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Effects of ultraviolet (UV) irradiation in air and under vacuum on low-k dielectrics

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This work addresses the effect of ultraviolet radiation of wavelengths longer than 250 nm on Si-CH_3 bonds in porous low-k dielectrics. Porous low-k films (k = 2.3) were exposed to 4.9 eV (254 nm) ultraviolet (UV) radiation in both air and vacuum for one hour. Using Fourier Transform Infrared (FTIR) spectroscopy, the chemical structures of the dielectric films were analyzed before and after the UV exposure. UV irradiation in air led to Si-CH_3 bond depletion in the low-k material and made the films hydrophilic. However, no change in Si-CH_3 bond concentration was observed when the same samples were exposed to UV under vacuum with a similar fluence. These results indicate that UV exposures in vacuum with wavelengths longer than ~250 nm do not result in Si-CH_3 depletion in low-k films. However, if the irradiation takes place in air, the UV irradiation removes Si-CH_3 although direct photolysis of air species does not occur above ~242nm. We propose that photons along with molecular oxygen and, water, synergistically demethylate the low-k films. © *2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).* [http://dx.doi.org/10.1063/1.4959277]

Advanced interconnects for ultra-large scale integration (ULSI) devices on sub 22nm technology nodes requires implementation of ultra low-k dielectric films with k < 2.5 to reduce resistance-capacitance (RC) delay, dynamic power consumption, and crosstalk noise. The reduction of the dielectric constant (k value) is achieved by using low-polar chemical bonds (such as C-C, C-H, etc.) and introducing porosity in the dielectric films. At present, most porous SiCOH (pSiCOH) low-k materials are deposited by plasma-enhanced chemical vapor deposition (PECVD). The structures of these films are similar to conventional SiO_2, with terminating Si-CH_3 groups that keep the materials hydrophobic.[1–4] In order to enhance the dielectric and mechanical properties of low-k dielectric materials, UV-light assisted curing is commonly used.[5] The curing process removes organic porogens and improves the material properties.[2,7] The effects of the UV exposure on ULK films during curing and UV and VUV exposure during plasma-based processes subsequent to curing have been a topic of high interest in the semiconductor industry and have been investigated in detail.[1,5–7]

VUV exposure is known to be a factor in plasma damage to pSiCOH low-k films during nanofabrication.[8–10] Plasma-induced damage results in the removal of methyl groups (demethylation) by radicals and VUV photons, compromising the hydrophobic nature of the dielectric material. The role of UV photons in low-k film damage is less clear. Kao *et al.*[10] reported that UV curing with 200-450 nm wideband UV lamps under He/Ar atmosphere led to significant loss in Si-CH_3 bond concentration. However, Prager *et al.*[7] reported quantum-chemical calculations on model SiCOH clusters that suggests that photons with wavelengths shorter than 200 nm are required to deplete the Si-CH_3 bonds in pSiCOH low-k films. However experimental data from the same paper shows

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that Si-CH_3 is depleted by photon irradiation in nitrogen. This effect is much more pronounced with 172 nm VUV irradiation as compared to 222 nm UV, where some >200nm UV-induced Si-CH_3 loss was observed. The Si-CH_3 degradation also increases with nitrogen pressure before reaching a saturation point. Rakhimova *et al.*[11] published a comprehensive study of Si-CH_3 depletion in pSiCOH low-k films due to vacuum ultraviolet (VUV) and extreme ultraviolet (EUV) irradiation. In that report, it was shown that the loss of Si-CH_3 was small at 193 nm compared to shorter wavelengths because of the low photoabsorption. As there are conflicting reports on this topic a full explanation of the damage mechanism from UV radiation is yet to be attained. To further address this question, we examined the damage to pSiCOH films from 254-nm UV light in air and under vacuum.

P-SiCOH films (32% porosity, k = 2.3) were deposited by PECVD and UV cured to remove porogen on 300-mm Si wafers. The thickness of the as deposited films was measured using an ellipsometer and found to be approximately 250 nm. The fully cured films were then exposed to 254-nm UV radiation using a Cole-Parmer Standard Pen-Ray UV lamp. During the UV exposure, the samples were placed 2 centimeters from the lamp. The UV exposures were performed under two different conditions: a) in air and b) in vacuum. The exposures were made for 1 hour and 2.5 hours to treat the samples with a total photon dose of 9×10^{21} photons/cm^2 and 2×10^{22} photons/cm^2 respectively. The vacuum exposures were made in a vacuum chamber that was pumped down to a pressure below 8×10^{-4} torr. The samples were placed inside the vacuum chamber and taped to a UV-grade sapphire window using Kapton tape. The UV lamp was placed on the other side of the window outside the chamber. The UV-sapphire window used for these experiments has 90% transmission at 250 nm. Fourier transform infra-red (FTIR) measurements were performed in transmission mode with a resolution better than 4 cm^{-1}, averaging 64 spectra within the 400–4000 cm^{-1} range. For each FTIR analysis, the background and the Si substrate spectra were subtracted and the absorbance normalized to film thickness. The typical FTIR features of the low-k films included CH_x stretching (2850-3000 cm^{-1}), Si-CH_3 deformation (1270 cm^{-1}), Si-O cage stretching (1130 cm^{-1}) and Si-O network stretching (1050 cm^{-1}). Water absorption is indicated by a 'hump' in the spectrum around 3500 cm^{-1}.

Figures 1 and 2 show the FTIR absorption spectra for an untreated sample and a sample that was exposed to 254 nm UV in air and under vacuum, respectively. The sample that was exposed to UV radiation in air shows a significant loss in Si-CH_3 bond concentration (1270 cm^{-1}), which can be seen from the differential FTIR spectra shown in Figure 3. The loss of methyl groups increases with longer UV-exposure times. As mentioned earlier, the depletion of methyl groups in low-k films leads to degradation in the hydrophobic nature of the material. This is evident from the FTIR spectra in Figure 1, which shows significant water uptake by the film after UV exposure in air. In comparison, the FTIR absorption spectrum for the sample that was exposed to 254 nm UV radiation under vacuum (Figures 2 and 3) does not show any indication of depletion in Si-CH_3 bond concentration or other chemical modifications in the dielectric film.

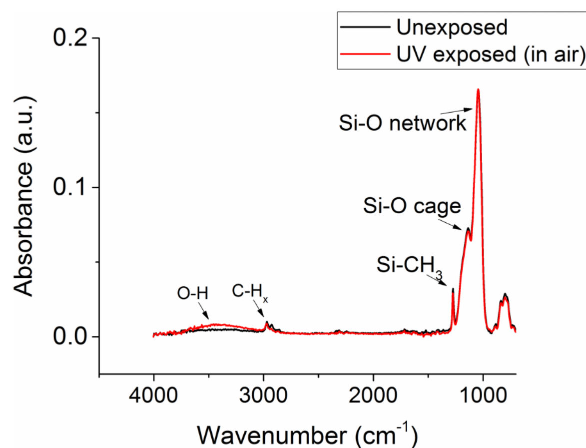

FIG. 1. FTIR spectra before and after UV exposure in air. The sample was exposed to UV radiation for 1 hour.

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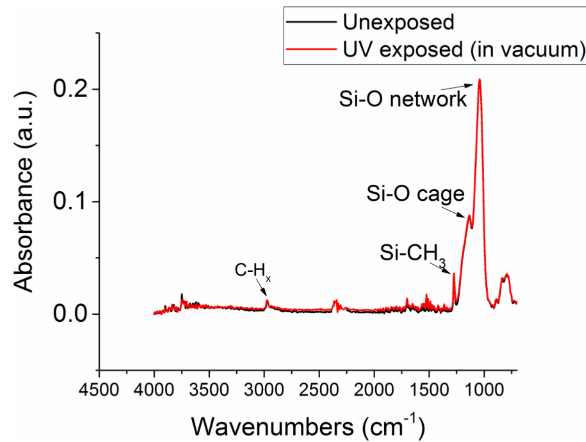

FIG. 2. FTIR spectra of pSiCOH exposed to UV under vacuum.

It is well known that oxygen radicals can cause significant modifications to pSiCOH films.[12,13] However, the direct photodissociation of air constituents (O_2, CO_2, H_2O) at 254 nm is unlikely to generate significant numbers of radicals, if any, because the absorption cross-sections are very small and the photon energy is not high enough to dissociate these molecules even at room temperature.[14] Therefore any effects due to radical interactions during 254 nm irradiation must be ruled out. Instead, we propose a synergistic effect of UV photons and molecular oxygen or water along with a possible reaction mechanism as follows.

If UV photons at 254 nm can break the Si-C bonds in the low-k film to create $^*CH_3$ radicals then, under vacuum conditions, the resulting radicals can be trapped within the dielectric layer and then recombine to recreate the Si-CH_3 bonds. Hence, no appreciable loss in $SiCH_3$ bond concentration would be observed after the UV exposure in vacuum consistent with observation. However, in the presence of air, the $^*CH_3$ radicals can react with molecular oxygen and water trapped in the pores of the dielectric film and thus an overall loss in $SiCH_3$ bond concentrations would be observed. A similar mechanism was proposed by Graves *et al.*[15] to explain the depletion of Si-CH_3 bonds in low-k films due to the synergistic effects of VUV photons and molecular oxygen.

According to the quantum calculations presented by Prager,[7] the scission of Si-C bonds requires photons with wavelengths below 200 nm. However, they did not explain their experimentally observed Si-CH_3 loss at 222nm, which suggests Si-C bond scission can occur at >200 nm by direct bond scission. However, it is also possible that the inert ambient used in their study contained

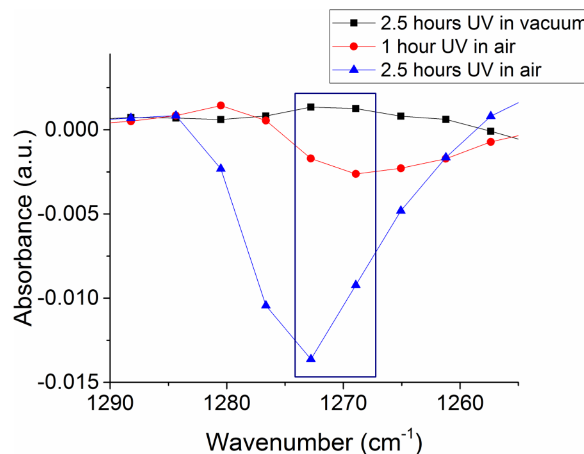

FIG. 3. Differential FTIR spectra of the Si-CH_3 peak area. The Si-CH_3 peak area is marked by the rectangular box.

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residual O_2 or H_2O, which could have led to some $SiCH_3$ loss. Recent results from Zhang, et al.,[16] suggest this as a possible explanation. They observed $SiCH_3$ loss and Cu oxidation during UV exposure under an inert ambient in one commercial UV chamber but not in another chamber made by a different supplier.[16] This data strongly indicates that residual O_2 or H_2O is present in the chamber where $SiCH_3$ and oxidation was observed.

If 254 nm photons cannot break the Si-C bond, another possibility to explain our results is that the photons break the weaker C-H bonds. In vacuum, the fragments are trapped and may recombine so no loss is observed. However in the presence of air, they can react with the oxygen and water trapped within the pores before recombining. As a result, an overall decrease in $SiCH_3$ bond concentration in the dielectric film is observed. C-H bond scission could also lead to the formation of cross-linked Si-CH_2-Si or Si-CH_2-CH_2-Si networks,[8] but we see no evidence for this in our FTIR spectra.

In conclusion, no changes in the chemical structure of pSiCOH films were observed after 254nm UV exposure in vacuum. We propose that any photon-induced scission of Si-C or C-H bonds quickly recombine as the fragments are trapped. Thus, 254-nm photons alone do not lead to Si-CH_3 depletion. In the presence of air, Si-CH_3 bonds were depleted significantly and the loss of methyl groups increased for longer UV-exposure times. It is proposed here that the 254-nm photons and molecular oxygen or water synergistically affect the pSiCOH films, which leads to $SiCH_3$ depletion. Below 242 nm direct photolysis of molecular oxygen (and water at $<$200nm) become possible resulting in a second mechanism for Si-CH_3 loss when oxygen or water are present.

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