the $Si–O^-$ dangling bonds, as shown for steps 2 and 3 (in Fig. 7). The $Si–O^-$ dangling bond is very unstable, which easily reacts with the hydrogen of the water molecule. Consequently, the reaction converts the $Si–O^-$ dangling bonds into Si–OH bonds. Furthermore, the hydroxide ions (OH^-) will be generated simultaneously due to the hydrolysis reaction, as shown for steps 4 and 5 (in Fig. 7). Hence, the partial OSG film will be partially dissolved by the repetition of the hydrolysis reaction (from steps 2 to 6) to the Si–O bonds of the OSG film.

However, the OSG film contains a large amount of hydrophobic methyl groups. The hydrophobic methyl groups can resist wet stripper solution approaching the OSG surface, which partially prevents the hydroxide ions (OH^-) in wet stripper from attacking the Si–O bonds of OSG film at the liquid–film interface. This will reduce the opportunity of the reaction between the OSG film and the wet stripper solution so that the degree of the hydrolysis reaction will be reduced at the OSG surface, as compared with the silica (without methyl groups content). Although the slight change of the OSG structure caused by the slight hydrolysis reaction is difficult to observe by utilizing the FTIR spectra, the increase of the leakage current and the dielectric constant can demonstrate that the slight hydrolysis reaction really occurs on the OSG film.

The hydrophilic Si–OH groups caused by O_2 plasma or wet stripper treatment easily induce moisture uptake, which can be proved by Fig. 4. As a result, the moisture content of samples O and S are higher than that of sample STD. Consequently, the leakage current density and the dielectric constant will increase when OSG film undergoes O_2 plasma or wet stripper treatment (Figs. 1 and 2).

Figures 8(a) and 8(b) show the FTIR spectra of samples O and S undergoing TMCS treatment. After the O_2 plasma-treated OSG film (sample O) undergoes TMCS treatment, the intensities of the $Si–CH_3$ peaks (781, 1273 cm^{-1}) and the Si–O peaks (1029, 1122 cm^{-1}) increase, whereas the intensities of the Si–OH groups (933 cm^{-1}) decrease, as shown for sample T1 [in Fig. 8(a)].

Another Si–O peak appeared in the absorption band (1072 cm^{-1}) assigned to the reference peak, which is characteristic of silica and resulted from the O_2 plasma treatment to the OSG film. When sample O undergoes TMCS treatment, it is found that the peak-intensity ratio of (Si–C, 781 cm^{-1})/(S–O, 1072 cm^{-1}) on the FTIR spectra increases from 0.542 to 0.571, and the peak-intensity ratio of (Si–C, 1273 cm^{-1})/(S–O, 1072 cm^{-1}) increases from 0.514 to 0.540.

Furthermore, after TMCS treatment, the intensity ratio of (Si–O, 1122 cm^{-1})/(S–O, 1072 cm^{-1}) increases from 0.850 to 0.871, and meanwhile the intensity ratio of (Si–O, 1029 cm^{-1})/(S–O, 1072 cm^{-1}) increases from 1.015 to 1.128, as shown in the FTIR spectra for sample T1 [Fig. 8(a)]. Both the absorption bands (1122, 1029 cm^{-1}) are characteristic for the Si–O vibration in $Si–OSi(CH_3)_3$ groups and moreover the absorption bands (1273, 781 cm^{-1}) are characteristic for the $Si–CH_3$ vibration in $Si–OSi(CH_3)_3$ groups. These results indicate that the TMCS can convert the Si–OH groups into $Si–OSi(CH_3)_3$ groups via Eq. (1). As a result, the con-

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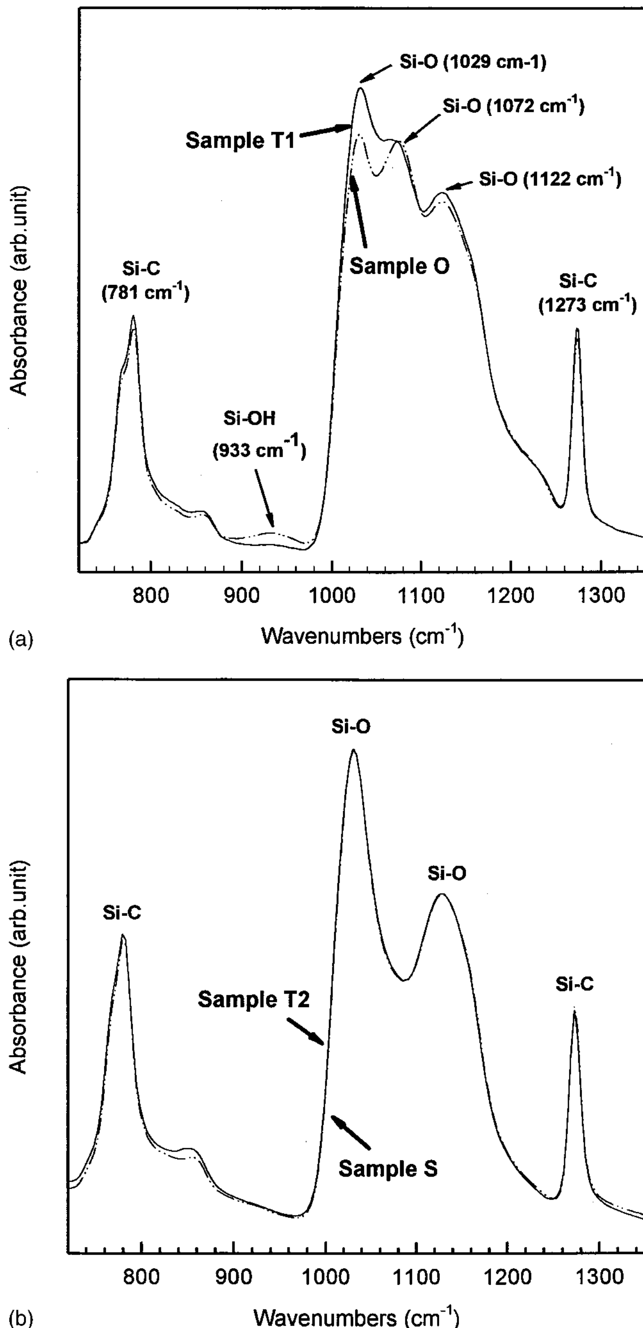

FIG. 8. (a) FTIR spectra of sample O (OSG with O_2 plasma ashing for 1 min) and sample T1 (sample O with TMCS treatment). (b) The FTIR spectra of sample S (OSG with wet stripper dipping at 60 °C for 10 min) and sample T2 (sample S with TMCS treatment).

tent of the $Si-OSi(CH_3)_3$ groups increase, and the content of the Si–OH groups decrease, as shown for sample T1.

Moreover, in comparison with sample T2, Fig. 8(b) shows that the FTIR spectra of sample S are not observed to undergo a conspicuous change after TMCS treatment. This may because since the damage caused by the slight hydrolysis reaction is too slight to be observed, the negation to the slight damage is difficult to examine by utilizing FTIR spectra. However, the decrease of the leakage current and the dielectric constant can still surely demonstrate that the slight damage is negated by TMCS treatment.

TMCS treatment can transform the OSG surface from hydrophilic into hydrophobic due to the hydrophobic $Si-OSi(CH_3)_3$ groups. Therefore, the content of the moisture uptake in the OSG film will be reduced by the TMCS treatment. Hence, both the leakage current density and dielectric constant of the damaged OSG film can be reduced by TMCS treatment. These results indicate that TMCS treatment can negate the OSG damage originating from O_2 plasma ashing and wet stripper dipping.

V. SUMMARY

O_2 plasma ashing and wet stripper treatment lead to the dielectric degradation in OSG film during photoresist removal processing. The dielectric degradation results from the moisture uptake. The TMCS treatment can negate some of the OSG damage after photoresist removal. TMCS treatment can convert the Si–OH groups into $Si-OSi(CH_3)_3$ groups, which makes the damaged OSG surface become more hydrophobic. For this reason, the content of the moisture uptake can be decreased by the TMCS treatment, leading to the decrease of the leakage current and dielectric constant. Therefore, TMCS treatment is an effective method to negate the dielectric degradation in the OSG film for the photoresist removal application.

ACKNOWLEDGMENTS

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