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Influence of porosity on electrical properties of low-k dielectrics irradiated with vacuum-ultraviolet radiation

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During plasma processing, low-k dielectrics are exposed to high levels of vacuum ultraviolet (VUV) radiation emitted from the plasma. The porous structure of these materials makes them more sensitive to modification because of their low density and consequently deep penetration of active species into the film. Here, we investigate the changes to electrical properties of porous low-k dielectrics as a function of porosity after VUV irradiation. Organosilicate low-k films of porosities between 30% and 50% were exposed to synchrotron VUV radiation at 8 eV with a fluence of approximately 5×10^{14} photons/cm^2. Capacitance-voltage measurements showed an increase in the dielectric constant along with a flat-band voltage shift. FTIR results show methyl depletion as well as water uptake after VUV treatment. These show that deterioration of the electrical properties after VUV exposure and the degree of damage are found to be higher for the more porous films. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4962899]

In this work, a measurement of the effects of porosity (30%–50%) on the electrical properties of dielectric materials irradiated with 8-eV photons is presented. The properties measured after vacuum ultraviolet (VUV) irradiation are compared with the intrinsic properties of pristine samples to determine the damage caused by the VUV photons.

Advanced interconnects for ultra-large scale integration devices on the sub-22 nm technology nodes require implementation of ultra low-k (ULK) dielectric films with dielectric constant $(k) < 2.5$.[1,2] These are needed to reduce RC delays[3,4] and crosstalk, which increases as the scaling of the Cu interconnects decreases. The most common materials used for this purpose are organosilicate glasses (OSG) usually deposited with a plasma-enhanced chemical vapor deposition (PECVD) process. To obtain even lower k-values, artificial porosity is introduced in the dielectric layer.[5–7] This is often done by co-deposition of a SiO_2-like matrix and an organic porogen. A UV-assisted thermal cure then removes the porogen, creating the pores.[6,7]

When the k-value of low-k materials drops below 2.3, the pore radius and porosity typically increase up to ~3–5 nm and ~50%, respectively.[20] Large pore size and high porosity create severe problems with plasma processing and integration.[15] The higher porosity of these low-k films is usually associated with inferior mechanical and chemical properties.[6,8–10] It has been reported that the Young's modulus is typically lower for the porous films and the material is less resistant to damage by etch-and strip-plasma treatments.[3,10] The porous materials are also extremely sensitive to modification during processing because of easier diffusion of active species from the processing plasma into the interconnected pores.[11] Other than the energetic neutrals, free radicals, and charged particles from the plasma, vacuum ultraviolet (VUV) radiation emitted from a processing plasma can also induce damage to the dielectric material.[12–19]

These VUV photons have sufficient energy for chemical modification and can lead to Si-CH_3 bond depletion in these porous materials, making them hydrophilic in nature and degrading their intrinsic reliability.[13,14] In this work, a measurement of the effects of porosity (30%–50%) on the electrical properties of dielectric materials irradiated with 8 eV VUV photons is presented. Previous work has shown that 8 eV photons cause significant damage to low-k films because of the deep penetration of the photons into the dielectric film.[15] The properties measured after VUV irradiation are compared with the intrinsic properties of pristine samples to determine the damage caused by the VUV photons.

The materials used for this study are ultra-low-k films prepared using PECVD technology. The films are cured at a temperature of 400 °C–430 °C and simultaneously exposed to a monochromatic broadband UV source ($\lambda > 200$ nm) to produce ALKB (ALKB is IMEC's internal abbreviation).[16] To avoid formation of amorphous carbon-like porogen residue, the films were exposed to H_2 downstream plasma before UV curing.[17] The porosities of these films were measured by ellipsometric porosimetry[18] and they range from about 30% to 50%. Table I below lists the properties and specifications of the three films used in this work. The thickness of the films is approximately 250 nm and their k values range from 1.9 to 2.4 depending on their porosity. The advanced low-k (ALK) films are deposited on p-type silicon substrates.

TABLE I. Advanced low-k (ALK B) film characteristics.

Material name	k-value (±0.07)	Open porosity (%)
D13	2.3	31
D9	2.2	38
D2	1.9	45

Monochromatic VUV radiation exposures were made at the National Synchrotron Radiation Research Center (NSRRC) in Taiwan using the apparatus shown in Figure 1. For this study, samples of different porosities were irradiated with 8-eV photons. This energy was chosen because previous work has shown that 8 eV photons can cause substantial damage to porous low-k films.[19] The photon flux was monitored *in-situ* using a photodiode (AXUV100) to ensure samples were irradiated with a fluence of approximately 5×10^{14} photons/cm^2, which is comparable to the photon fluence emitted during plasma processing.

Metal-insulator-semiconductor (MIS) structures were fabricated with e-beam evaporated 1000-nm thick, 80-μm diameter titanium electrodes through a stencil mask. Electrical measurements were made using a probe station (Signatone) in a dark box kept at 300 K. The MIS structures were biased such that the Si substrate was at a negative potential relative to the contact. Capacitance Voltage (CV) measurements were made using a HP 4285A Precision LCR meter along with a LabVIEW program. Ramped-voltage measurements were made by stepping a variable-voltage source in 0.125 V increments. This rate was found to provide the most reproducible results. Using this procedure, the C-V measurements were found to be highly repeatable, and the observed trends were found to be consistent across multiple samples.

In order to characterize the chemical bonds present in each dielectric sample and determine their relative concentrations, *ex-situ* FTIR measurements were made both before and after VUV exposures. The instrument used for this measurement was a Nicolet Magna-IR 560 spectrometer. All the measurements were made in transmission mode in order to obtain a spectrum from the bulk of the film. The wavenumber resolution was 4 cm^{-1} for all measurements. The spectrometer was purged with nitrogen to maintain a dry and clean environment during the measurements. Two hundred and fifty-six scans of spectra ranging from 400 to 4000 cm^{-1} were collected. The final spectrum is the average of the 256 scans. Since the low-k films were usually deposited on the Si substrate, the FTIR spectrum of the background, i.e., that of the Si substrate, was obtained first by removing the deposited film with buffered HF. The FTIR spectrum of the dielectric was then obtained by subtracting the background spectrum. Omnic software (Thermo Fisher Scientific, USA) was used to process the FTIR spectra.

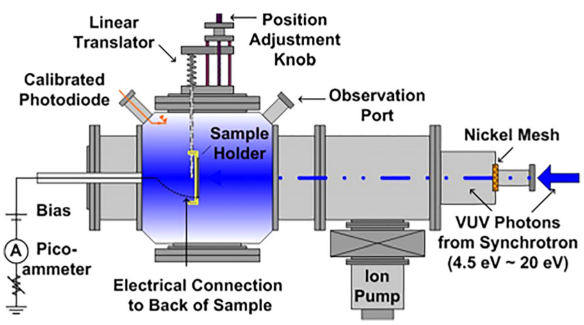

FIG. 1. Experimental arrangement for VUV irradiation of dielectric samples.

C-V measurements on the pristine and VUV irradiated samples were made at 10 MHz using the probe station and a high-precision LCR meter. The corresponding k values of the porous samples were calculated from the CV measurements. Figure 2 shows the CV characteristics of samples D2, D9, and D13 after an 8-eV VUV exposure. The CV measurements showed that the k values of all the samples increase after VUV exposure. It was also observed from the measurements that the increase in the k values is higher for the more porous

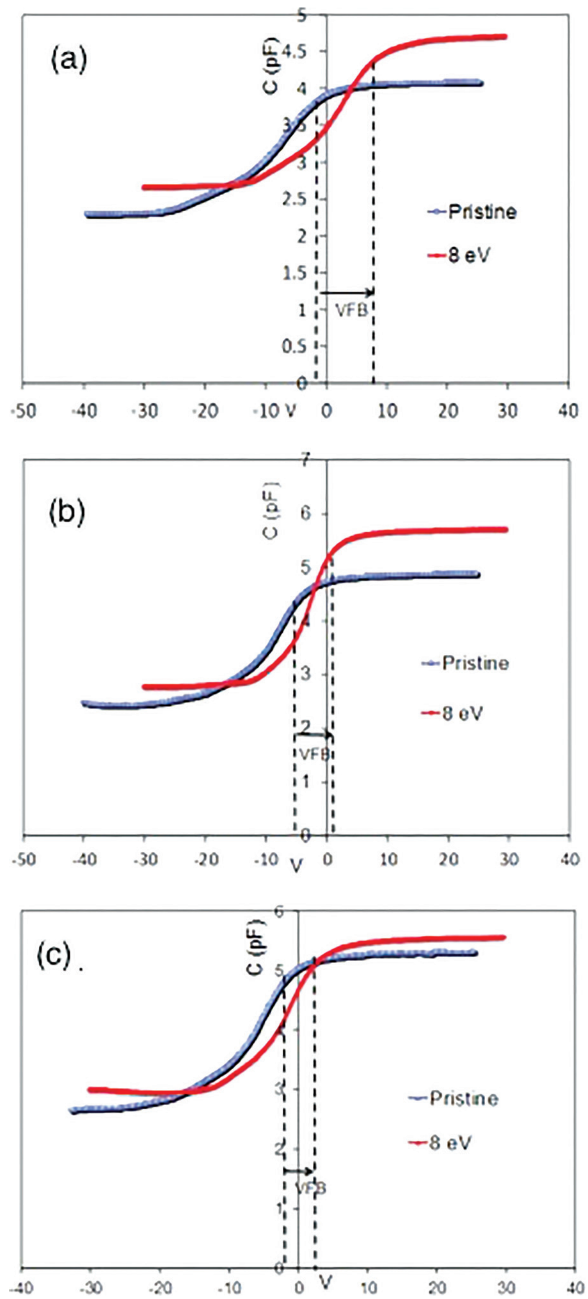

FIG. 2. CV characteristics of (a) D2 (46% porosity), (b) D9 (38% porosity), and (c) D13 (32% porosity), respectively. The double vertical lines at the mid-plane of each graph show the flat-band voltage (V_{FB}) shifts for each sample.

TABLE II. Change in k value after 8-eV VUV exposure.

Porosity (%)	k (pristine)	k (after VUV)	Increase in k	% Change
31	2.3	2.4	0.1	4.3
38	2.2	2.55	0.35	15.9
45	1.9	2.3	0.4	21.1

samples. Table II lists the k values of the pristine and VUV irradiated samples as well as the increase in k values as a function of porosity.

It has been reported in previous work that an increase in the k value can be due to water uptake by the dielectric film.[20] Although the low-k films were initially hydrophobic, chemical modifications to the bond structure of the material can compromise the hydrophobicity of the films and lead to water uptake. In order to test this hypothesis, FTIR measurements were performed on all the pristine and VUV treated samples and the bond concentrations were compared. The FTIR results are discussed as follows.

Ex-situ FTIR spectroscopy was used in order to detect the changes in chemical-bond concentrations in low-k samples. The terminal Si-CH_3 bonds observed via the Si-CH_3 deformation mode at wavenumber 1275 cm^{-1} are responsible for the hydrophobic nature of these materials.[21] The FTIR spectrum of pristine, UV-cured ALK film is shown in Figure 3. No observable Si-OH peak (3500 cm^{-1} to 4000 cm^{-1}) was present in the pristine samples, which indicates that there is no significant absorbance of moisture under ambient conditions. After the samples were exposed to 8-eV photons, a rise in the Si-OH "hump" was observed (see Figure 4) as well as depletion of methyl groups. The fraction of $SiCH_3$ remaining in each sample after VUV treatment is listed in Table III. The results show that 8-eV photons break chemical bonds in the low-k films and the samples start absorbing moisture when they are brought out of the vacuum chamber. This will directly affect the film properties and lead to an increase in the dielectric constant as observed from the CV characteristics.

From the CV measurements, a positive flat-band voltage shift was also observed after VUV exposure for all three samples. Table IV lists the flat-band voltage for each sample before and after VUV treatment. The CV measurements show that the flat-band voltage shift is higher for more porous low-k films after they have been exposed to the same dose and energy of VUV photons. The positive flat-band voltage shift indicates that there are negative mobile charges within the dielectric layer and the magnitude of the flat-band voltage shift is proportional to the amount of negative mobile charge.[22] These results can be explained as follows.

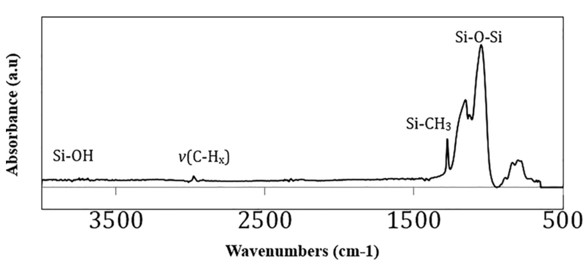

FIG. 3. FTIR spectrum of pristine ALKB films.

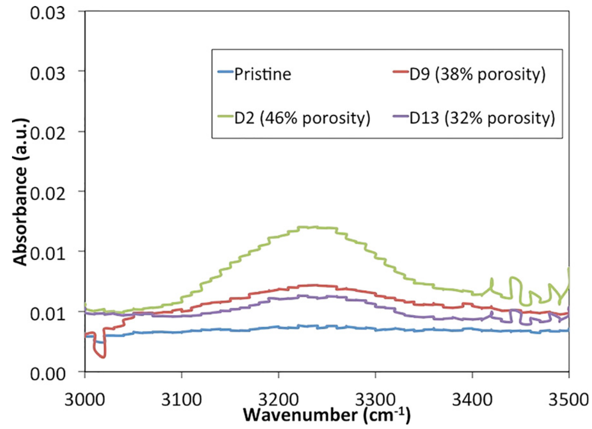

FIG. 4. Moisture uptake by ALK films after VUV exposure. The Si-OH "hump" is shown in the figure above.

TABLE III. Fraction of $SiCH_3$ remaining after 8-eV VUV exposure.

Material	Porosity	$[SiCH_3]_{exposed}/[SiCH_3]_{pristine}$
D13	31	0.55
D9	38	0.35
D2	45	0.28

It is well known that VUV irradiation causes photoinjection, photoconduction, and photoemission in thin dielectric films.[12,22–25] Energetic photons can penetrate deep into the dielectric layer and cause photoinjection of electrons from the silicon[25] dielectric-substrate interface into the dielectric layer.[12,22,25,26] This leads to additional negative charges within the dielectric layer as indicated by a positive flat-band voltage shift in the CV curve. The films with higher porosity are less dense which allows more photons to penetrate through the films to the substrate. This leads to a higher degree of photoinjection and increased flat-band voltage shift. Although VUV photons can also cause photoemission of electrons from the dielectric layer to the vacuum, the energy required for photoemission is much higher than the energy required to photoinject electrons from the silicon substrate into the dielectric layer. Hence the photoinjected negative charges will accumulate in the dielectric layer and cause a positive flat band voltage shift that increases with porosity. This is because the density of the dielectric films decreases with increasing porosities that allows deeper penetration of the VUV photons into the dielectric film. Deeper penetration of photons with increasing porosity leads to a higher number of electrons photoinjected into the dielectric film from the silicon substrate. The amount of negative charge accumulation in the dielectric layer after the VUV treatment is directly related to the magnitude of the flat-band voltage shift observed from the CV measurements.

TABLE IV. Flat-band voltage shift after 8 eV VUV exposure.

Material	Porosity	V_{FB} (pristine) (V)	V_{FB} (VUV) (V)	ΔV_{FB} (V)
D13	31.4	0	5	5
D9	38.3	−5	1	6
D2	45.4	−2	6	8

This work shows that the degree of VUV-induced damage is higher for the more porous films indicating that the introduction of pores makes the low-k films more susceptible to damage from photon bombardment. This was determined by examining the influence of porosity on advanced low-k dielectrics irradiated with 8-eV VUV photons. CV measurements were made after VUV irradiation, which showed increasing k values and flat-band voltage shifts as a function of film porosity. FTIR measurements showed that VUV photons break Si-CH_3 bonds in the dielectric films followed by water uptake leading to an increase in k values. The $SiCH_3$ depletion and water uptake by the low-k film also increased as a function of porosity after VUV exposure. It is likely that VUV photons can penetrate deeper into the dielectric film as the porosity increases because of the lower density of the film. This can lead to photoinjection from the substrate into the dielectric layer that became evident from the positive flat-band voltage shift, which was observed from the CV measurements. Besien *et al*. previously reported that pristine low-k films with increasing porosity show higher leakage currents and lower breakdown fields.[8] The increased leakage currents with increasing porosity for the pristine films can be attributed to the presence of more porogen residue.

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