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Effect of the C-bridge length on the ultraviolet-resistance of oxycarbosilane low-k films

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The ultra-violet (UV) and vacuum ultra-violet (VUV) resistance of bridging alkylene groups in organosilica films has been investigated. Similar to the Si-CH₃ (methyl) bonds, the Si-CH₂-Si (methylene) bonds are not affected by 5.6 eV irradiation. On the other hand, the concentration of the Si-CH₂-CH₂-Si (ethylene) groups decreases during such UV exposure. More significant difference in alkylene reduction is observed when the films are exposed to VUV (7.2 eV). The ethylene groups are depleted by more than 75% while only about 40% methylene and methyl groups loss is observed. The different sensitivity of bridging groups to VUV light should be taken into account during the development of curing and plasma etch processes of low-k materials based on periodic mesoporous organosilicas and oxycarbosilanes. The experimental results are qualitatively supported by *ab-initio* quantum-chemical calculations. © 2016 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4939449>]

Low-k dielectrics are needed in order to reduce the resistance $\times$ capacitance (RC) delay and the capacitive-power dissipation with the downscaling metal interconnect dimensions in next generation ultra-large-scale integration devices.^{1,2} The semiconductor industry has so far been using silica-based films for inter-metal and inter-layer dielectrics³ mostly deposited by plasma enhanced chemical vapor deposition (PECVD). The silica based-materials seem likely to continue to be used because of material breakthroughs which could alleviate the current low-k integration challenges. In this regard, the organosilicate materials containing Si-R-Si (R=(CH₂)_x), called oxycarbosilane, and, by extension, the PMO⁴⁻⁶ films have been shown to possess higher cohesive and adhesive fracture energies⁷ as well as higher Young's modulus (E)^{8,9} than amorphous silica and methylsilsequioxane or carbon-doped oxides (CDOs), the two latter materials containing C only in the form of methyl groups. Additionally, the control over the pore organization leads to further improvement of E.⁹⁻¹¹ All these advantages make oxycarbosilane based materials very promising for sub 10-nm technology nodes because further scaling of dielectric constant of PECVD deposited materials meets fundamental problems.¹²

Besides the mechanical properties of the low-k films, the common challenge of silica based low-k materials hindering their integration is the plasma induced damage (PID). However, the presence of bridging alkylene groups has been shown to lead to reduction in the PID^{13,14} as compared with only methyl groups. Additionally, quantum chemical calculations have revealed improved oxidation resistance for alkylene compared with methyl groups.¹⁵ Furthermore, it has been

reported that the length of the bridging group influences the cohesive fracture energy,⁷ the E, and the hardness.⁹ The control over the pore structure is also limited by the length and the rigidity of the bridging organic group.¹⁶ Notably, while the plasma-enhanced chemical-vapor deposition is the established deposition approach throughout the IC industry, the sol-gel route can provide better compositional and structural control over the film properties.¹⁷

The effect of UV light on low-k is of major interest in two main contexts: (i) UV-assisted thermal porogen removal (UV-cure) and (ii) plasma processing. For porogen removal the energy of the radiation can be independently controlled in order to optimize polymer decomposition and low-k properties enhancement.¹⁸⁻²⁰ On the other hand, in plasma processing the energy and intensity of the photons are determined by the required chemistry and plasma conditions. For example, the typical fluorocarbon-based plasmas used for low-k etching emit photons in the wavelength range 100–350 nm²¹ and the extent of their impact correlates with the penetration depth.²² Therefore, it is of paramount importance to quantify the contribution of the UV light to the PID.²³⁻²⁵ There are numerous studies reporting the effect of UV on CDO films^{18,19,22} but it has not been investigated in detail for alkylene-bridged films.^{26,27}

In the present study, we have utilized Fourier-transform infra-red (FTIR) spectroscopy to investigate the stability of ethylene and methylene bridging groups during UV (KrCl* excimer, 222 $\pm$ 1.2 nm; I = 130 W/m²) and VUV (Xe₂* excimer, 172 $\pm$ 12 nm; I = 15 W/m²) exposure. The low-k films investigated here are spin-coated hybrid oxycarbosilane films. The first material obtained through the acid-catalyzed polycondensation of 1,2-bis(triethoxysilyl)ethane contains ethylene groups (EtLK) while the second material which was obtained from 1,2-bis(triethoxysilyl)methane and triethoxymethylsilane contains methylene and methyl groups (MeLK).

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FIG. 1. FTIR spectra of the reference (thermally treated) (a) EtLK and (b) MeLK.

A nonionic PEO-hydrocarbon $((C_{2n}H_{4n+2}O_{n+1})-(C_mH_{2m+1}))$ block copolymer was employed as a template. The UV irradiation time was varied between 1 and 10 min. The processing chamber was evacuated down to 5 mbar before flushing with N_2 to maintain a pressure of 20 mbar. Afterwards, the temperature was increased by a heater element from room temperature to 400°C within ~ 2 min. Reference samples were annealed at 400°C for 3, 5, and 10 min²⁸ without irradiation.

The FTIR spectra in the $500\text{--}4000\text{ cm}^{-1}$ range associated with the only thermally treated reference samples EtLK and MeLK films are presented in Fig. 1. The band at $1250\text{--}950\text{ cm}^{-1}$ is usually attributed to the absorption from three different oxide structures—network, cage, and suboxide.²⁹ However, overlapping in this region is the signal from the alkylene bridges: $\text{Si-CH}_2\text{-Si}$ ^{30,31} at $\sim 1080\text{--}1040\text{ cm}^{-1}$ and $\text{Si-CH}_2\text{-CH}_2\text{-Si}$ ³² at 1160 cm^{-1} . While the band below 900 cm^{-1} is often ascribed to $\text{Si}(\text{CH}_3)_x$ groups,²⁹ for EtLK it has been explained in terms of tilting vibrations and translational oscillations of the ethylene unit against the rest of the molecule.³³ Nevertheless, contribution from $\text{Si}(\text{CH}_3)_x$ is not excluded due to conversion of the alkylene groups into alkyl.^{34,35} Furthermore, the region below 3000 cm^{-1} contains the signals associated with the C-H stretch vibrations in $-\text{CH}_3$ (2975 and 2905 cm^{-1}) and $-\text{CH}_2$ (2930 and 2880 cm^{-1}) units. The CH_3 groups in MeLK are bonded to the matrix as Si-CH_3 while the CH_2 signal is mainly attributed to the remaining template. On the other hand, due to the ethylene

groups in the matrix, the spectrum of EtLK is characterized by intense CH_2 bands even when the surfactant is virtually removed. Next, the peak at 1275 cm^{-1} in MeLK is attributed to Si-CH_3 . However, in EtLK we attribute the peak at 1270 cm^{-1} mainly to C-H bending in $\text{Si-CH}_2\text{-CH}_2\text{-Si}$ although the formation of Si-CH_3 is not excluded due to the thermal instability of organic species but it has not been demonstrated.

We estimate the concentration of the ethylene bridges by the absorption at $\sim 1415\text{ cm}^{-1}$ which has been attributed to out-of-plane rocking of Si-C and deformational vibrations of C-H bonds.^{15,31,36} The latter band is a suitable indicator since it does not overlap with band(s) produced by the organic template. However, the cleaving of the $\text{Si-CH}_2\text{-CH}_2\text{-Si}$ chain, which is expected to result into Si-alkyl groups, leads to absorption at the same frequency.^{35,37} On the other hand, the $\text{Si-CH}_2\text{-Si}$ is monitored by the signal at about 1360 cm^{-1} which has been attributed to C-H bending mode.^{29,31,38} The latter overlaps with a broad peak centered at $\sim 1350\text{ cm}^{-1}$ originating from the hydrocarbon chain of the template.³⁹ Consequently, the concentration of methylene bridges before the UV cure cannot be unambiguously estimated by FTIR. Nevertheless, the absorption due to the template can be shown to be negligible between the 3 and 10 min UV cure for both of the photon energies of 222 and 172 nm .²⁷

Fig. 2 depicts the peaks assigned to the alkylene groups. Exposure of EtLK to 222 nm photons leads to about 10%

FIG. 2. FTIR spectra zoomed in the region attributed to $\text{Si-CH}_2\text{-CH}_2\text{-Si}$ in EtLK after (a) 172 nm (b) 222 nm and to $\text{Si-CH}_2\text{-Si}$ in MeLK after (c) 172 nm (d) 222 nm UV cure.

decrease of the ethylene peak intensity when comparing 3 min with 10 min cure. On the other hand, 172 nm cure results in $\sim 75\%$ intensity reduction between 1 and 10 min cure which decreases the associated signal down to noise level. In comparison, the methylene peak in MeLK is also diminished by about 10% by the exposure to the 222 nm light. However, only 40% intensity loss of the methylene peak is observed after exposure to 172 nm photons.

In general, the Si-C bonds are less affected by photons with $\lambda = 222$ nm as compared with $\lambda = 172$ nm.²⁸ However, there is a significant difference in how the irradiation affects these two films. While for MeLK the decrease of the methylene peak can be attributed to a self-hydrophobization process³⁵ which is also supported by the increased intensity of the bands assigned to Si-O-Si and Si-CH₃, the decrease of the ethylene peak in EtLK cannot. On the contrary, we observed an increase of about 10% of the intensity of the peak at 1415 cm^{-1} with anneal time for the reference EtLK samples when compared with the not-annealed spectrum. The increase is attributed to the higher concentration of the absorbing species such as C-H bonds caused by the thermally induced bond rearrangement as a result of which the $-\text{CH}_2-$ groups are transformed into $-\text{CH}_3$. Since we do not expect any detrimental effect on the Si-alkyl groups²⁹ we attribute the 222 nm UV-induced decrease of the 1415 cm^{-1} peak to fragmentation of the Si-CH₂-CH₂-Si chain. Additionally, Si-H bonds formation is evident from the bands at 885 cm^{-1} and 2250 cm^{-1} , whose intensities and calculated areas under the curves (AUC) increase with exposure time. Fig. 3 depicts the evolution of the absorption at 885 cm^{-1} . Furthermore, Si-H is not present in the reference EtLK films indicating that it is generated during the exposure to UV light. The observed Si-H bond signals hint at formation of Si dangling bonds passivated by H atoms or radicals. The latter are present as a result of the UV-assisted template decomposition which involves C-H bonds breaking.⁴⁰ Fig. 3 further emphasizes the different effects of the 222 nm light on EtLK and MeLK by showing no Si-H bond formation for MeLK.

The damaging effect of the VUV light ($\lambda < 200$ nm) on the organic component of the hybrid low- k and specifically on the methyl groups is well-known.^{22,29} While our results conform to the previous reports, we observe about twice more significant effect on the ethylene as compared with the methylene groups (Figs. 2(a) and 2(c)). Additionally, after

FIG. 3. Area under the curve (AUC) observed for the peak at 885 cm^{-1} attributed to Si-H after 222 nm UV cure.

10 min VUV exposure the intensity of the peak attributed to Si-CH₃ (not shown) in MeLK decreases to $\sim 70\%$ compared with its intensity after 1 min cure similar to the Si-CH₂-Si peak which decreases to $\sim 60\%$ compared with its intensity after 1 min cure (Fig. 2(c)).

Rakhimova *et al.*²² reported an increase of the quantum yield for breaking Si-CH₃ bonds by VUV photons for films with $\sim 50\%$ porosity compared with films with $\leq 45\%$ porosity. The latter suggests that the differences we have discussed so far might be due to the porosity difference between a 55% porous EtLK with respect to 45% porous MeLK. This hypothesis was tested by depositing EtLK (38%–40%) and MeLK ($\sim 33\%$ –38%) with the same target porosity and exposing them at 400°C to 172 nm light for 2, 5, and 10 min. This experiment was performed with a different lamp whose intensity is not available. Fig. 4 shows the intensity changes of the peaks attributed to the alkylene groups relative to the first measured point. The intensity of the methylene peak decreases by about 10% increasing the exposure time from 2 to 10 min but the ethylene peak is reduced by 60% in the same time range. The effects observed in this additional experiment seem to be less pronounced than those discussed earlier which is probably related to the different intensity of the Xe₂⁺ excimer source or to the fact that the shortest VUV irradiation was 2 min instead of 1 min. The latter seems especially relevant when we consider the large difference in peak intensity after 1 and 3 min exposure in Fig. 2(a). Nevertheless, this result confirms our observation that the ethylene bridging groups are consumed faster than the methylene groups and porosity does not play a significant role under the investigated experimental conditions.

Quantum chemical calculations were performed using the Density Functional Theory (DFT) B3LYP method^{41,42} (Jaguar version 8.3 program⁴³) to study VUV spectra and energetics of reactivity of various polymer compositions. The structures of model polymers were optimized at B3LYP/6–31(d,p) level. The frequency analysis was made at the same level of theory to obtain thermodynamic parameters such as total enthalpy (H) and Gibbs free energy (G) at 298 K. The reaction enthalpies (ΔH) and Gibbs free energies of reaction (ΔG) were calculated as the difference of the calculated total enthalpies and Gibbs free energies between the reactants and products, respectively. The energies of excited

FIG. 4. Evolution of the peak intensity attributed to the bridging alkylene groups after 172 nm cure.

FIG. 5. Results of DFT quantum chemical calculations: (a) energy scheme of the radicals formation after excitation; (b) model structures used for calculations; molecular orbitals are given for the case of structure (III).

states and electronic transition spectra were calculated using the Time Dependent⁴⁴ (TD) DFT method at B3LYP/6-31+G(d,p) level of theory.

The results of the calculations are shown in Fig. 5. The energy schema shows the formation of reactive triplet state T₁ after absorption of a high energy photon (e.g., 172 nm). The dissociation reactions X₁ and X₂ lead to formation of two radicals through Si-C bond and C-C bond scission, respectively (Fig. 5(b)). The C-C bond scission is energetically more favorable than Si-C bond ones. However, it should be noted that the σ -electron from the highest occupied molecular orbital, which has bonding character, is strongly localized on Si-C bond (as shown for the structure (III)). After excitation into the lowest unoccupied molecular orbital, which has σ -character, this Si-C bond will be weakened, facilitating dissociation reaction X₁. From the comparison of the possible dissociation reactions it can be seen that decomposition of model polymer (II) with only one CH₂ group is energetically less favorable than that of (III).

In conclusion, it was demonstrated that the UV and VUV irradiation have more detrimental effect on ethylene-bridged oxycarbosilane films as compared with those containing methylene groups. While it is known that photons with lower energy ($\lambda = 222$ nm) do not have any detrimental effect on the Si-CH₃ content, we showed that this also applies for the bridging methylene groups. On the other hand, the concentration of the bridging ethylene groups is reduced even by the 222 nm light. The difference in the stability of these two alkylene groups is more apparent when these films are exposed to 172 nm light. The ethylene groups are depleted by more than 75% while methylene loss is limited to only 40%. The experimental results were qualitatively supported by DFT quantum chemical calculations. Finally, the different sensitivity of bridging groups to VUV light should be taken into account during the development of curing and plasma etch processes of PMO and oxycarbosilane based low-k materials that are considered as the most promising candidates for sub 10 nm technology nodes.

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