

Dielectric Damage

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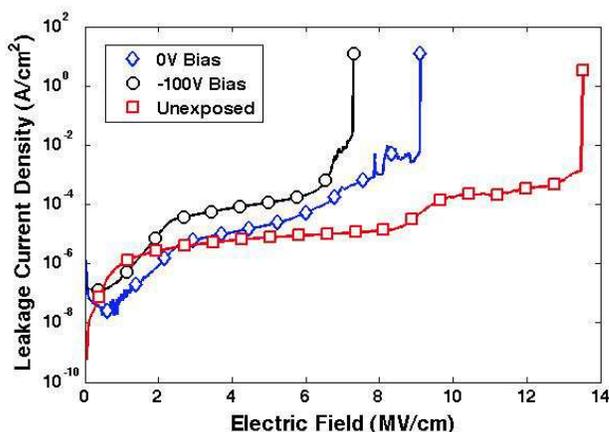
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More and more high- and low-k dielectrics are used in microfabrication today. However, as is well known, these materials are easily damaged during processing or during operation in a device. Sources of damage include plasma and/or VUV exposure, water uptake, free radicals as well as cosmic rays. A description of the damage effects on dielectrics from water uptake, plasma and/or VUV exposure, and neutron exposure is presented. Although the results for neutron exposure are presented for a high-k dielectric, HfO₂, they can easily be extended to low-k dielectrics.

The Effects of Plasma Exposure and Vacuum Ultraviolet Irradiation on Photopatternable Low-k Dielectric Materials¹

The effects of plasma exposure and vacuum-ultraviolet (VUV) irradiation on photopatternable low-k dielectric materials (PPLK) were investigated. In order to examine these effects, current-voltage measurements were made on PPLK materials before and after exposure to a variety of inert plasma-exposure conditions. In order to examine the effects of photon irradiation alone, PPLK samples were also exposed to



monochromatic synchrotron radiation with 10-eV photon energy. It was found that plasma and/or VUV exposure causes significant degradation in electrical characteristics, resulting in increased leakage-currents and decreased breakdown voltage.

Figure 1. Effect of argon plasma exposure and r.f. bias on current-voltage characteristics of UV-cured PPLK.

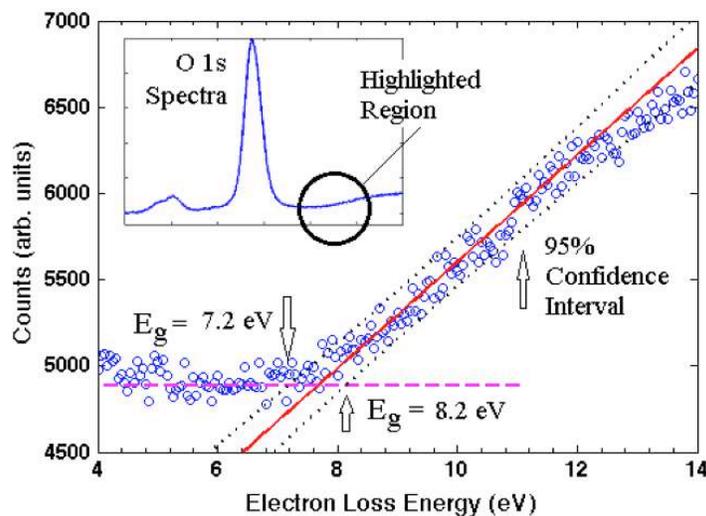
Figure 1 shows the effects of plasma exposure and r.f. bias on leakage currents of PPLK dielectrics under VUV exposure. In addition, XPS measurements also showed appreciable carbon loss near the sample surface after plasma exposure. Conversely, VUV exposure was found to increase breakdown voltage and reduce leakage-current magnitudes.

Bandgap measurements of low-k porous organosilicate dielectrics using x-ray photoelectron spectroscopy and vacuum ultraviolet irradiation

X-ray Photoelectron Spectroscopy (XPS)

XPS is used to analyze the binding energies of the atomic core-level electrons in a material. These core-level spectra are representative of the chemical composition of the material near the surface (*i.e.*, within the electron-escape depth) and, among other things, can give detailed information about changes in the atomic structure near the surface due to processing-induced damage. In addition to measuring the photoelectron intensities of core-level peaks, XPS can also be used to analyze the inelastic collisions that occur during photoexcitation and photoemission of electrons from the sample. These inelastic processes include band-to-band electronic transitions and excitation of “plasma waves” by Coulomb interaction with other electrons below the Fermi level, or equivalently for insulators and semiconductors (assuming there are no defect states below the Fermi level), with electrons in the valence band. Analysis of these inelastic processes can be used to determine the bandgap energy near the surface of the dielectric.

By measuring the onset of inelastic loss relative to the O 1s core level peak, the bandgap



energies for organosilicate films can also be determined. To further verify the efficacy of fitting a linear extrapolation about the inelastic loss peak, bandgap energies were measured for 644-nm $k=2.75$ as-deposited SiCOH films. Extrapolating a linear fit to the loss yielded a bandgap energy of $E_g = 7.0$ eV.

Figure 2. Electron energy loss spectrum showing linear fit (solid line) with 95% confidence interval (dotted lines) for UV-cured SiCOH. Inset: region of O 1s spectra corresponding to loss spectra.

Figure 3 shows the electron energy-loss spectrum for PPLK.

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Vacuum Ultraviolet Irradiation

Vacuum ultraviolet (VUV) photoemission spectroscopy is used to investigate the effect of VUV radiation on porous organosilicate (SiCOH) dielectrics during plasma processing. By comparing photoemission spectroscopic results before and after VUV exposure, VUV irradiation with photon energies less than 9.0 eV was found to be beneficial in depleting

accumulated charge in SiCOH films while VUV photons with higher energies did not have this effect. Moreover, VUV irradiation with 8.9 eV photons depletes the most charge. From this result, it can be concluded that 8.9 eV is the bandgap plus the electron affinity energy of SiCOH dielectrics.

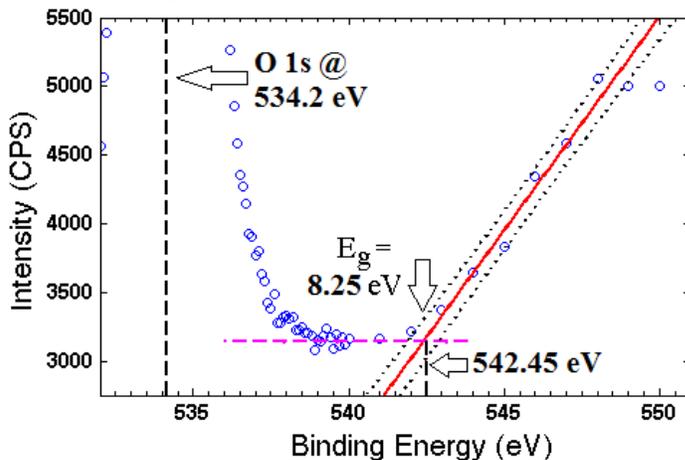


Figure 3. Bandgap measurements for $k = 2.75$ UV-cured PPLK materials showing 95% confidence interval.

Table I shows a summary of recent bandgap measurements of low- k dielectrics. According to the Grill group,² film thicknesses, optical properties, and band gaps in their cited papers were measured using a spectrometric reflectance tool, specifically the

N&K model¹⁹.

TABLE I. Bandgap Measurements in low- k organosilicates

Dielectric	K	E _g (eV)	Method	Reference
Dense SiCOH	3.99	4.74	Optical Reflectance	Grill, 1999 ³
Dense SiCOH	3.25	5.92	Optical Reflectance	Grill, 1999
Porous SiCOH	2.6	2.91	Optical Reflectance	Grill, 2003 ⁴
Porous SiCOH	2.1	3.62	Optical Reflectance	Grill, 2003
Porous SiCOH	2.55	9.0	VUV spectroscopy	Lauer 2010 ⁵
Porous SiCOH	2.65	7.7 ± 0.5	XPS	This Work
Porous SiCOH	2.3,2.8	8.0 ± 0.4	REELS	King, 2013 ⁶
As-dep. SiCOH	2.75	7.2	XPS	This Work
PPLK	2.75	8.25 ± 0.5	XPS	This Work
Thermal SiO ₂	3.9	8.8	XPS	This Work

According to the manufacturer, the range of wavelengths used by this tool is between 190-1000 nm, and it calculates optical constants from reflectance data using the Forouhi-Bloomer (F-B) relations. However, as noted by others, the F-B equations were originally derived for use in the interband energy region of a material.⁷ In other words, they were meant to be applied to measured data that is taken using photon energies *higher* than the bandgap energy. Since the wavelength range of the N&K analyzer used in the above-cited work is limited to a maximum photon energy of 6.53 eV (190 nm wavelength), the vast majority of the measured optical data corresponds to photon energies lower than *the*

reported bandgap measurements of ~ 6 eV. Hence, it is plausible that the light source used in previous work by the Grill group was not capable of emitting short-enough wavelengths for accurate determination of the optical bandgap energy of the films that were studied.

The effect of water uptake on the mechanical properties of low-k organosilicate glass⁸

Interconnect resistive-capacitive (RC) delay is a major challenge for the further downscaling of integrated circuits. To reduce the capacitance, materials with lower dielectric constants are being used in back-end-of-line (BEOL) integration. Recently, low-k porous organosilicate glasses (OSG or SiCOH), i.e., porous SiO₂ with hydrophobic methyl groups (-CH₃) lining the pores, have attracted much attention and are widely accepted due to their enormous potential as an alternative to conventional SiO₂ for inter-metal dielectrics.^{9,10,11} However, these originally hydrophobic porous-structured low-k dielectrics, have been found to become hydrophilic after plasma processing (e.g., photoresist stripping and cleaning).¹² For example, CF_x polymers that are deposited during the etching of SiCOH in fluorocarbon plasma can introduce hydrophilic properties to SiCOH because they are not as hydrophobic as -CH₃ groups. Additionally, oxygen plasma, usually used to remove organic photoresist polymers, can also remove the original hydrophobic groups (-CH₃) and create some free radical sites (-SiO₂•), resulting in the formation of hydrophilic -SiO₂-OH groups. These hydrophilic groups enable significant amounts of water to be absorbed from humid air following diffusion into the SiCOH bulk through interconnected pores.¹³

For these dielectrics, which include free-radical sites (-SiO₂•), it has been reported that there exist four types of water-related chemical groups attached to the Si-based siloxane groups. The α -bonded and β -bonded water components, often called physisorbed water and chemisorbed water, respectively, are water molecules that are hydrogen-bonded to the hydrophilic hydroxyl groups. Unlike α -bonded water molecules that are loosely bonded to each other and to surface hydroxyl groups, β -bonded water is tightly hydrogen-bonded to two neighboring hydroxyl groups. The existence of these water molecules will increase the dielectric constant of the material and thus detract from efforts to develop low-k dielectrics. Fortunately, these hydrogen-bonded water components can be desorbed at specific annealing temperatures for each component, without changing or damaging the chemical structure and integrity of the SiCOH.¹⁴ This will degrade the dielectric properties and worsen reliability. Previous work¹⁵ has shown that for these types of OSG, both the hardness and elastic modulus can vary significantly with ambient humidity. Nanoindentation measurements were made on dehydrated organosilicate glass during exposure to varying humidity conditions.

The elastic modulus and hardness for as-deposited SiCOH are intimately linked to the nature and concentration of the absorbed water in the dielectric. The elastic modulus varies with the absorbed water components for as-deposited SiCOH films. Water-saturated films (with both α - and β -bonded water in the bulk) have the highest modulus of 5.5 ± 0.2 GPa, α -bonded water-removed films have a lower modulus of 5.1 ± 0.2 GPa, and both α - and β -bonded water removed films have the lowest modulus of 4.2 ± 0.2 GPa. These results indicate that reduced water in SiCOH decreases the film's elastic modulus, which is consistent with Broussous' results¹⁵. Further analysis shows that, compared with the water-saturated samples, the elastic modulus of samples with only β -bonded water does not decrease substantially (7.3%), while for the both α - and β -bonded water-removed sample, the modulus value has a larger drop (23.6%). The decrease in the

modulus for initially both α - and β - bonded water removed SiCOH is more than three times of that for only α -bonded water removed SiCOH. This may indicate that the β - bonded water has a more significant effect on the elastic modulus than α -bonded water for as-deposited SiCOH.

For as-deposited SiCOH, the sample hardness of water-saturated, only with α -bonded water was removed and with both α - and β -bonded water removed were measured to be 0.35 ± 0.01 GPa, 0.32 ± 0.01 GPa and 0.27 ± 0.01 GPa respectively under a humidity of 10%. Compared with the water-saturated samples, dehydration of only α -bonded water and dehydration of both α - and β -bonded water induces hardness degradations of 8.6% and 22.8% separately, demonstrating that dehydration of SiCOH decreases the hardness. In addition, the β -bonded water has a more significant effect than α -bonded water. These trends are in good agreement with that for the elastic modulus for as-deposited SiCOH. When the humidity was increased to 38% and then to 73% from 10%, the hardness of the water-saturated SiCOH film almost remains stable; while for the dehydrated films, the hardness increases and tends to approach the value of the water-saturated samples. It can be concluded that these hardness variations can be reversed through mild annealing.

The same measurements were also carried out on UV-Cured OSG, and it was found that the mechanical properties of UV-cured OSG were dependent on absorbed water, although to a lesser extent because UV curing depopulates the hydrophilic chemical groups in the OSG bulk and thus lowers the degree of its hydrophilicity. Thus, UV-curing can be used to resist the water uptake induced property variations and increase reliability.

Effects of neutron irradiation of ultra-thin HfO₂ film

Continued exposure cosmic-ray irradiation can cause single-event upsets (SEU)¹⁶ that can contribute to time-dependent dielectric breakdown (TDDB)¹⁷ and also decrease the reliability of devices. Although the results presented here are for a high-k dielectric film, the method can easily be applied to low-k dielectrics. In the past, radiation hardening of devices was one of the principal drivers for damage measurements as a function of fluence (dose) for military and space applications. Initially, radiation hardening was investigated for basic devices utilizing SiO₂ on Si.¹⁸ However, "Cosmic-ray induced computer crashes have occurred and are expected to increase with frequency as devices (for example, transistors) decrease in size in chips. This problem is projected to become a major limiter of computer reliability in the next decade," Intel Corporation. Following this, studies were undertaken to investigate SEUs to understand "random" malfunctions of DRAM and SRAM and currently RRAM. SEUs are typically produced by two mechanisms, (1) energetic charged particles, such as alpha particles and protons, produced by radioactive metallic impurities¹⁹ and (2) charged particles produced by neutron recoil.²⁰ The former can be prevented with a relatively thick polymer coating, such as polyimide, of the Si chip after removing radioactive impurities in the metal interconnects, while the latter can be reduced with careful design for devices and the introduction of parity bits for memory.

The leakage currents of the pristine sample and samples irradiated by three different neutron fluences are shown in Figure 4. Each leakage-current measurement was repeated five times for each neutron fluence, and the results shown in Figure 4 are the averages of the data. It is clear that the leakage currents decrease when the radiation fluence increases. This is believed to be due to the decrease in the number of Pb-type defect states as was shown in electron-spin resonance measurements. For pristine samples, the Pb-type defect states that are very near the Si/HfO₂ interface reduce the barrier at the surface of HfO₂

which enhances Poole-Frenkel conduction.²¹ However, after neutron irradiation, the number of Pb-type defect states decreases, with a concomitant reduction in leakage current. It should be noted that in this experiment, although the E' state concentration increases at high neutron fluence, this defect has a negligible effect on the leakage current since the number of E' states is very small compared with the number of Pb-type states.

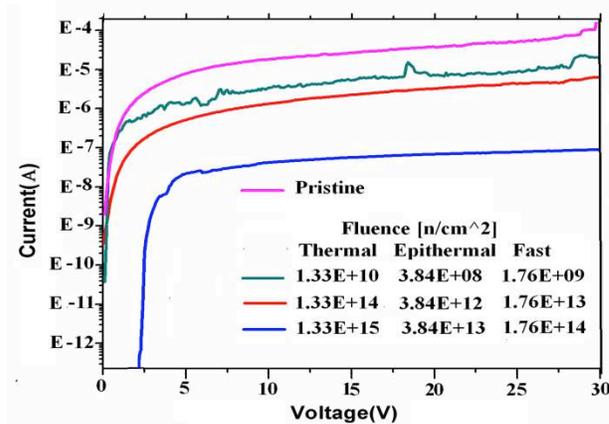


Figure 4. I-V characteristics of pristine and neutron-irradiated HfO₂. The highest fluence produces the lowest leakage current.

Acknowledgments

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