Electronic Supplementary Information

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

Dielectric Materials

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SFG experimental and calculation

Briefly, the SFG system used here was purchased from EKSPLA, and a Nd:YAG laser was used to generate the visible and infrared input beams. The fundamental output from the Nd:YAG laser was a 1064 nm beam with a 50 Hz repetition rate and a \sim 30 ps pulse duration. The fixed frequency 532 nm visible input beam and the infrared beam with tunable frequency in the range of 2.3–10.0 µm were overlapped spatially and temporally at the surface of PMSQ films on fused silica prisms using a prism face-down geometry (shown in Figure 1c). The input angles of the two input beams are 60° and 53° versus the surface normal, respectively. The pulse energies for the visible and infrared beams were about 9 and 90 µJ, respectively. Both laser beam diameters were about 500 µm at the PMSQ film surface. The SFG spectra were collected with the ssp (s-polarized sum frequency output, s-polarized visible input, and p-polarized IR input) polarization combination.

The output SFG intensity in the reflection mode can be written as: ¹

$$I(\omega) = \frac{8\pi^3 \omega^2 sec^2 \beta}{c^3 n_1(\omega_1) n_1(\omega_2) n_1(\omega)} |\chi_{eff}^{(2)}|^2 I_1(\omega_1) I_2(\omega_2) AT$$
Equation S1

where β is the output sum frequency reflection angle, c is light speed, $n_i(\omega_i)$ is the frequency (ω_i) dependent reflective index of the medium, $I_1(\omega_1)$ and $I_2(\omega_2)$ are the intensities of the input visible and IR fields, respectively. T is the input beam pulse width, A is the overlapping area of the two input beams at the sample surface or interface, and $\chi_{eff}^{(2)}$ is the effective second-order nonlinear optical susceptibility. We can see that I (ω) is proportional to $|\chi_{eff}^{(2)}|^2$. We collected ssp spectra in this paper, and $\chi_{eff}^{(2)}$, ssp can be written as: ¹

$$\chi_{eff,ssp}^{(2)} = L_{yy}(\omega)L_{yy}(\omega_1)L_{zz}(\omega_2)sin\beta_2\chi_{yyz}$$
 Equation S2

where β_2 is the input angle of the infrared beam, L_{ii} 's are the Fresnel coefficients responsible for the local field correction of the two input and one output beams, and χ_{yyz} is one tensor component of the second-order nonlinear susceptibility within the surface-fixed coordinate system.

An SFG spectrum can usually be fitted using the following equation: ²

(2)

$$\chi_{ijk}^{(2)} = \chi_{NR} + \sum_{q} \frac{A_q}{\omega_2 - \omega_q + i\Gamma_q}$$
 Equation S3

where χ_{NR} is the non-resonant background arising from the electric polarization of the surface or interface and the adjacent media, and A_q , ω_q , and Γ_q are the strength, resonant infrared frequency, and damping coefficient of the *qth* vibrational mode, respectively.

For a methyl group with C3 υ symmetry, we can determine the relationship between different components of the second-order nonlinear susceptibility in the lab coordinate system and the molecular hyperpolarizability in the molecular coordinate system by assuming a δ -function distribution of θ .² Therefore, for the C-H symmetric stretch of CH₃, we have: ²

$$\chi_{yyz,ss} = \frac{1}{2} N_s \alpha_{ccc} [\langle \cos\theta \rangle (1+r) - \langle \cos^3\theta \rangle (1-r)]$$
Equation S4

While for the asymmetric stretches, we have:²

$$\chi_{yyz,as} = -\frac{1}{2} N_s \alpha_{caa} (\cos\theta - \cos^3\theta)$$
 Equation S5

where "ss" stands for symmetric stretch, "as" stands for asymmetric stretch, N_s is the molecular number density, α is the molecular hyperpolarizability tensor element, and r is the ratio of the hyperpolarizability components α_{aac} and α_{ccc} .²

Therefore, we can have:

$$\left|\frac{\chi_{yyz,as}}{\chi_{yyz,ss}}\right| = \left|\frac{\alpha_{caa}}{\alpha_{ccc}}\left(\frac{\langle \cos\theta - \langle \cos^{3}\theta \rangle \rangle}{\langle \cos\theta \rangle (1+r) - \langle \cos^{3}\theta \rangle (1-r)}\right)\right|$$

Equation S6

Additionally, a Gaussian distribution function can be generally used to describe the average tilt angle and its distribution:

$$f(\theta) = Cexp\left[\frac{(\theta - \theta_0)^2}{2\sigma^2}\right]$$
Equation

S7

where θ_0 is the averaged tilt angle, σ is the angle distribution, and C is the normalization constant.^{2, 3}

Figure S1 shows the calculated $|\chi_{yyz,as}/\chi_{yyz,s}|$ value as a function of the average tilt angle for a δ distribution (σ =0). From SFG fitting, we know that the fitted $|\chi_{yyz,as}/\chi_{yyz,s}|$ values are about 0.41 and 0.71 for the untreated and plasma-damaged PMSQ samples. Thus from Figure S1, we can deduce that the possible orientations of the Si-CH₃ groups at the PMSQ surfaces before and after oxygen plasma treatment are about 37 ° and 48 ° assuming a δ angle distribution.

After obtaining the possible orientation of Si-CH₃ groups at the PMSQ surface before and after oxygen plasma treatment for 5 s, we can have:

$$\left|\frac{\chi_{yyz,ss,after}}{\chi_{yyz,ss,before}}\right| = \left|\frac{\frac{1}{2}N_{s,after}\alpha_{ccc}[\langle \cos\theta_{after}\rangle(1+r) - \langle \cos^{3}\theta_{after}\rangle(1-r)]}{\frac{1}{2}N_{s,before}\alpha_{ccc}[\langle \cos\theta_{before}\rangle(1+r) - \langle \cos^{3}\theta_{before}\rangle(1-r)]}\right|$$

Equation S8

Since $\chi_{yyz,ss}$ and θ for both cases before and after oxygen plasma treatment are known, for r=4, we can deduce that the molecular number density ratio of methyl before and after oxygen plasma treatment for 5 s is: $N_{s,after}/N_{s,before} = \sim 0.66$.



Fig. S1 Calculated value of $|\chi_{yyz, as}|/|\chi_{yyz, ss}|$ for the Si-CH₃ groups at the PMSQ/air interface as a function of the tilting angle θ with a δ distribution (σ =o) and the deduced possible orientation angles of the Si-CH₃ groups at the surfaces before and after oxygen plasma treatment for 5 s.



Fig. S2 Water stability of PTMS SAMs at the PMSQ surfaces after silvlation. (a) ssp SFG spectra collected from the surface of repaired PMSQ thin film before and after immersing in water for 1 h, 2 h and 3 h. (b) The C-H stretching frequency region of the normalized ssp SFG spectra of the same SFG spectra shown in Figure S2a.

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