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

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ABSTRACT

This work addresses the issue as to whether ultraviolet radiation of wavelengths longer than 200 nm can break Si-CH\(_3\) bonds in porous low-k dielectrics. To resolve this issue, porous SiCOH films (k = 2.3) were exposed to 4.9 eV (254 nm) ultraviolet (UV) radiation in both air and vacuum for 1 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 photons themselves with wavelengths longer than ~250 nm do not modify the chemical structure of the low-k film. However, if the irradiation takes place in air, the photons can indirectly cause damage to the samples. This is due to the fact that UV radiation can break down the air components and create radicals and active species that affect the low-k films.
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, low-k materials are deposited by plasma-enhanced chemical vapor deposition (PECVD) and spin-on glass (SOG) technology. The structures of these films are similar to conventional SiO₂, with terminating Si-CH₃ groups that keep the materials hydrophobic.¹,²,³ In order to enhance the dielectric and mechanical properties of low-k dielectric materials, UV-light assisted curing is commonly used.⁴ The curing process removes organic porogens and improves the material properties.²,⁷ The effects of the UV cure have been a topic of high interest in the semiconductor industry and have been investigated in detail.⁴,⁵,⁶

Although the UV-curing process has several major advantages as mentioned above, it has been reported that it can also cause damage to low-k films.⁷,⁸,⁹ The damage is caused mainly by the removal of methyl groups, compromising the hydrophobic nature of the dielectric material. Kao et. al. reported that UV curing with 200-450 nm wideband UV lamps under He/Ar atmosphere led to significant loss in Si-CH₃ bond concentration.⁹ However, Prager et. al.⁶ reported quantum-chemical calculations on model SiCOH clusters that suggest that photons with wavelengths shorter than 200 nm are required to deplete the Si-CH₃ bonds in low-k films. Experimental data from the same paper shows that Si-CH₃ is depleted by UV irradiation in nitrogen. However, this effect is a lot more
pronounced with 172 nm irradiation compared to 222 nm UV. The Si-CH$_3$ degradation also increases with nitrogen pressure before reaching a saturation point. Rakhimova et. al. published a comprehensive study of Si-CH$_3$ depletion in 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$_3$ is small at 193 nm compared to shorter wavelengths because of the low photoabsorption. $^{10}$ There are several conflicting reports on this topic and a clear explanation of the damage mechanism of UV radiation is yet to be attained. To resolve this discrepancy, we examine the damage to low-k dielectric films from 250nm UV light in air and under vacuum.

Advanced low-k (ALK) films (32% porosity, k = 2.3) deposited by PECVD on 300-mm Si wafers were used in this work. The thickness of the as deposited films was measured using an ellipsometer and found to be approximately 250 nm. The films were exposed to 254 nm UV radiation using a Cole-Parmer 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 x 10$^{21}$ photons/cm$^2$ and 2 x 10$^{22}$ photons/cm$^2$ respectively. The vacuum exposures were made in a vacuum chamber that was pumped down to a pressure below 8x10$^{-4}$ torr. The samples were placed inside the vacuum chamber and taped to an 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 250nm. Fourier transform infrared (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 every FTIR analysis, the background spectrum and the Si substrate spectrum 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 differential spectra are obtained by subtracting the spectrum of the pristine sample from that of the UV-treated ones. The loss in 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. These results indicate that the UV photons with wavelengths greater than 250 nm do not affect the chemical structure of the low-k films. This result is in agreement with the quantum-chemical calculations presented by Prager et. al.\(^6\) showing that UV radiation over 200 nm cannot modify the Si-CH\(_3\) bonds in SiCOH. This paper
concluded that the light absorption at wavelengths shorter than 200 nm leads to the excitation of the first singlet cluster state. Then the excitation due to the intersystem crossing transforms to the excited triplet state after which the Si-CH₃ bond dissociation can occur. More detail on the quantum-chemical calculation can be found in reference 6.

However, UV irradiation in air can modify the chemical structure of the films as seen in Figures 1 and 3. It is known that UV irradiation in air can lead to the photochemical production of appreciable levels of reactive ions, radicals and reactive-oxygen species (ROS) from the air constituents (O₂, H₂, N, H₂O, etc.).¹¹ These active species can interact with the dielectric material and cause damage. In particular, it has been reported that oxygen radicals can significantly modify and degrade low-k films.¹²,¹³ Thus any residual oxygen or water in the sample chamber during UV irradiation can lead to damage to the material and the extent of damage increases with longer exposure times. It is also shown in other reports that the presence of nitrogen and even inert gasses such as argon can deplete the Si-CH₃ in the low-k films.⁶,⁹ It is possible this is due to the interaction of the dielectric material with thermalized ions that are produced by the UV. Many authors have studied the effects of ion bombardment on low-k films and reported significant degradation of the films induced by ions from processing plasmas including Si-CH₃ loss and water uptake.¹⁴,¹⁵,¹⁶,¹⁷

In conclusion, no changes in the chemical structure of the samples were seen after UV exposure in vacuum. The results indicate that 254 nm UV does not break the Si-CH₃ bond in low-k dielectrics as long as the irradiation takes place in vacuum. However, such
bonds can be broken indirectly with this wavelength irradiation in air because active species can be formed by the UV in air that degrades the low-k dielectrics. These results suggest that reports of Si-CH$_3$ loss during UV irradiation may be due to residual moisture or other species in the chamber.

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Figure Captions

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

FIG 2: FTIR spectra of low-k sample before and after UV exposure in vacuum.

FIG. 3: Differential FTIR spectra (pristine – UV exposed) of the Si-CH$_3$ peak area for one and 2.5 hour UV exposures. The Si-CH$_3$ peak area is marked by the rectangular box.
REFERENCES


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