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The effect of vacuum ultraviolet irradiation on the time-dependent dielectric breakdown of organosilicate dielectrics

D. Pei,¹ P. Xue,¹ W. Li,¹ X. Guo,¹ Y. H. Lin,² H. S. Fung,² C. C. Chen,² Y. Nishi,³ and J. L. Shohet¹

 ¹Plasma Processing and Technology Laboratory and Department of Electrical and Computer Engineering, University of Wisconsin-Madison, Madison, Wisconsin 53706, USA
²National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan
³Department of Electrical Engineering, Stanford University, Stanford, California 94305, USA

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In this work, the effect of vacuum ultraviolet (VUV) exposure on the time-dependent dielectric breakdown (TDDB) properties of porous low-k films was investigated. Synchrotron irradiation was used to simulate the VUV photon irradiation from processing plasmas without any particle flux. The synchrotron flux varies with the wavelength, so the irradiation time was chosen to produce the same fluence at various photon energies. The deterioration of TDDB and generation of negative mobile charge were observed in the film after exposure to the VUV photons with 9 eV or higher energy. These effects were not observed in the films exposed with 7-eV photon energies or less. The creation of paramagnetic defects was observed with the ESR measurement and believed to be the reason for TDDB degradation. Depletion of carbon and breakage and rearrangement of the Si-O-Si structure were observed and believed to be the reason for mobile charge generation and the change in TDDB, chemical, and mechanical properties. *Published by AIP Publishing*. [http://dx.doi.org/10.1063/1.4962949]

To reduce resistance-capacitance (RC) delays and capacitive-power dissipation in the back-end-of-the-line (BEOL), low-k dielectric materials¹⁻⁴ are being used as the inter-layer dielectric (ILD) in integrated circuits. Porous organosilicate, often called p-SiCOH, is the currently used material for this purpose.² A serious problem for using p-SiCOH is the plasma-induced damage (PID).^{5,6} The p-SiCOH films are exposed to multiple plasma-processing steps during the manufacturing process, including dielectric etching and photoresist stripping.⁷ As a result of PID, degradation of both the electrical and mechanical properties has been observed.⁸ PID is induced by the bombardment of various plasma species, such as reactive radicals,^{9,10} charged particles,¹¹ and photons (primarily vacuum ultraviolet (VUV) photons).^{12,13} Intensive research has been undertaken on the effect of reactive radicals and charged particles on the properties of low-k. However, the effects of VUV photons on the electrical properties of the p-SiCOH films, especially the photon energy dependence of their effects, have not been fully understood in relation to the electrical, chemical, and mechanical properties of the films.

In this work, the effect of VUV photon exposure on the electrical, mechanical, and chemical properties of the p-SiCOH films was investigated with particular emphasis on time-dependent dielectric breakdown (TDDB). Synchrotron radiation was used as the VUV photon source. The p-SiCOH films were exposed to monochromatic VUV photons of various energies. The electrical properties of the VUV exposed p-SiCOH film, including TDDB, capacitance-voltage (C–V) characteristics, and the dielectric constant (k value), were measured and compared with those of the pristine films. The results were also used to compare changes in the chemical and mechanical properties as well.

The p-SiCOH films used in this work were deposited on the (100) Si substrates using plasma enhanced chemical vapor deposition (PECVD). After deposition, the film was UV cured.¹⁴ The thickness of the film was measured to be 500 nm. From the C–V characteristics, the *k* value was calculated to be 2.55. The film density was 1.24 g/cm^3 , as measured with X-ray reflectivity. The porosity of the film was measured to be 15%–20% with the ellipsometric porosimetry (EP).

The UV-cured p-SiCOH (referred to as pristine p-SiCOH) films were then exposed to monochromatic synchrotron radiation using the stainless-steel Seya-Namioka (SEYA) beamline of National Synchrotron Radiation Research Center (NSRRC), the apparatus as previously described.¹⁵ The VUV photon beam was oriented to be incident normally on the surface of the p-SiCOH film with a beam cross-section of ~ 15 (horizontal) \times 4 mm (vertical). The beam was scanned vertically in eight steps with 1.5 mm step size over the surface of the film in order to achieve a nearly uniform exposed area of at least $10 \,\mathrm{mm} \times 10 \,\mathrm{mm}$. Four different photon energies, 7, 9, 12, and 15 eV, were used for the VUV exposure. The energies were chosen as representing the range of the VUV spectrum of a typical processing plasma.¹⁶ The VUV photon flux of each energy was measured with a calibrated photodiode (AXUV100). The exposure time of each photon energy was controlled; therefore, the total fluence was 2×10^{16} ph/cm² at all energies.

After VUV exposure, the TDDB of the p-SiCOH film was measured, using a method described previously.¹⁷ A 100 nm thick titanium hexagonal pattern was deposited on the p-SiCOH, followed by a layer of 400 nm silver. The size of each hexagon was 8.6×10^{-4} cm². Titanium was chosen as the first layer because titanium is non-diffusive to p-SiCOH. The purpose of using silver, a softer metal, is to help release any mechanical pressure from the pin probe when making electrical contact. To measure the TDDB, a voltage

stress was applied between the deposited metal and the silicon substrate. The voltage was ramped at 1 V/s until the desired TDDB measurement voltage was reached. The voltage was then kept constant, and the leakage current was measured as a function of time. The time to failure (TTF) is the time when a sudden increase of leakage current of more than three orders of magnitude was observed. The measurement was repeated for several times and Weibull statistics were applied.

The TDDB of p-SiCOH exposed with the VUV photons of different energies was measured at 130 °C under an electric field of 3.4 MV/cm. The Weibull plots of the films are shown in Figure 1. Compared with the pristine films, the TDDB lifetime of p-SiCOH irradiated with 7-eV photons does not display much. However, the TDDB degradation was observed for the p-SiCOH irradiated with 9, 12, and 15 eV photons, as the probability curves are seen to move to the left. Thus, there is a photon energy threshold between 7 and 9 eV for the TDDB degradation effect.

The TDDB of dielectric films can be affected by the mobile charge and defect state concentrations within the film. To obtain this, the C-V characteristics of the pristine and VUV-exposed p-SiCOH were measured. The C-V characteristics were obtained using the same hexagonal titanium structure. The frequency and the amplitude of the voltage modulation were 1 MHz and 0.1 V, respectively. The C-V characteristics of the pristine and 12-eV photon-exposed films are shown in Figure 2. The C-V curves were measured with both positive and negative directions of ramping voltage, as illustrated by the red (decreasing voltage) and black (increasing voltage) arrows. Significant C-V hysteresis was observed on the samples irradiated with the VUV photons with energies equal or larger than 9 eV. Compared with pristine films, the red curve remained at the same horizontal position while the black curve shifted to the left. For samples exposed with 7 eV photons, no C-V hysteresis was observed. The overall slope showing the transition from accumulation to depletion on the C-V curve was not changed after the VUV exposure, indicating no interface trap states were created by the VUV exposure. The amount of C-V hysteresis of the film exposed with VUV with different energies is shown in Figure 3. Again, there is a photon



FIG. 2. C–V characteristics of the pristine and 12-eV photon-exposed films. The C–V curves with the increasing voltage are in black (squares) and those with the decreasing voltage are in red (triangle).

energy threshold between 7 and 9 eV for this C–V hysteresis effect, similar to that for TDDB.

The C–V hysteresis was believed to be created from the generation of mobile charge inside the dielectric film during VUV exposure. The fact that the black curves shifted, but the red curves did not shift, indicates that the mobile charge generated by the VUV exposure was negative. When the C–V characteristic measurements started from a positive voltage and decreased to a negative value, the negative mobile charge



FIG. 1. The probability plots of the TTF of pristine and VUV exposure p-SiCOH film.



FIG. 3. The magnitude of C–V hysteresis as a function of the photon energy of the VUV exposure.

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within the dielectric film moves to the titanium metal electrode side under the electric field. While the mobile charge is at the titanium electrode, it provides no contribution to the flat-band voltage shift,¹⁸ and the C–V curve remained the same as the pristine one. When the C–V measurement started with a negative voltage and increased to a positive voltage, the negative mobile charge will move to the silicon-substrate electrode. At this position, the mobile charge makes its maximum contribution to the flat-band voltage shift resulting in the C–V curve being shifted to the right compared with the pristine one. If the mobile charge was positive, the C–V hysteresis would shift over in the opposite direction. That is, the black curve (increasing voltage) would stay the same, but the red curve (decreasing voltage) would shift to the left.

The TDDB of the low-k dielectric film is believed to be related to the Poole-Frenkel tunneling of charge carriers via defects in the film.¹⁹⁻²¹ X-band electron paramagnetic resonance (EPR) can measure the paramagnetic defect states of dielectric films^{22,23} and was applied to the p-SCOH films, as shown in Figure 4. A defect with g-factor of 2.0054 and bandwidth of 7G was detected. The defect is a bulk state as the EPR signal does not depend on the direction of the magnetic field. Thus, it cannot be an interface state like P_b. Instead, the isotropic nature of the defect indicates that it is likely to be an E' center as the film is amorphous. However, due to the complexity of the structure of p-SiCOH, the g-factor of this defect may differ from E' centers found in silicon-oxide materials. Compared with the pristine film, higher amplitudes of the EPR signals were observed from the films exposed with 9, 12, and 15 eV photons. The highest increase was observed in the 12-eV exposed film. However, no significant change was observed for the films exposed with 7 eV photons. With a higher density of defect states, the TTF of the p-SiCOH will be shorter.

The effective k value of the p-SiCOH film was also determined from the C–V characteristics. It is assumed that the effect of the VUV photons on the p-SiCOH film is not uniform from the vacuum interface to the substrate. Therefore, the effective k value obtained from the C–V characteristics is an average value for the entire thickness. The measured effective k values of the p-SiCOH films are shown in Table I. Only 15-eV photon-irradiated films show a statistically significant



FIG. 4. The EPR signal of the pristine and VUV-exposed film.

TABLE I. The measured effective k value and water contact angle of pristine and VUV exposed p-SiCOH film.

Exposure energy	Pristine	7 eV	9 eV	12 eV	15 eV
Effective k value	2.55 ± 0.03	2.54 ± 0.04	2.57 ± 0.05	2.63 ± 0.05	2.69 ± 0.05
WCA (deg)	117 ± 2	89 ± 5	72 ± 5	45 ± 4	39 ± 3

increase (about 5% in the k value compared with the pristine film). For other photon energies, there may be small changes of k, but none of them were statistically significant in this measurement. The increase in the k value can be explained by the loss of Si-CH₃ during the VUV exposure and the formation of Si-OH after the exposure when the film was exposed to air. This was confirmed by a water contact angle (WCA) measurement, shown in Table I. Compared with the Si-CH₃ terminated surface, the Si-OH surface may oxidize the later-deposited Ti electrode and contribute to TDDB degradation.

The bandgap of the p-SiCOH film can also affect the TDDB and was measured using the inelastic energy-loss spectrum, using a method previously described.²⁴ The bandgap of the pristine p-SiCOH was measured to be $7.9 \pm 0.2 \text{ eV}$. The bandgap values of the VUV-exposed films were found to be between 7.8 and 8.0 eV. No statistically significant change in the bandgap was observed after the VUV exposure with any of the energies used here. This is likely because the density of states of the defects generated by the VUV photons is much smaller than the density of states of the valance band. However, research has shown that very high-energy ion sputtering (4 keV) can significantly narrow the bandgap of the low-k materials.^{25–27}

To examine the chemical changes to the p-SiCOH film, the Fourier transform infrared spectrum (FTIR) of the film was measured. The amplitude of each peak in the absorption spectrum of the low-k material is well understood.²⁸ To evaluate the changes in the FTIR spectrum, the differential FTIR of the VUV exposed film was obtained by subtracting the spectrum of the pristine film from that of the VUV-exposed film. The differential FTIR of the films is shown in Figure 5. The result is similar to the previous studies of VUV effects on low-k dielectrics where somewhat different photon energies were used.²⁹ Two effects were observed. The first one is that the VUV photons reduced the CH₃ (methyl) groups in the p-SiCOH films. Both the symmetric bending mode $(1270 \text{ cm}^{-1})^{30}$ and the stretching mode $(780 \text{ cm}^{-1})^{31}$ show a decreasing trend. The removal of the methyl groups occurs for all VUV-photon energies from 7 to 15 eV. For the higher photon energies, larger decreases of the methyl group peaks were observed. Therefore, this loss of the less polarizable Si-CH₃ bonds will lead to an increase in the k value^{1,32} after exposure to 15-eV photons. The second effect of VUV exposure is the modification of the Si-O-Si structure. For samples irradiated with 9, 12, and 15 eV photons, a decrease in the cage-structure peak $(150^{\circ} \text{ bond angle}, 1145 \text{ cm}^{-1})^{33}$ and an increase in the network-structure (144° bond angle, 1065 cm^{-1} ³³ were observed. The amount of conversion of Si-O-Si from cage to network gets larger as the irradiation



FIG. 5. The differential FTIR of the VUV-exposed film (by comparing with the pristine film).

energy increases. No change of the Si-O-Si structure was observed in the film irradiated with 7 eV photons. This energy dependence is in the same direction as the TDDB degradation, paramagnetic defect state creation, and mobile charge generation measured in this work, indicating that it is likely that these are caused by the same process. Interestingly, in an another work about the effect of VUV irradiation on the effect of mechanical properties of low-k material, a similar energy dependence was reported.²⁹

The photon-energy dependence of the methyl group and Si-O-Si structure observed in the FTIR can be explained by the bond-dissociation energy. The bond-dissociation energy of Si-CH₃ is 4.7 eV and that of Si-O is 8.3 eV.³⁴ Thus, the VUV photons of 9eV or higher can break the Si-O bonds. When the Si-O bonds were reformed, they will coalesce in a more stable network structure than less stable cage structure. However, some of the broken bonds will not be reformed, and can result in dangling bonds. This explains the EPR results in Figure 4. The breakage of the Si-O bonds may also be the reason for the creation of negative mobile charge. Hydroxide (OH⁻) can be formed by breaking the Si-OH structure in the film, which can explain the generation of negative mobile charge during the VUV exposure. The mobile charge should not be CH₃⁻ because no mobile charge generation was observed when the film was exposed to 7 eV photons.

In summary, the electrical, chemical, and mechanical properties of the VUV-exposed p-SiCOH films were measured and compared with the pristine p-SiCOH films. TDDB degradation, negative mobile-charge generation, and paramagnetic defect-state creation were observed in the p-SiCOH exposed to the VUV photons of 9 eV or higher energy. However, none of these effects were observed in the films exposed to 7-eV photons. Thus, there is an energy threshold between 7 and 9 eV for the degradation of electrical properties. Above this threshold, the Si-O bonds in p-SiCOH can be broken. This can be shown by examining the FTIR spectra, which indicates that some Si-O-Si cage structures were transformed into a more stable network structure. Dangling bonds can also be created from the breaking of the

Si-O bonds, which will shorten the TDDB lifetime of the film. The negative mobile charge is believed to be hydroxide generated by breaking a Si-OH bond. For all photon energies from 7 to 15 eV, a decrease of methyl groups in the film was observed after the exposure. This methyl loss can lead to the increase of the *k* value of the film.

With the results above, it is concluded that the VUV photons with enough energy can damage the electrical properties of low-k films. Reducing the exposure to high energy VUV photons should be helpful in the processing of low-k materials.

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