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ARTICLE TYPE

Probing the Molecular Structures of Plasma-damaged and Surface-repaired Low-k Dielectrics

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Fully understanding the effect and the molecular mechanisms of plasma damage and silylation repair on low dielectric constant (low-k) materials is essential to the design of low-k dielectrics with defined properties and the integration of low-k dielectrics into advanced interconnects of modern electronics. Here, analytical techniques including sum frequency generation vibrational spectroscopy (SFG), Fourier transform infrared spectroscopy (FTIR), contact angle goniometry (CA) and X-ray photoelectron spectroscopy (XPS) have been employed to provide a comprehensive characterization of the surface and bulk structure changes of poly (methyl)silsesquioxane (PMSQ) low-k thin films before and after O_2 plasma treatment and silylation repair. O_2 plasma treatment altered drastically both the molecular structures and water structures at the surfaces of the PMSQ film while no bulk structural change was detected. For example, ~34 % Si-CH_3 groups were removed from the PMSQ surface, and the Si-CH_3 groups at the film surface tilted toward the surface after the O_2 plasma treatment. The oxidation by the O_2 plasma made the PMSQ film surface more hydrophilic and thus enhanced the water adsorption at the film surface. Both strongly and weakly hydrogen bonded water were detected at the plasma-damaged film surface during exposure to water with the former being the dominate component. It is postulated that this enhancement of both chemisorbed and physisorbed water after the O_2 plasma treatment leads to the degradation of low-k properties and reliability. The degradation of the PMSQ low-k film can be recovered by repairing the plasma-damaged surface using a silylation reaction. The silylation method, however, cannot fully recover the plasma induced damage at the PMSQ film surface as evidenced by the existence of hydrophilic groups, including C-O/C=O and residual Si-OH groups. This work provides a molecular level picture on the surface structural changes of low-k materials after plasma treatment and the subsequent silylation repair.

Introduction

The continuous downscaling of integrated circuits (ICs) demands constant innovations in both the electrical conductor and the electrical insulators of the interconnect layers in order to improve the overall chip performance and power dissipation.[1, 2] As the feature sizes shrink, the demand to decrease resistance-capacitance (RC) delay, cross-talk noise, and dynamic power consumption has become the driving force for interconnects. In 1997, copper was introduced by IBM[3] and Motorola[4] to replace aluminum as the electrical conductor to produce interconnects with lower resistivity and higher reliability. In order to further reduce RC delay, the conventional interlayer dielectric, silicon dioxide (SiO_2), has been gradually replaced by new electrical insulators with lower dielectric constants, that is, so-called low-k materials.[2] Several generations of low-k materials, including organosilicate glass (SiCOH), have been prepared by plasma-enhanced chemical vapor deposition (PECVD), have been successfully integrated with copper interconnects in several generations of products since 2001.[2, 5-8]

The implementation of low-k materials into Cu interconnects requires plasma etching for low-k patterning.[9] Plasma etching or reactive ion etching (RIE) technology is widely applied to pattern transfer into low-k dielectrics, removal of residual photoresist, cleaning, or surface treatments.[10-14] Unfortunately, uncontrolled plasma exposure can be very harmful to low-k dielectric materials, especially porous low-k films. Among all of the plasma treatments, oxygen plasma is one of the most aggressive in inducing damage to low-k materials. The plasma-induced low-k dielectric damage is manifested in both degradation of properties of low-k dielectrics as well as structural changes such as bonding configuration changes, carbon-depletion, film shrinkage, and surface densification.[9] In particular, the removal of hydrophobic groups and the formation of a carbon depleted layer will result in the adsorption of moisture that can greatly increase the dielectric constant and leakage current, and hence degrade the reliability.

In order to minimize the detrimental effects of plasma exposure, a comprehensive and in-depth understanding of all factors is required for the optimization of processing parameters and for meeting Cu/low-k material integration requirements. Traditionally, many techniques including Fourier transmission infrared vibrational spectroscopy (FTIR), x-ray photoelectron spectroscopy (XPS), secondary ion mass spectroscopy (SIMS), thermal desorption spectroscopy, and ellipsometry, have been used to evaluate the plasma damage of bulk low-k materials after plasma exposure.[8, 15-18] However, none of them can provide *in situ* nondestructive observation of interfacial molecular structural changes and various interfacial water behaviors after plasma damage. As the interconnects in ICs continue to scale down, the surface and interface of low-k materials became more and more important, especially as low-k materials with high porosity become entirely integrated into advanced interconnects. Simulation results pointed out that ~0.4 vol% chemisorbed water on the pore inner surface would result in a 17-23 % increase of the k value.[19] However, few studies have provided direct evidence of how low-k materials change after plasma damage at the surface and buried interface of low-k material at the molecular level. Especially, in some processing steps, low-k dielectric may only be exposed to plasma for a few seconds. Many bulk techniques, for instance, FTIR, would not be able to distinguish the plasma effect due to insufficient detection limits. Therefore, it is of great importance to find techniques that can provide nondestructive detection of the molecular structure changes at the low-k dielectric surface. Combination of molecular structural information with other complimentary results should provide a comprehensive characterization of low-k materials. Molecular structural information can then be correlated to property changes of low-k materials after plasma damage.

Although plasma exposure will induce large enhancement of the k value and degradation of the electrical performance and reliability of low-k materials, it is inevitable in some processing steps. Therefore, it is vital to solve/fix the problems associated with plasma damage, that is, to recover the dielectric properties of plasma-damaged low-k materials. In general, dielectric recovery can be mainly achieved in two different ways:[9] 1) silylation, i.e. restoration of methyl groups by utilizing some silylation agents at the plasma-damaged surface; 2) deposition of hydrophobic groups at the plasma-damaged low-k materials by hydrocarbon plasma, such as CH_4 or CF_4. During dielectric recovery, thermal treatment/UV annealing is additionally used to remove adsorbed water from low-k materials. The silylation method has been widely studied by many research groups. Normally, silylating agents with hydrophobic groups (hydrogen, alkyl, aryl, allyl, phenyl, or vinyl moiety) react with silanol groups on the damaged low-k surface to recover the hydrophobicity of the low-k surface and reduce the moisture uptake which repairs the dielectric.[9] There are few studies that present molecular level observation of dielectric recovery. Especially, the water structures at the low-k material after repair have not been directly related to the restoration of the dielectric constant and the reliability of dielectric properties. Therefore, it's very important to provide *in situ* investigation of water behavior and molecular structures at the surface after repairing the plasma damaged low-k material by silylation to clarify the repair mechanism which will aid in finding the best repair method for low-k materials after plasma damage.

Previously, our group has developed a method to provide *in-situ* nondestructive observation of water uptake and molecular structures at the surface and buried interface of a low-k film by combined studies using sum frequency generation vibrational spectroscopy (SFG) and FTIR.[20] SFG is a second-order nonlinear optical vibrational spectroscopy, which has been developed into a powerful tool to directly probe the molecular structures at the polymer/air surface, polymer/liquid (e.g. water) interface, polymer/polymer interface, polymer/metal interface, and polymer/semiconductor interface in the past 10 years.[21-38] By combining the SFG and FTIR, we were able to directly detect the molecular structures, especially water structures, at the surface and buried interface of a PMSQ film and thus correlate the molecular structures to the low-k property and reliability. It was found that water molecules tend to form strong hydrogen bond with PMSQ at the PMSQ/air surface (chemisorbed water) and PMSQ/SiO_2 buried interface while more weakly hydrogen bonded water was observed in the bulk (physisorbed water),[20] which provided direct evidence that water at the surface/buried interface plays more important roles in the low-k reliability and property degradation than that in the bulk because chemisorbed water cannot be completely removed by normal annealing process compared to physisorbed water.[39] These results are very consistent with simulation results and can well explain the water related time-dependent-dielectric-breakdown (TDDB) mechanism.[19, 39] Herein, following the previous developed methodology, the effects of plasma treatments and silylation repair on the surface and bulk structure of PMSQ were fully investigated. In addition to SFG and FTIR, static contact angle (CA) and XPS were also utilized here to provide surface hydrophilicity change, elemental composition, and chemical states of elements at the PMSQ surface after plasma treatment and repair which provided a more comprehensive characterization of low-k materials after plasma damage and repair. We hope that this research will clarify the understanding of the effect of plasma damage and the subsequent repair on low-k dielectrics and will thus aid in the adjustment of processing parameters of Cu/low-k material integration.

Experimental

Materials

Poly(methyl silsesquioxane) (PMSQ) (≥99.5% purity) was obtained from Gelest. Phenyltrimethoxysilane (PTMS, ≥99.5% purity) and Tetrahydrofuran (THF; ≥ 99.9% purity) were purchased from Sigma-Aldrich (St. Louis, Mo) and were used as received. Right angle fused silica prisms (Altos Photonics) were used as substrates for all SFG measurements and Calcium fluoride (CaF_2) windows (Lambda Optics) were used as substrates for all FTIR experiments.

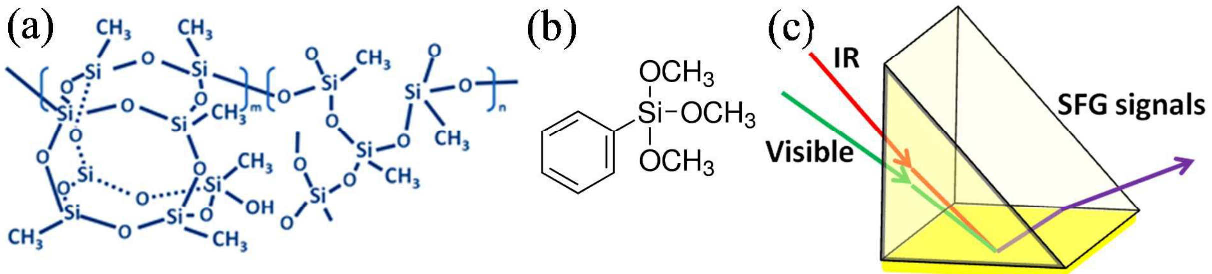

Fig.1 molecular structures of (a) poly PMSQ and (b) PTMS as well as (c) the SFG experimental geometry (prism face-down geometry)

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Sample preparation

The sample preparation method has been reported and will not be repeated in detail here.[20] After the sample preparation, a commercial plasma system (PE-50, Plasma etch) was used to provide oxygen plasma treatment on as-deposited thin films. The treatment time was 5 s at 200 mbar pressure, with O_2 gas flows of ~ 2 sccm (standard cubic centimeters per minute). For silylation, a small amount of PTMS molecules (50 μL) and the plasma-damaged PMSQ thin film were placed inside a vacuum dessicator (Fisher Scientific) under vacuum (~10^{-3} torr) for 1 h to fully complete the silylation reaction of PMTS and Si-OH groups at the PMSQ surface. Film thicknesses were measured by a depth profilometer (Dektak 6 M Stylus Surface Profilometer, Veeco) and the average thicknesses of thin films before and after plasma treatment were around 200 nm, which indicates that 5 s O_2 plasma treatment did not greatly affect the film thickness.

Equipments

A commercially available SFG system (EKSPLA) was utilized for SFG study. The detailed setup has been reported previously.[20, 35, 40] All the SFG spectra collected in this paper were in the ssp (s-polarized signal output, s-polarized visible input, and p-polarized IR input) polarization combination. When using a prism face-down geometry, the ssp SFG signals collected from PMSQ thin films have been shown to be mainly generated from the PMSQ/air surface and the signals from PMSQ/SiO_2 buried interface can be neglected.[20] Herein, a similar prism face-down geometry (Figure 1c) was applied in all SFG experiments. For each sample, spectra were collected from five different spots; for each spot, five spectra were detected to ensure the film homogeneity and data collection reproducibility. The SFG fitting equation and the details about surface coverage and orientation calculations are discussed in the Electronic Supplementary Information (ESI). A Nicolet 6700 FTIR spectrometer controlled by software (OMINC) was used for all FTIR experiments. A CAM 100 optical contact meter (KSV Instruments) was used to perform static water contact angle measurements. At least three samples were used for contact angle measurements and the contact angles from five spots were averaged. XPS measurements were performed by an X-ray photoelectron spectrometer (Kratos Axis Ultra DLD) at the University of Michigan's Electron Microbeam Analysis Laboratory (EMAL). All the XPS spectra were processed and fitted using CasaXPS software.

Results and Discussion

In order to characterize the bulk structure change of low-k film after 5 s O_2 plasma treatment, transmission FTIR spectra were collected from untreated and plasma-damaged PMSQ thin films (Figure 2). The molecular structure of PMSQ is displayed in Figure 1a. A PMSQ molecule consists of two kinds of Si−O structures which are commonly called "cage" and "network" structures. In addition to Si−O bonds, Si-CH_3 groups are also part of the PMSQ structure. Figure 2 exhibits that the FTIR spectral features are almost unchanged before and after O_2 plasma treatment for 5 s, which also resembles most carbon-doped oxide low-k films.[5, 7, 8] In the C−H stretching frequency region, only a sharp CH_3 peak (~2971 cm^{-1}) and a broad water peak (~3400 cm^{-1}) were observed. This broad water peak has been assigned to weakly hydrogen bonded water inside the PMSQ bulk, indicating that most of water molecules in the bulk are physisorbed water.[15, 41] In the fingerprint region, several pronounced peaks were detected, including a strong peak around 1272 cm^{-1} (Si-CH_3 bending mode) and two strong overlapped peaks around 1109 and 1035 cm^{-1}, which were attributed to the caged and network Si−O bond structure, respectively.[8] Undetectable changes in the FTIR spectra acquired from low-k film before and after plasma damage (Figure 2) indicate that almost no structure changes occurred in the PMSQ bulk after exposure to O_2 plasma for 5 s or that the structural changes in the PMSQ bulk were not substantial enough to be detected by FTIR.

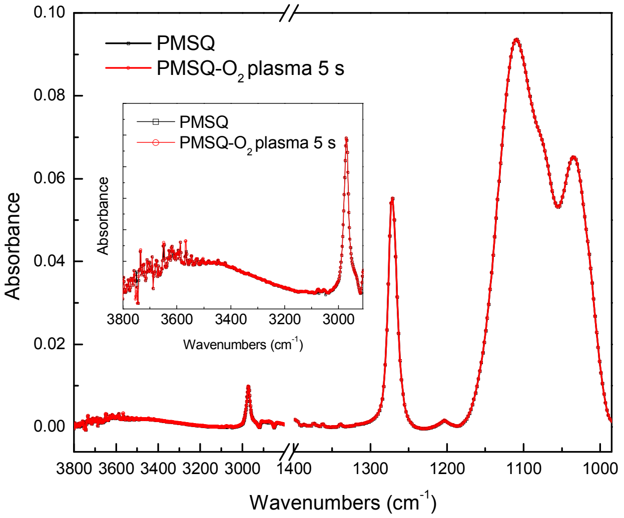

Fig. 2 FTIR spectra acquired from PMSQ thin films before and after oxygen plasma treatment for 5 s

To investigate the effect of plasma on the PMSQ surface, SFG measurements were collected from untreated and plasma-damaged PMSQ thin films, respectively. Different from FTIR results, Figure 3 clearly shows that the SFG spectral features were drastically changed after oxygen plasma for 5 s. Similar to the case of untreated PMSQ shown in Figure 3a, the ssp SFG spectrum collected from the PMSQ thin film after 5 s plasma treatment was also dominated by two peaks located at 2915 and 2970 cm^{-1}, however, the ratios of two peaks are significantly different and the intensities became much weaker compared to the peaks in the SFG spectra collected from the untreated film. These results suggest that the surface of the plasma-damaged PMSQ thin film is still covered by Si-CH_3 groups, but the surface coverage and/or the possible orientation of Si-CH_3 groups were influenced even though the film was only exposed to O_2 plasma for 5 s. This clearly indicates that SFG is much more sensitive than transmission FTIR to surface structural changes.

To obtain more details about the effect of short-term oxygen plasma on the molecular structure changes at the PMSQ surface, the possible orientations of Si-CH_3 groups at the PMSQ surface before and after plasma treatment were deduced. In addition, the surface coverage of Si-CH_3 groups after oxygen plasma exposure was deduced. The detailed calculation method can be found in ESI. SFG spectra fitting results were displayed in Figure 3a-b and the fitting parameters and the calculation results were included in Table 1. The average orientation of Si-CH_3 groups at the surface of untreated PMSQ thin film was ~37 ^{o} (schematic illustration is shown in Figure 3c) which indicates that the Si-CH_3 groups tilt up at the PMSQ surface. Whereas, after exposure to O_2 plasma for only 5 s, the surface orientation of Si-CH_3 groups was ~48 ^{o}, indicating that the Si-CH_3 groups lie down to the surface more compared to the untreated sample. The schematic illustration of a plasma-damaged PMSQ surface is shown in Figure 3d. After determining the possible orientation of methyl groups at the low-k/air interface before and after plasma treatment, the surface coverage change before and after O_2 plasma treatment was deduced using equation S8 (ESI). The coverage change (molecule number density after plasma treatment/molecule number density before plasma treatment) was determined to be ~66 %, suggesting that 5 s oxygen plasma exposure removed ~34 % methyl groups from the PMSQ surface.

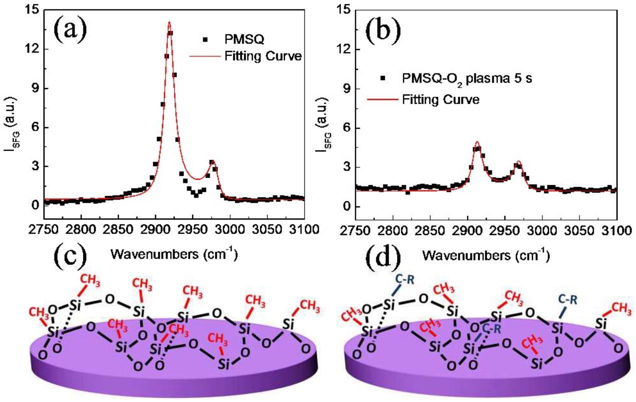

Fig. 3 ssp SFG spectra of a PMSQ thin film before (a) and after (b) oxygen plasma treatment, and the schematic illustrations of the corresponding surface structures of untreated (c) and plasma-damaged (d) PMSQ films

Table 1 Fitting parameter and the corresponding calculation result

Peak	Fitting Parameter	Untreated	O_2 plasma 5 s
Peak 1	A_1	29	15
	Peak center1 (cm^{-1})	2919	2915
	Γ_1 (cm^{-1})	8	8
	$X=A_1/\Gamma_1$	3.6	1.9
Peak 2	A_2	-12	-10.7
	Peak center 2 (cm^{-1})	2980	2970
	Γ_2 (cm^{-1})	8	8
	$X=A_2/\Gamma_2$	-1.5	-1.3
	$\lvert\chi_{yyz,as}/\chi_{yyz,ss}\rvert$	0.4	0.7
Possible orientation (deg.)		~37	~48

After elucidating the molecular structure at the surface and in the bulk of PMSQ thin film after short-term O_2 plasma treatment, the previous-developed method was applied to investigate the effect of a silylation repair treatment on the molecular structure at the surface and in the bulk of plasma-damaged PMSQ thin films.

After repairing the plasma-damaged PMSQ thin film using a silylation reaction, two strong new peaks were detected in the SFG spectrum acquired from the PMSQ surface (Figure 4). These two new peaks were located at ~3020 cm^{-1} and ~3050 cm^{-1}, which can be assigned to υ_{20b} mode and υ_2 mode of aromatic C-H stretching of phenyl rings, respectively.[26] The appearance of pronounced phenyl signals implies that the silylation reaction between PTMS molecules and the plasma-damaged PMSQ thin film was effective. To confirm the chemical reaction instead of physical adsorption of PTMS at the PMSQ surface, the repaired film was rinsed by water and then the surface was examined by SFG. The corresponding result was shown in Figure S2 (ESI); we will discuss these data later. Here, the strong phenyl υ_2 peak and the weak phenyl υ_{20b} peak indicate that the phenyl rings were oriented near the PMSQ surface normal after repair[26]. The corresponding schematic illustration of PTMS at the PMSQ surface after silylation is exhibited in Figure 4b.

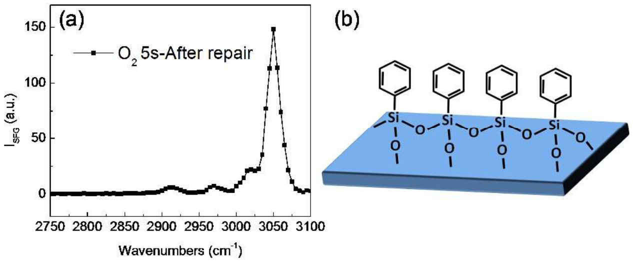

Fig.4 (a) ssp SFG spectrum of plasma-damaged PMSQ thin film after repair, (b) schematic illustration of PTMS deposited on plasma-damaged PMSQ thin films surface

Subsequently, FTIR measurements were performed on the repaired PMSQ thin film to investigate the bulk structure change after silylation. Figure 5 indicates that no phenyl peaks were detected in the FTIR spectrum collected from the repaired film. Combined with the SFG spectrum collected from the repaired PMSQ thin film (Figure 4a), this suggested that only a small amount of PMTS molecules reacted with plasma-damaged PMSQ thin film.

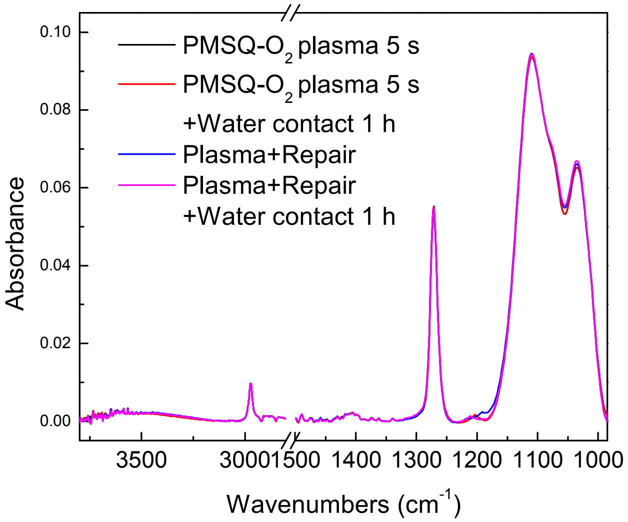

Fig. 5 FTIR spectra of the plasma-damaged PMSQ film before and after contacting with water for 1 hour, and the repaired PMSQ thin films before and after contacting with water for 1 hour

In order to study the repair effect of PTMS silylation, one method is to directly detect water adsorption on the repaired PMSQ thin film. First, water adsorption in the bulk of plasma-damaged and repaired PMSQ was compared by FTIR. The corresponding samples were immersed into water for 1 hour, and then FTIR tests were performed (shown in Figure 5). Almost no spectral features were altered after water immersion for both plasma-damaged and repaired PMSQ thin films, indicating that no more detectable water was present in the bulk of both plasma-damaged and repaired samples. However, degradation of low-k electric reliability and properties after short-term oxygen plasma treatment has been reported in several previous studies,[39, 42] and it was also reported that silylation treatment cannot fully recover the low-k materials.[43] Apparently, more detailed characterization needs to be done here to get a clearer picture about the effect of plasma damage and silylation repair on PMSQ thin films.

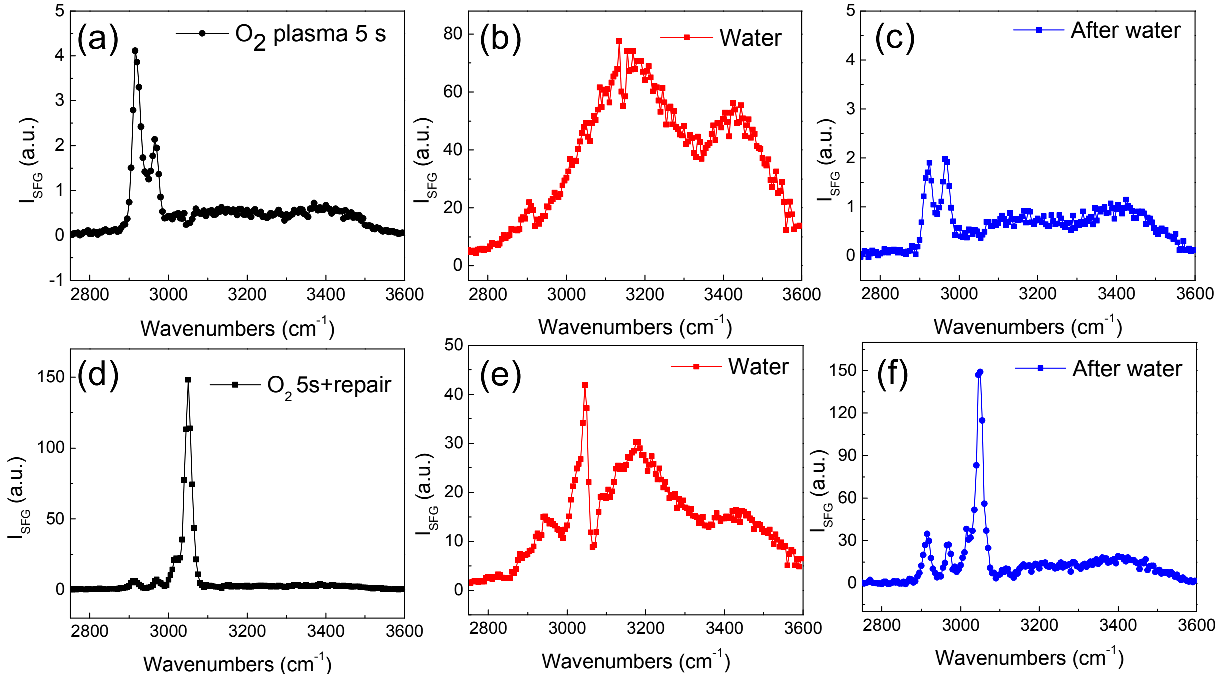

Fig. 6 ssp SFG spectra of the plasma-treated PMSQ thin film before (a), under (b) and after (c) contacting with water, and ssp SFG spectra of the repaired PMSQ thin film before (d), under (e) and after (f) contacting with water

Therefore, *in situ* SFG measurements were implemented next to directly probe the surfaces of PMSQ thin films after O_2 plasma treatment for 5 s and silylation repair to investigate the molecular structures and water behavior during exposed to water. SFG measurements were thus performed at the surfaces of plasma-damaged and repaired PMSQ thin film before and during contact with water and after water removal. Figures 6a-c show the ssp SFG spectra collected from PMSQ thin films in the C-H and water O-H stretching frequency region (2750 – 3600 cm^{-1}) after 5 s O_2 plasma exposure before, during, and after contacting with water, respectively. First, we can see from Figure 6a that only very weak water peaks were detected except for pronounced Si-CH_3 signals, indicating that not much water or not much ordered water molecules were present at the PMSQ/air surface after exposure to O_2 plasma for 5 s. This is slightly different from the untreated PMSQ surface, at which no ordered water was detected.[20] Also, this is very different from the bulk, where physisorbed water was detected in the bulk even before contacting with water (a broad water peak located at ~3400 cm^{-1} was detected by FTIR).

However, during contact with water, two strong water peaks centered near 3150 cm^{-1} and 3400 cm^{-1} were immediately observed in the SFG spectrum (Figure 6b). The water peak near 3200 cm^{-1} has been assigned to strongly hydrogen bonded water (chemisorbed water), while the water peak near 3400 cm^{-1} has been assigned to weakly hydrogen bonded water (physisorbed water).[15, 37, 41] The presence of an SFG peak centered near 3150 cm^{-1}, which is shifted from the 3200 cm^{-1} peak to a lower wavenumber, implies the formation of stronger hydrogen bonds at the PMSQ/water interface. Additionally, these two water peaks are so pronounced that the Si-CH_3 peaks become almost undetectable, indicating that water structures almost dominate the surface of plasma-damaged PMSQ thin films as contacting with water. All these phenomena are distinct from the case of the untreated film, in which only one water peak centered at 3150 cm^{-1} was observed at the PMSQ/water interface. These results suggest that O_2 plasma for only 5 s can highly enhance water adsorption at the PMSQ surface. Oxygen plasma treatment can thus lead to the formation of strongly hydrogen bonded water with PMSQ (~3150 cm^{-1}) and weakly hydrogen bonded water (~3400 cm^{-1}) at the PMSQ/water interface. Combining FTIR and SFG results above (Fig. 5 and Figs. 6a-c), we can conclude that water structures at the PMSQ surface after plasma treatment are also very different to the bulk, i.e., water molecules are more flexible in the bulk, and they prefer to stay in the bulk by forming weak hydrogen bonds (evidenced by FTIR result). Furthermore, the intensity of the SFG water peak did not change much during contact with water, showing that the formation of hydrogen bonded water at the PMSQ surface is quite fast, which is very similar to the untreated case. Additionally, based on the previous studies, the chemisorbed water components are much more difficult to be removed compared to the physisorbed water from the low-k network.[15, 39] However, the direct detection of such water components at the pore inner surfaces is quite challenging because the amount of these water components is still very small, especially after short-term plasma treatment (almost no water changes can be detected by FTIR shown in Figure 6). Here, following the previous developed method,[20] it's capable of providing the direct evidence that water adsorption was highly enhanced at the PMSQ surface and two kinds of water components, especially chemisorbed water, dominated the PMSQ surface even exposed to O_2 plasma for only 5 s. Therefore, considering the similar chemical environment in the pore inner surface for porous low-k materials, it's suggested that even after 5 s oxygen plasma exposure, as water molecules reach the pore inner surfaces, the formation of strong hydrogen bonds between water molecules and the low-k material at the pore inner surfaces could be highly enhanced, which would induce the degradation of low-k dielectric and decrease the low-k reliability;[17, 39] Meanwhile, there was also a large amount of weakly hydrogen bonded water retained at the plasma-damaged PMSQ/water interfaces, and this part of water will also contribute to the increase of dielectric constant.[17] Since these chemisorbed water components have been closely related to the TDDB failure mechanism of low-k materials,[39] we believe the great increase of the chemisorbed water molecules at the pore inner surfaces even after 5 s O_2 plasma exposure is the main reason for these negative effects on low-k material properties rather than the water components in the bulk. In addition, after contacting with water, the molecular structures at the low-k/air interface were found to be permanently changed. Figure 6c shows that the ratio of two Si-CH_3 peaks is different from the one before water contact. More importantly, there are some ordered water components detected on the plasma-damaged PMSQ surface. Since these two kinds of water components are not easily removed at room temperature, we believe the weaker water signals shown in Figure 6c are due to less ordered water after water contact rather than less water left at the interface.

Subsequently, similar SFG measurements were performed on the repaired PMSQ thin films to examine the repair effect of PTMS silylation on restoration of the PMSQ thin film. Figures 6d-f show the ssp SFG spectra collected from plasma-damaged PMSQ thin films in the C-H and water O-H stretching frequency region (2750 cm^{-1} – 3600 cm^{-1}) after silylation repair before, during, and after contacting with water, respectively. Different from the plasma-damaged sample shown in Figure 6a, Figure 6d exhibits that almost no water was detected after the silylation repair. To examine the quality of PTMS grown at the surface of plasma-damaged PMSQ thin film, an as-grown PMSQ thin film after silylation was immersed into water for various times. The water stability of repaired PMSQ thin film was thus tested. The ssp SFG spectra of repaired PMSQ thin film before and after water immersion for 1 h, 2 h and 3 h were shown in Figure S2a in ESI. In order to see the spectra feature changes more clearly, the ssp SFG spectra shown in Figure S2a were normalized and the C-H stretching regions were shown in Figure S2b. Figure S2 shows that the intensity of phenyl peaks did not change much after water immersion, meanwhile the relative peak ratio of two phenyl peaks was only altered a little bit. More importantly, the intensities of Si-CH_3 groups were increased. This indicates that possible restructuring occurred at the repaired PMSQ surface after water immersion. It's notable that after immersing in water for 2 h, the SFG spectra features remained very similar, that is, the ratios of Si-CH_3 and phenyl peaks were very similar after water immersion for 2 hours, indicating that the surface structures became more stable after water immersion for 2 hours. It's possible that in addition to the silylation reaction, there are some PTMS molecules physically absorbed at the repaired PMSQ surface, and after water immersion, the physisorbed PTMS molecules no longer stayed at the repaired PMSQ surface which changed the surface molecular structure. It's also possible that the changes of spectral features are due to the water-induced restructuring at the repaired PMSQ surface. Besides, some weak water signals, that is, a clear 3400 cm^{-1} peak and some weak signals at lower wavenumbers near 3200 cm^{-1}, can also be detected in Figure S2a after water immersion, indicating that some ordered water structures were also formed after water immersion.

Since the molecular structures remained unchanged after immersion in water for 2 hours, the *in situ* molecular structure changes and water behavior at the repaired PMSQ surface as contacted with water were thus observed to elucidate the repair effect of PTMS silylation on the plasma-damaged low-k material. Figure 6f shows the *in situ* ssp SFG spectrum of repaired PMSQ thin films in contact with water. We can see that phenyl peak located at ~3050 cm^{-1} still dominates the spectrum. Besides, Si-CH_3 peaks are also detectable here which were overlapped with broad water peaks. More importantly, the intensities of two water peaks are highly depressed after PTMS repair compared to the plasma-damaged one shown in Figure 6b, although the ~3200 cm^{-1} peak is still more pronounced than ~3400 cm^{-1}. This means either less water components and/or less ordered water components were formed at the repaired PMSQ/water interface. More techniques including CA and XPS were utilized next for further characterization of the PMSQ surface after plasma damage and repair to clarify the surface structure change.

Static water contact angle measurements were carried out at the plasma-damage and repaired PMSQ thin films next. The CA results of PMSQ thin films before and after oxygen plasma treatment for 5 s and then repaired by PTMS molecules are shown in Table 2. For untreated PMSQ thin films, the surface CA is ~94.6 ^{o}, indicating that the untreated PMSQ film is quite hydrophobic. However, after exposure to O_2 plasma for only 5 s, the surface CA drastically decreased to ~32.9 ^{o}, suggesting that even short-term O_2 plasma treatment will highly increase the surface hydrophilicity. This is very consistent with our SFG results shown above that indicated that CH_3 groups were removed from PMSQ surface by O_2 plasma thus the surface become more hydrophilic. Whereas after repairing the plasma-damaged PMSQ surface by PTMS silylation, the surface CA increased from ~32.9 ^{o} to ~63.6 ^{o}, indicating that growing a PTMS layer on the plasma-damaged PMSQ surface can repair a part of Si-OH groups. However, the PMSQ surface hydrophobicity was not completely recovered, which is very consistent with previous research. [43, 44]Also, this is also very consistent with our SFG observation above (Figure 6). In Figure 6e, we can see that there are still two pronounced water peaks on the repaired surface as contacting with water, but the overall intensities of these water peaks decreased substantially compared to the plasma-damaged one shown in Figure 6b. Combining the CA results, we believe that the decrease of SFG water peaks in the repaired PMSQ surface could be attributed to the less water components formed on the repaired surface instead of less ordered water components.

Table 2 Static water contact angles of PMSQ films before and after oxygen plasma treatment for 5 s, as well as after repair.

Samples	Contact angle (deg.)
Without treatment	94.6 ± 3.7
After O_2 plasma treatment for 5 s	32.9 ± 3.9
After repair	63.6 ± 3.2

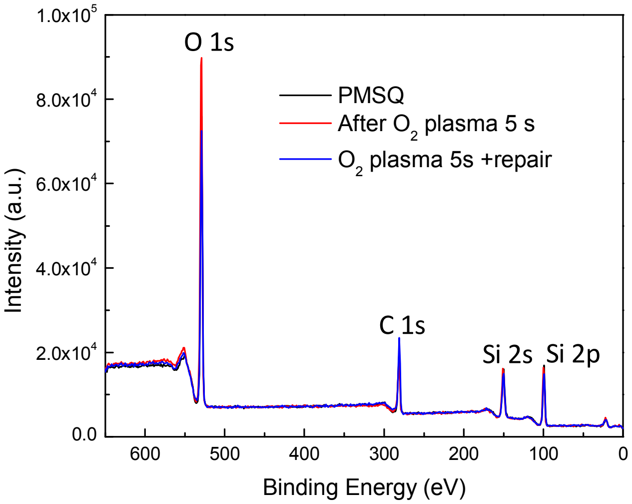

Fig. 7 XPS survey spectra of untreated, plasma-damaged and repaired PMSQ thin films

Next, XPS measurements were utilized to give more information about element compositions and chemical binding before and after O_2 plasma treatment and PTMS repair. First, XPS survey spectra were collected from the untreated, plasma-damaged, and repaired PMSQ thin films, respectively, to provide information about element composition changes. Figure 7 shows the XPS survey spectra collected from three samples in the energy range of 0 - 650 eV. Clearly, the intensity of the oxygen 1s peak at ~529 eV increased after oxygen plasma treatment for 5 s, while after PTMS silylation, this peak decreased again and became similarly strong as the untreated one. However, the changes of other peaks, such as C 1s, Si 2p, cannot be seen as clearly as O 1s peak in Figure 7. Therefore, in order to get more quantitative details, the XPS spectra shown in Figure 7 were fitted and the fitting results were displayed in Table 3. We can see from Table 3 that after 5 s oxygen plasma treatment, the atomic percentage of O 1s increased from 40.67 to 47.95 %, and then returned to 40.75 % after PTMS repair. Meanwhile, the C 1s content decreased from 34.22 to 29.10 %, and then increased to 37.80 % after repair. The XPS spectra shown here (Figure 7 and Table 3) imply that the oxygen content at PMSQ surface after 5 s plasma treatment increased and was recovered to the similar level as the untreated sample after repair by PTMS silylation. The carbon signal decreased after the oxygen plasma treatment and then increased again by PTMS silylation. These results are very consistent with our SFG and CA results, indicating that the damaged surface was effectively repaired by PTMS silylation. More discussions about the comparison of the experimental results collected from varous techniques will be presented later.

Table 3 Quantitative fitting results of XPS survey spectra of untreated, plasma-damaged and repaired PMSQ thin films.

	Before treatment	After O_2 plasma 5 s	After repair
	Atomic %	Atomic %	Atomic %
C 1s	34.22	29.10	37.80
O 1s	40.67	47.95	40.74
Si 2p	25.12	22.95	21.46

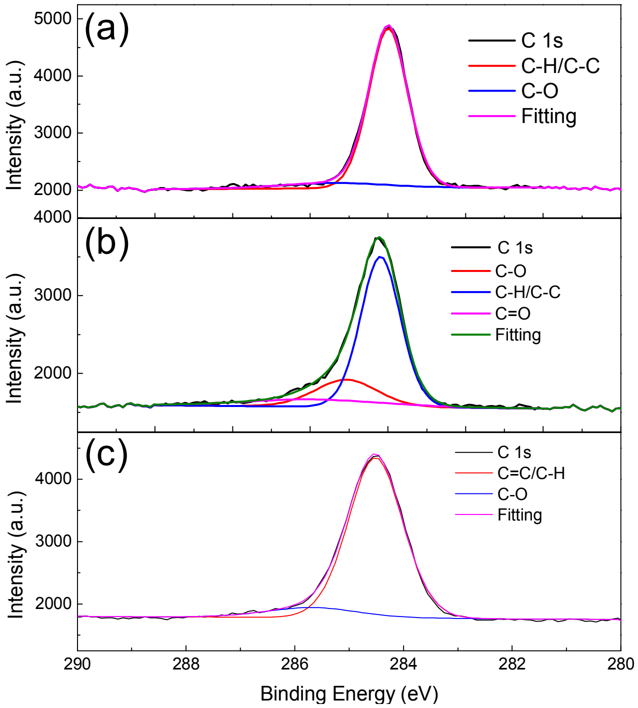

Fig. 8 C 1s high resolution XPS spectra collected from (a) the untreated, (b) plasma-damaged and (c) repaired PMSQ thin films

Furthermore, high-resolution XPS measurements were carried out on the untreated, plasma-damaged and repaired PMSQ thin films to obtain more information about the chemical state changes. That is, the local chemical binding energy changes of a specific element were examined to provide more information about O_2 plasma treatment and PTMS repair of PMSQ thin films. Here, a typical C 1s envelope provides local binding information about carbon. Additionally, all high-resolution XPS spectra were fitted to get more quantitative information about the PMSQ samples. The fitting results as well as the experimental spectra are exhibited in Figure 8 and all the fitting parameters are listed in Table 4. We can see from Figure 8 and Table 4 that for untreated PMSQ, the majority of the carbon near the surface is in the form of C-C/C-H bonds, only very small amounts of C-O (3.37%) were detected which may be due to slow natural oxidation in air. However, oxygen plasma treatment leads to a increase in the percentage of C-C/C-H bonds from 96.63 % to 69.04 %, meanwhile both C-O and C=O signals became higher, indicating breaking of the C−C/C-H bonds as well as the formation of new bonds such as C−O and/or C=O bonds after O_2 plasma exposure.

In addition, in the case of plasma-damaged PMSQ thin film after silylation repair by PTMS, the trend is opposite. That is, both C-O and C=O signals became lower while the C-C/C-H bonds increased from 69.04 % to 91.55 %, suggesting that the repaired surface is dominated by C-C/C-H bonds again. These results are very consistent with SFG, CA as well as XPS survey results.

The cumulative results show a clear picture about the effect of oxygen plasma treatment and surface silylation repair on the surface structural changes of PMSQ thin films at the molecular level. Even though FTIR is not sensitive enough to monitor the molecular structure changes after oxygen plasma treatment and surface repair by silylation, utilizing high surface-sensitive techniques, including SFG, CA and XPS, enabled us to get more information about the surface structure changes. In particular, *in situ* SFG observation is capable of providing quantitative molecular structure changes and the various components of water structures at the surfaces of PMSQ thin films after different treatments. The surface structure changed dramatically even after exposure to O_2 plasma for only 5 s, the possible orientation of Si-CH_3 groups increased from 37 ^{o} to 48 ^{o} vs. the surface normal, meanwhile about 34% CH_3 groups have been removed from the PMSQ surface by 5 s O_2 plasma treatment. Besides, XPS results indicated that 5 s oxygen plasma treatment also increased the C-O/C=O bonds at the PMSQ surface. The removal of CH_3 groups and the formation of new C-O/C=O bonds at PMSQ surface lead to a more hydrophilic surface (CA decreased from ~94.6 ^{o} to ~34.9 ^{o}), which highly facilitate the water adsorption at the plasma-damaged PMSQ surface. *In situ* SFG observation indicated that oxygen plasma treatment not only enhanced the overall water adsorption but also influenced the water structures formed at the PMSQ surface. That is, during exposure of low-k surfaces to water, two kinds of water structures, chemisorbed water and physisorbed water, were directly detected at the plasma-damaged PMSQ/water interface. More importantly, ordered strongly hydrogen bonded water (chemisorbed water) dominate the plasma-damaged PMSQ/water interface, which should be the main reason for the degradation of low-k property and reliability. However, after repairing the plasma-damaged PMSQ surface by PTMS silylation, a PTMS layer was grown at the plasma-damaged PMSQ surface. SFG spectra displayed pronounced phenyl peaks after repair, suggesting that the phenyl groups stand up more at the repaired PMSQ surface. The restoration of plasma-damaged PMSQ by PTMS molecules containing phenyl groups makes the PMSQ surface more hydrophobic, evidenced by the CA which increased to ~63.6 ^{o}. Additionally, XPS results indicated that there are still some C-O bonds left at the PMSQ surface even after silylation. *In situ* SFG results show that although overall water adsorption at the repaired PMSQ surface is highly suppressed, some ordered water structures were still formed during contact with water. Combing all these results together, it is suggested that the ordered water signal detected at the repaired PMSQ surface may be due to uncompleted silylation between PTMS and Si-OH groups (which can be proved by water stability test shown in Figure S2) or C-O/C=O bonds caused by O_2 plasma. This is why PTMS silylation method cannot fully recover the plasma-damaged PMSQ surface. Considering the similarity of PMSQ/air surface and the surfaces of pores inside the PMSQ film, we believe that the plasma effect and the repair discussed in this paper could also reveal the water interactions on the surfaces of the pores inside the porous low-k materials after exposed to O_2 plasma and silylation repair.

Table 4 Fitting results of C 1s peaks in high resolution XPS spectra shown in Fig. 8

Atomic Cont (%)	C-C/C-H	C-O	C=O
Untreated	96.63	3.37	/
Plasma-treated	69.04	19.54	11.42
Repaired	91.55	8.45	/

Conclusions

In conclusion, a detailed characterization using various analytical techniques, including FTIR, SFG, CA and XPS, has been implemented to analyze the molecular structures and water structures at the surfaces and in the bulks of the PMSQ thin films before and after oxygen plasma treatment for 5 s, as well as after surface repair by PTMS silylation. First of all, it was found that almost no bulk structure changes could be detected by FTIR after 5 s O_2 plasma treatment and silylation repair. However, both the surface molecular structures and water structures were found to be changed significantly even after exposure to O_2 plasma for 5 s. ~34 % Si-CH_3 groups were removed from the PMSQ surface by 5 s oxygen plasma treatment, and the possible orientation of Si-CH_3 groups at the PMSQ surface was determined to be tilted towards the surface more compared to the untreated case. These changes of the Si-CH_3 groups and the partial/full oxidation by O_2 plasma treatment for 5 s (increase of C-O/C=O bonds) highly facilitate the water adsorption at the PMSQ surface (because the surface became more hydrophilic), especially strongly hydrogen bonded water (chemisorbed water) was found to dominate the plasma-damaged PMSQ surface during exposure to water, meanwhile weakly hydrogen bonded water (physisorbed water) was also detected. Herein, we provide direct evidence that even 5 s O_2 plasma treatment will cause permanent changes of the molecular structures at the surface, increasing both chemisorbed and physisorbed water, which may be one of the main reasons leading to the degradation of low-k properties and reliability. Furthermore, after repairing the plasma-damaged PMSQ surface by PTMS, the surface hydrophilicity can be recovered to a certain degree. However, the existence of hydrophilic groups including C-O/C=O and some possible Si-OH groups induce both chemisorbed and physisorbed water formed at the repaired PMSQ surface as exposed to water; we believe that this is the main reason why silylation method would not be able to fully recover the PMSQ surface after oxygen plasma damage. As we discussed above, plasma treatment may remove the hydrophobic groups such as methyl groups and form a carbon depleted layer, resulting in the adsorption of moisture that can greatly increase the dielectric constant and leakage current, and hence degrade the reliability. This research demonstrates that SFG can be used as a unique and powerful technique to quantify the surface coverage and molecular orientation of methyl groups on low-k material surfaces, as well as the adsorbed water interfacial structure before and after plasma treatment, providing molecular level understanding on the impact of plasma treatment on low-k materials. In addition, SFG can quantify the surface coverage and molecular orientation of methyl groups on low-k material surface after the surface repair, testing the effectiveness of the repair process directly at the molecular level. We believe that SFG can be developed into a power tool to characterize not only low-k materials but also other organic and polymer materials used for modern microelectronics.

Notes and references

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†Electronic Supplementary Information (ESI) available: The calculation method and details about how to deduce the possible orientation of Si-CH_3 groups and the relatively change of the surface, and ssp SFG spectra collected from the repaired PMSQ thin films after immersion in water for 1 h, 2 h and 3 h to examine the water stability of PTMS film grown in plasma-damaged PMSQ surface are demonstrated in the ESI. See DOI: 10.1039/b000000x/

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