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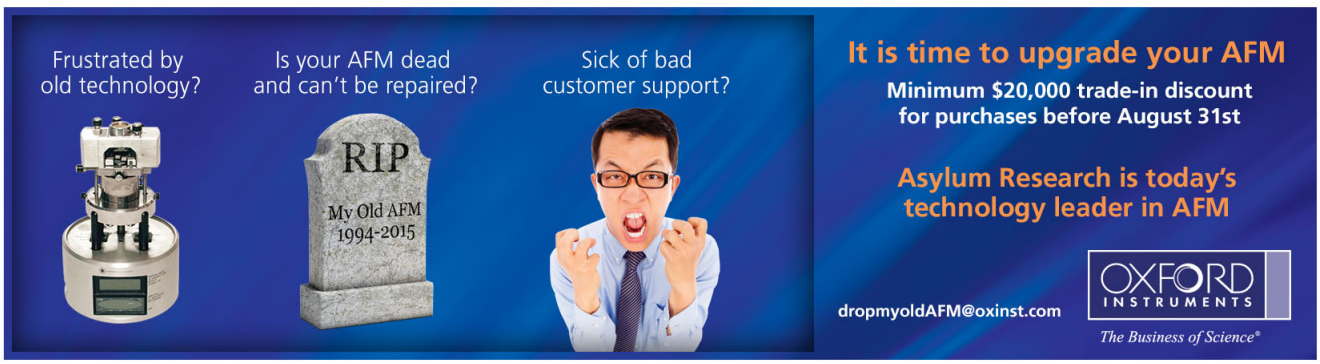

Effects of vacuum ultraviolet irradiation on trapped charges and leakage currents of low-k organosilicate dielectrics

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Vacuum ultraviolet (VUV) photoemission spectroscopy is utilized to investigate the distribution of trapped charges within the bandgap of low dielectric constant (low-k) organosilicate (SiCOH) materials. It was found that trapped charges are continuously distributed within the bandgap of porous SiCOH and the center of the trapped states is 1.3 eV above the valence band of the tested sample. By comparing photoemission spectroscopic results before and after VUV exposure, VUV irradiation with photon energies between 7.6 and 8.9 eV was found to deplete trapped charge while UV exposure with photon energies less than 6.0 eV induces more trapped charges in tested samples. Current-Voltage (IV) characteristics results show that the reliability of dielectrics is improved after VUV irradiation with photon energies between 7.6 and 8.9 eV, while UV exposure results in an increased level of leakage current and a decreased breakdown voltage, both of which are harmful to the reliability of the dielectric. This work shows that VUV irradiation holds the potential to substitute for UV curing in microelectronic processing to improve the reliability of low-k dielectrics by mitigating the leakage currents and trapped charges induced by UV irradiation.
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The next generation of integrated circuit (IC) fabrication requires the utilization of low-k materials as inter-layer dielectrics (ILDs) and etch-stop layers (ESLs).[1–3] One of the significant concerns about this emerging insulating dielectric material is its electrical reliability in MOS structures. The reliability is directly linked to the presence and creation of trapped charges,[4,5] especially after plasma processing. Therefore, much work has been done in order to develop metrologies to measure these defect-state concentrations. Specifically, electron-spin resonance (ESR) spectroscopy has been used to detect and identify defect-state concentrations in dielectric films,[6,7] but the distribution of trapped charges within the band gap of low-k dielectrics cannot be detected with ESR measurements[6] and is still an open question.

In this letter, vacuum-ultraviolet (VUV) photoemission spectra are utilized to solve this problem. It was found that 7.6–8.9 eV vacuum-ultraviolet irradiation depletes trapped charges while ultraviolet exposure with lower photon energies causes an increased level of trapped charges in SiCOH which contributes to the degradation of the dielectrics.[5,8] This indicates that VUV irradiation could overcome some of the disadvantages of ultraviolet curing by depleting trapped charges within dielectrics and holds the potential to be the next generation curing light source for low-k thin film deposition.

VUV irradiation of dielectrics often results in electron-hole pair generation, photoconduction, photoemission, and photoinjection of electrons from the substrate into the dielectric.[9,10] These processes depend on the incident photon energy and the dielectric thickness. Electron-hole pairs will be formed if electrons are excited into the conduction band from the valence band or from bandgap defect states within the dielectric.[11,12] Depending on their energy, the electrons and holes can travel in the dielectric with a number of them being photoemitted. Electrons dominate photoconduction, photoemission, and photoinjection, since the mobility of electrons is larger than the mobility of holes.[5] When the energy supplied by irradiation is greater than the sum of the band-gap energy and the electron affinity, photoemission can occur from the dielectrics.[12,13] By measuring the VUV photoemission spectra, peaks in the measured photoemission currents at various photon energies can be detected. By comparing the photon energy at which the electrons are excited with the measured bandgap of the tested samples reported in the previous work,[14] the presence of electron traps and their energy distribution can be found.

The samples used for this work, 150 nm-thick porous SiCOH/Si wafers ($k = 3.05$), were fabricated in a plasma-enhanced chemical-vapor-deposited (PECVD) reactor. These samples were rapidly scanned with monochromatic VUV synchrotron radiation. The advantage of a synchrotron is that it generates radiation with no charged particles and can be varied over a continuum of photon energies.[15] In this work, the photon energy range was chosen to be 4.5–8.9 eV. This range was chosen because (1) 4.5 eV is the lowest photon energy that could be selected from the stainless Seya-monochromator utilized in the synchrotron beamline and (2) 8.9 eV is the threshold energy for photoemission of electrons from the valance band of dielectrics into vacuum.[14] Higher photon energies were not selected since they could also generate large charge accumulation and affect the reliability of SiCOH films.[13] In addition, based on the relation between the wavelength of the VUV photons and their penetration depth in low-k dielectrics,[16] those photons with

energies from 4.5 to 8.9 eV can easily penetrate through the dielectric layer. Finally, the normalized photoemission currents induced by different photon energies in these ranges are comparable.

For VUV photoemission spectroscopy, the exit slit of the synchrotron-beam monochromator was set to 40 μm to minimize the photon flux so that modification of the dielectric by VUV photons was minimized. The VUV photons were normally incident on the surface of the SiCOH sample at a pressure of 10^{-8} Torr and the VUV beam on the surface of the wafer had a cross-sectional area of 3×0.1 cm^2.

Figure 1 shows a comparison between the VUV photoemission spectroscopic measurements of a pristine SiCOH dielectric film and the dark current measured without photon irradiation. The photoemission current was normalized by dividing the measured photoemission current by the incoming VUV photon flux. It was found that the photoemission current is at least three orders of magnitude higher than the dark current. The photoemission current is still present for photon energies much less than the bandgap of the tested SiCOH sample. This shows that the trapped charges must be distributed within the bandgap of the dielectric. The higher the normalized photoemission current means the higher the level of trapped charges within the bandgap of the pristine SiCOH samples. The highest peak was observed in the VUV photoemission spectrum at an energy of 7.6 eV. Since 7.6 eV is lower than the band gap of the tested sample,[14] electrons in the valence band of SiCOH could not absorb enough energy from these photons to be emitted into the vacuum. Therefore, this implies that there must be a defect center within the band gap of SiCOH from which level the electrons could be emitted into vacuum condition after absorbing 7.6 eV from the irradiated photons. Since the threshold energy for electrons in the test samples to be emitted from the valance band of dielectrics into vacuum is 8.9 eV,[14] it is plausible that the trap center is located 1.3 eV above the valence band of SiCOH. In addition, it can be concluded that VUV irradiation with photon energies between 7.6 and 8.9 eV can efficiently reduce the trapped charges within the dielectrics by photoemission. That is, the trapped charges within the bandgap of SiCOH can absorb energy from the VUV photons and be photoemitted. It must be mentioned although the density of trapped charges is relatively small,[3,7,8] that post treatment (e.g., UV exposure[12,13] and hydrogen annealing[17,18]) might still be needed to make sure that there is no significant net charge generated due to photoemission.[13] As a result, the trapped charges within the bandgap of the dielectric are reduced, the defect states are passivated and electrical activity is mitigated[19] since trapped charges are shifted out of the band-gap of the low-k dielectric.[20]

To prove this hypothesis, monochromatic photons between 7.6 and 8.9 eV were exposed on the samples. The exit slit width of the synchrotron monochromator was now set to 500 μm to maximize the photon flux. The accumulated photon fluence for VUV exposure was set to be 1.3×10^{14} photons/cm^2 by using a photodiode (AXUV100). This is comparable to the VUV photon fluence emitted during a typical plasma process.[8,14,21] Photon energies were specifically selected to mimic those emitted by processing plasmas.[22] Specifically, photons of 8.4 eV energy (147.6 nm wavelength) were used to mimic the strong emission lines generated from a Xe plasma[23] which is a typical inert feed gas utilized in thin-film deposition.

Figure 2 shows a comparison of VUV photoemission spectroscopic measurements for a SiCOH dielectric film before and after irradiation with 8.4 eV photons. It can be seen that the normalized photoemission current decreases drastically after the 8.4 eV VUV irradiation. This indicates that the level of trapped charges has been reduced significantly. It must be mentioned that VUV photoemission spectroscopy spectra are not shown for VUV exposures other than 8.4 eV over the desired energy range (7.6–8.9 eV) because these results are similar to those shown in Figure 2.

To further understand and investigate the effect of VUV irradiation on reliabilities of low-k dielectrics, Figure 3 shows the IV characteristics for both pristine and 8.4 eV VUV-exposed SiCOH samples. To measure the characteristics, a 300-nm titanium metal layer was uniformly deposited on the surface of the dielectric to form a Metal-Oxide-Silicon (MOS) structure. The dimensions of all test structures were the same since the changes in the metal contact area could affect the breakdown voltage and IV measurements.[24,25] Hexagonal patterned masks were used to define the metal contact area of the tested structures. The area of each hexagon is 2.8×10^{-4} cm^2. For current-voltage (I-V) measurements, a computer-controlled combination high-

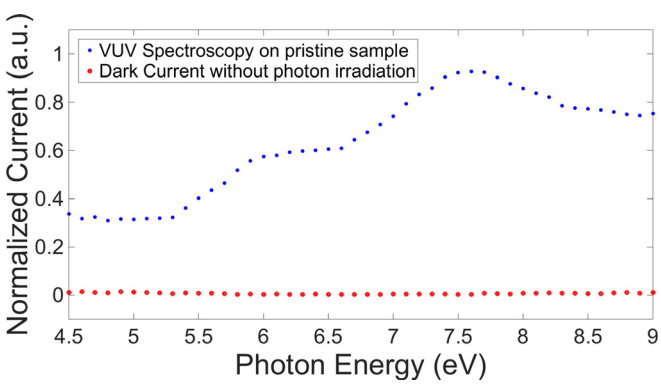

FIG. 1. Comparison of VUV photoemission spectroscopic measurements on 150 nm SiCOH and normalized dark current.

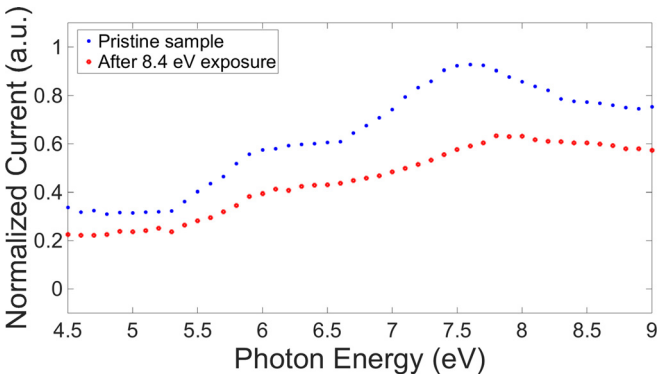

FIG. 2. VUV photoemission spectroscopic measurements on 150 nm SiCOH before and after 8.4 eV VUV irradiation with 1.3×10^{14} photons/cm^2 fluence.

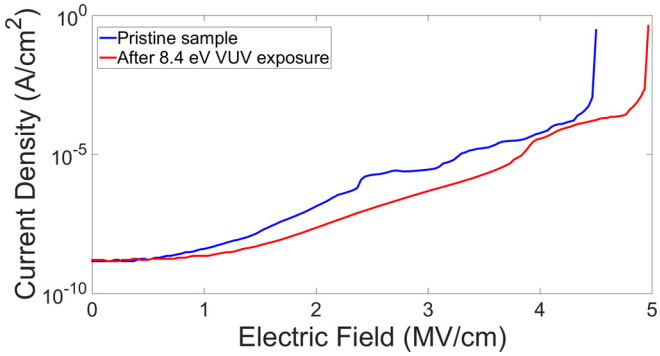

FIG. 3. Comparison of I-V characteristics of 150 nm SiCOH test samples before and after 8.4 eV VUV irradiation with 1.3×10^{14} photons/cm^2 fluence.

voltage supply and a Keithley 6487 picoammeter was used. Labview was used to automate the data collection.[26]

Figure 3 shows the comparison of the I-V characteristics before and after 8.4 eV exposure on the samples. For each IV curve, seven test structures were measured and averaged to help ensure that the results are repeatable and convincing. The most significant result from this data is that the 8.4 eV VUV exposure appears to *reduce* the magnitude of the leakage currents measured in the pristine films. In addition, the slope of the current as a function of voltage *decreases* after VUV exposure. Finally, 8.4-eV VUV exposure results in an increase in the breakdown voltage (V_{bd}) of the SiCOH samples: for the pristine sample, the breakdown voltage is 67.2 ± 0.8 V and after 8.4 eV VUV exposure, the breakdown voltage is 74.3 ± 1.0 V, which shows a good improvement in this quantity for low-k dielectrics. Therefore, it is plausible that trapped charges within the dielectric produces leakage currents and the resulting photoemitted trapped electrons under VUV irradiation contribute to the improvement of the electrical properties and reliability of low-k thin films.

Furthermore, the current density versus electric field curves shown in Figure 3 indicates multiple conduction mechanisms dominating at different electric field regimes.[26] The dominant conduction mechanisms for the organosilicate analyzed in this work are Schottky emission,[27] Poole-Frenkel emission,[28] and Fowler-Nordheim tunneling.[29] Here, the IV curves can be divided into four regions that correspond to different conduction mechanisms.[26] For the I-V curve of the pristine sample, the first region corresponding to very low electric fields from 0 to approximately 0.5 MV/cm, exhibits irregular behavior and does not appear to fit any plausible conduction model.[26] This behavior can be attributed to electrical and ambient noise since the measured current under extremely low bias is comparable to the noise level.[26] This result was also observed by Yiang *et al.*[30] and Nichols *et al.*[22] and explained in their work. The regions from 0.5 MV/cm to 1.5 MV/cm and from 1.5 MV/cm to 2.35 MV/cm fit well with the Schottky and Poole-Frenkel emission models respectively. Clear linear regions are seen for $\ln(J) \sim E^{1/2}$ and $\ln(J/E) \sim E^{1/2}$ where J stands for current density (A/cm^2) and E is the measured electric field (MV/cm).[26,30] Therefore, Schottky and Poole-Frenkel emission are indeed the dominating conduction mechanisms in these regions.[26] From 2.35 MV/cm toward the dielectric breakdown regime, another mechanism, Fower-Nordheim tunneling, occurs. The linear relation between $\ln(J/E^2)$ and E^{-1} in this region indicates Fower-Nordheim tunneling is the dominant conduction mechanism from 2.35 MV/cm to breakdown.[22,26]

The I-V curve for the 8.4 eV VUV-exposed sample is also shown in Figure 3. The first region which is produced by electrical and/or ambient noise is similar to the I-V curve for the pristine sample (0–0.5 MV/cm), while Schottky emission dominates an extended region from 0.5 to about 1.73 MV/cm.[22,26] A similar result is found for the third and fourth regions.[26,30] Poole-Frenkel emission is the dominating conduction mechanism from 1.73 to 3.7 MV/cm and the region between 3.7 MV/cm toward breakdown is dominated by Fower-Nordheim tunneling.[22,26] Thus, VUV exposure has changed the boundaries of the conduction mechanism regimes and, importantly, increased the breakdown electric field.[22]

It was found in previous work[8] that UV exposure and UV curing with photon energies less than 6.0 eV can induce higher leakage currents and a lower breakdown voltage of these dielectric films. It is thus important to differentiate between the effects of VUV and UV photon irradiation. Figure 4 shows a comparison of photoemission spectroscopic measurements for pristine 8.4 eV-VUV exposed and 4.9 eV UV-exposed SiCOH samples. In contrast to the measured photoemission spectra after VUV irradiation, after 4.9 eV irradiation with a photon dose of 1.3×10^{14} photons/cm^2, the VUV photoemission spectrum of pristine SiCOH *increased* over the band of photon energies between 4.5 and 8.9 eV. Two main effects contributed to these results.

First, since the penetration depth of 253 nm photons is much larger than the thickness of the tested low-k dielectrics (150 nm),[14] photons that are not absorbed in SiCOH can penetrate through the dielectric layer and directly impinge on the Si substrate. These photons can then be absorbed in the Si substrate and can create electron-hole pairs. Since the Si-SiCOH interface barrier is around 4.2 eV,[11] some of the electrons can overcome the Si-SiCOH interface barrier and are injected into the dielectric layer. If these electrons do not have enough energy to overcome the band-gap of the dielectric layer and be emitted into vacuum, they could be trapped in defect centers within the bandgap of the dielectric and

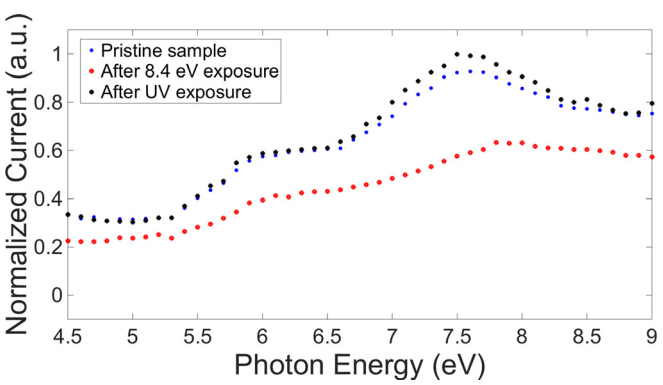

FIG. 4. Comparison of VUV photoemission spectroscopic measurements of pristine SiCOH samples and samples after 8.4 and 4.9 eV photon irradiation.

contribute to the increased level of trapped charges after UV irradiation.

Second, trapped charges within the bandgap of dielectrics cannot be efficiently photoemitted by photons in the UV range. For example, from VUV photoemission spectroscopic results, it was found that trapped electrons require photon energies equal to or larger than 7.6 eV to be emitted. Therefore, the UV light used (4.9 eV) does not provide sufficient energy to deplete the trapped charges. In Figure 4, this result can be easily observed from the photoemission spectra: after 4.9 eV irradiation, the normalized photoemission current does not decrease which indicates that trapped charges were not removed.

Both of these reasons lead to the conclusion that trapped charges within the SiCOH sample increased after UV exposure. In addition, the leakage current increased and the breakdown voltage decreased. This result shows that the optimal photon energy for low-k dielectric curing lies in the VUV range of the spectrum rather than the UV range. Thus, the disadvantage of UV curing that result in more trapped charges and increased leakage currents could be minimized by VUV exposure/curing under carefully selected conditions.

In summary, VUV spectroscopy was utilized to detect the distribution of trapped charges within the band gap of dielectrics. For our test samples, the trapped centers were found to be about 1.3 eV above the valence band of SiCOH. Moreover, VUV irradiation with photon energies between 7.6 eV and 8.9 eV was found to deplete the trapped charges in SiCOH films. The dielectric reliability of SiCOH was improved showing both an observed increased breakdown voltage and a decreased leakage current. This shows that VUV exposure holds the potential to cure low-k thin films after deposition and overcome the "trapped charge and leakage-current generation" drawback induced by UV curing.

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