



## Charge Trapping within UV and Vacuum UV Irradiated Low-*k* Porous Organosilicate Dielectrics

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Vacuum ultraviolet (VUV) spectroscopy is used to determine the valence-band structure and location of defect states within the bandgap of porous organosilicate (SiCOH) dielectrics both before and after VUV and UV irradiation. SiCOH dielectrics have bandgap energies of about 9 eV. In addition, positive charge is trapped by defect states located 1 eV above the top of the SiCOH valence-band edge. These defect states can be populated or depopulated with electrons during UV and VUV irradiation, respectively. This is verified by measuring the magnitude and polarity of the trapped charge after VUV irradiation using two techniques: (i) capacitance vs voltage characteristics obtained with a mercury probe and (ii) surface-potential measurements obtained with a Kelvin probe. Both techniques show that the defect states are uncharged when occupied with electrons and positively charged when depleted of electrons.

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UV and vacuum ultraviolet (VUV) radiation are often emitted<sup>1-3</sup> during plasma processing of interconnect microelectronic structures. The photons introduce photoconductive effects<sup>4,5</sup> which significantly affect the density and location of trapped charge within dielectrics.<sup>6-8</sup> Trapped charge within low-*k* dielectrics, such as porous organosilicate dielectrics (SiCOH), can adversely affect the capacitance,<sup>9</sup> breakdown voltage,<sup>10</sup> and leakage currents<sup>11,12</sup> through low-*k* intermetal dielectrics. Suitably optimizing or supplementing the “beneficial” spectrum of photon radiation during plasma processing can reduce charge accumulation within low-*k* dielectrics.<sup>7,8,13</sup> However, the mechanisms and photon spectra that determine the beneficial and damaging effects of UV and VUV irradiation of low-*k* porous SiCOH dielectrics have not been clear.<sup>14</sup>

In this work, we use a mercury probe and a Kelvin probe<sup>15,16</sup> to measure the accumulation and neutralization of the trapped positive charge<sup>17</sup> within porous SiCOH dielectrics after UV and VUV irradiation. We use VUV spectroscopy to determine the valence-band structure and location of defect states within the bandgap of porous SiCOH dielectrics both before and after VUV and UV irradiation. After VUV irradiation, the dielectric layer becomes positively charged due to photoemission, photoconduction, and positive-charge trapping. We are able to determine the bandgap energy of SiCOH to be 9.0 eV. Positive charge becomes trapped in defect states located 1 eV above the top of the valence-band edge of SiCOH. Next, these defect states can be populated with electrons during UV irradiation or depopulated with VUV irradiation.

For example, if the VUV-irradiated dielectric is irradiated with UV photons, the positively charged defect states become refilled with electrons due to UV-induced photoinjection of electrons from the Si substrate. From surface-potential measurements, we determine that the traps are uncharged when filled with electrons and positively charged when depleted of electrons. This is similar to the properties of oxygen-deficient Si centers within SiO<sub>2</sub> dielectrics.<sup>18</sup> Because, in addition to charged particle bombardment, both UV and VUV radiation are present during plasma processing, these and other competing processes can set the amount of charge accumulation within low-*k* dielectrics during plasma processing.

The competing processes that can occur during UV and VUV irradiation of dielectrics are (i) photoemission, (ii) photoconduction, (iii) population or depopulation of electrons from trap states, and (iv) photoinjection. The photon energy, dielectric thickness, and electric properties of the dielectric layer (defect states, valence-band struc-

ture, and bandgap) are critical to the determination of which of the above processes occur at a given photon energy. If the energy of the photons is greater than the bandgap of the dielectric, then it can create electron-hole pairs within the dielectric layer. Both the free electrons and holes within the dielectric layer are able to move throughout the dielectric layer (photoconduction) until they become trapped, recombine, or leave the dielectric. Typically, the mean free path of holes is much shorter than that of electrons,<sup>19</sup> and thus, holes become trapped within the dielectric, while electrons might escape from the dielectric layer. If electrons near the vacuum/dielectric interface have an energy greater than the electron affinity of the dielectric material, they can be photoemitted into the vacuum.

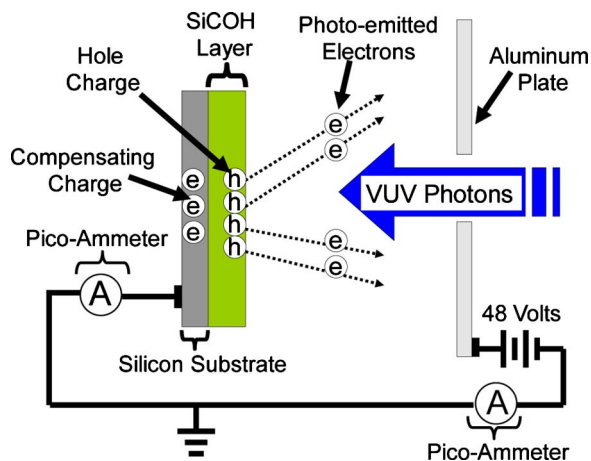
Photons with energies less than the bandgap of the dielectric (UV photons) can travel through the dielectric layer and excite electrons from defect states into the conduction band. In addition, these photons can be absorbed in underlying conductive or semiconductive layers. This can result in charge being injected into the dielectric layer. All four processes (photoemission, photoconductivity, trap depopulation, and photoinjection) can generate current flowing through the dielectric layer. As a result, these processes can significantly affect the charge trapped in defect states within low-*k* porous SiCOH dielectrics.

### Experimental

Low-*k* porous SiCOH dielectrics (*k* = 2.55, 2.65, and 2.75) were deposited by plasma-enhanced chemical vapor deposition with a Novellus Systems Vector Express system on 300 mm Si (<100>, 1–100 Ω/cm) p-type substrates. All three samples were produced with a single organosilane precursor. After deposition, the SiCOH samples (*k* = 2.55 and 2.65) were treated with UV irradiation on a Novellus System SOLA. The sample (*k* = 2.75) was as deposited. The VUV irradiation system<sup>20</sup> used in this work is shown in Fig. 1. It consists of a dielectric-coated wafer with an Al plate placed 3.5 cm in front of the wafer. The Al plate has an opening that allows the VUV photons to be normally incident on the surface of the wafer. This permits the simultaneous measurement of the photoemission current and the current drawn by the substrate during VUV exposure. This system was inserted in a vacuum chamber at a distance of 5 ft from the exit slit of a VUV monochromator at the UW Synchrotron Radiation Center. During VUV irradiation, the vacuum chamber was evacuated to a pressure of 10<sup>-8</sup> Torr. At the location of the wafer, the photon beam was elliptical and measured to be roughly 25 × 10 mm on the wafer surface. As shown in Fig. 1, the substrate was grounded during VUV irradiation, while a dc bias voltage of 48 V was placed on the Al plate to ensure that most

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**Figure 1.** (Color online) Experimental system used to measure the photoemission current and substrate current during VUV irradiation.

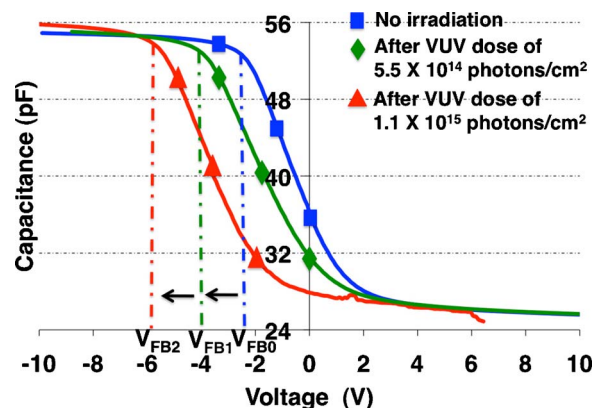
of the photoemitted electrons are collected by the Al plate. The photoemission current and the current drawn by the substrate were each measured with a Keithley 486 picoammeter.

With the arrangement shown in Fig. 1, we performed two types of experiments to characterize (i) the accumulation of charge within dielectrics during VUV irradiation and (ii) the valence-band structure and energy levels of trap states within the bandgap of the dielectrics using VUV spectroscopy. In both cases, we measured the currents drawn by the Al plate and the substrate during VUV irradiation. However, in case (i), a single photon energy was used, while in case (ii), the photon energy was scanned at low intensity, for example, between 5 and 15 eV.

The samples were also irradiated with UV in air at atmospheric pressure. A HgAr pen lamp was used as the source of UV radiation. VUV spectroscopy measurements were taken both before and after each UV or VUV irradiation step to determine the electron structure and occupation of defect states by electrons within the bandgap. After UV and VUV irradiation, the accumulated trapped charge was measured with a mercury probe and a Kelvin probe.

The mercury probe (Materials Development Corporation 862B-HV1000 Mapping Mercury Probe) was used to measure the capacitance vs voltage ( $C$ - $V$ ) characteristic across mercury/dielectric/semiconductor structures. The  $C$ - $V$  characteristics allow the measurement of trapped charge within the dielectrics before and after VUV irradiation. A mercury drop was placed on the surface of the dielectric to form a metal/oxide/semiconductor (MOS) structure. The MOS structure was positioned on a probing station, housed in a light-tight box to exclude room light, and was connected by shielded cables to an LCR meter. The LCR meter superimposes a small ac signal on top of a dc voltage that was stepped in increments of 1 V/min. The ac signal was 15 mV root-mean-square at a frequency of 100 kHz. The LCR detects the resulting ac current flowing through the MOS structure and determines the capacitance as a function of voltage. By comparing the flatband (FB) voltage before and after VUV and UV radiation, we can evaluate the degree of charge accumulation within the dielectric layer due to radiation exposure.

Surface-potential measurements,<sup>21-25</sup> obtained with a Kelvin probe, give useful information about the net charge deposited on and within the dielectric layer such as fixed charge, trapped charge, mobile charge, and surface charge.<sup>26</sup> A Kelvin probe is a noninvasive vibrating capacitor used to measure the surface potential of a charged dielectric on a conducting (or partially conducting) substrate.<sup>16</sup> Because the Kelvin probe is a noncontact device, the total charge on a dielectric can be measured without depleting/neutralizing any of the charge on the dielectric. As we show, the Kelvin probe can be important for the measurement of the trapped charge within dielectrics after VUV irradiation.



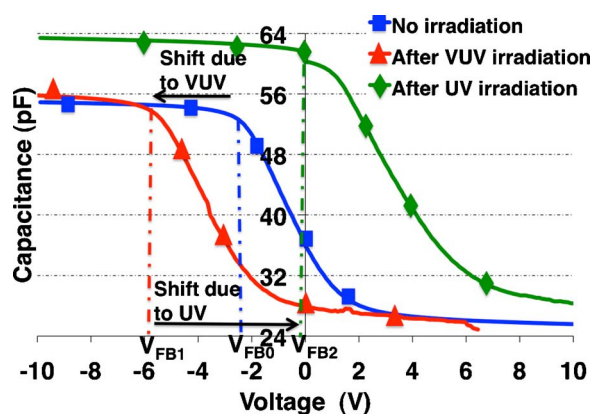
**Figure 2.** (Color online)  $C$ - $V$  characteristics measured on 266 nm of SiCOH ( $k = 2.65$ ) before (no irradiation) and after VUV irradiation with 8 eV photons for a total photon dose of  $5.5 \times 10^{14}$  and  $1.1 \times 10^{15}$  photons  $\text{cm}^{-2}$ , respectively. After VUV irradiation, the FB voltage shifts to larger negative values due to the accumulation of trapped positive charge within the SiCOH dielectric.

### $C$ - $V$ Characteristics

The mercury probe was used to measure the  $C$ - $V$  characteristics of SiCOH before and after VUV irradiation. We observed shifts in the FB voltage of the  $C$ - $V$  characteristics after VUV irradiation compared to no VUV irradiation. The shifts in the FB voltage indicate the accumulation of trapped charge within the dielectric layer, with a negative shift being due to positive trapped charge and a positive shift due to negative charge.

Figure 2 shows the normalized  $C$ - $V$  characteristics measured across a 266 nm layer of SiCOH with a  $k$  value of 2.65 (1) before VUV irradiation and (2) followed by 8 eV irradiation with photon densities of  $5.5 \times 10^{14}$  and  $1.1 \times 10^{15}$  photons  $\text{cm}^{-2}$ , respectively. We chose to irradiate the sample with 8 eV photons because, as will be shown later in this work, we believe photons of this energy are absorbed by defect states within the bandgap of SiCOH. The FB voltages for the three curves shown in Fig. 2 are labeled as  $V_{\text{FB0}}$ ,  $V_{\text{FB1}}$ , and  $V_{\text{FB2}}$ , which represent the FB voltage for no VUV irradiation and with photon doses of  $5.5 \times 10^{14}$  and  $1.1 \times 10^{15}$  photons  $\text{cm}^{-2}$ , respectively. Ideally, an uncharged dielectric should have a FB voltage of 0 V. However, we see that  $V_{\text{FB0}}$  is equal to about  $-2$  V. This indicates that the SiCOH dielectric has some residual positive charge before irradiation. We believe this residual charge is due to charging that occurred during the plasma deposition process. After irradiating the SiCOH dielectric with 8 eV photons with a total dose of  $5.5 \times 10^{14}$  photons  $\text{cm}^{-2}$ , we see that  $V_{\text{FB1}}$  has shifted to about  $-4$  V. This suggests that the 8 eV photons are inducing additional positive charge within the dielectric above the initial residual-trapped charge. In fact, the FB voltage shifts to more negative values as the total photon dose is increased until it eventually saturates at a FB voltage of about  $-6$  V. For example, as shown in Fig. 2, the FB voltage after  $1.1 \times 10^{15}$  photons  $\text{cm}^{-2}$  is about  $-6$  V.

Because charge accumulation within SiCOH dielectrics can result in unreliable performance of microelectronic devices, it is important to develop low temperature techniques that can neutralize accumulated trapped charge. One possible method is to utilize photoinjection of electrons from the substrate into the dielectric. We determine how the photoinjection of electrons affects the trapped positive charge accumulated during VUV irradiation. Papers have indicated that the threshold for the photoinjection of electrons from the Si substrate into a SiCOH layer is 4.2 eV.<sup>9</sup> Therefore, to photoinject electrons from the Si substrate into the SiCOH layer, the SiCOH samples were irradiated with UV light (as distinguished from VUV light) with a HgAr pen lamp. This lamp has a dominant emission line at 4.8 eV, which is above the threshold for photoinjection.



**Figure 3.** (Color online)  $C$ - $V$  characteristics measured before (no irradiation) VUV irradiation, after VUV irradiation, and after VUV followed by UV irradiation on 266 nm of SiCOH ( $k = 2.65$ ).

UV irradiation can also reduce the porosity of SiCOH dielectrics.<sup>27</sup> Reduced porosity causes an increase in the dielectric constant and a decrease in the dielectric thickness. Both of these result in an increase in the capacitance of the dielectric.<sup>28</sup>

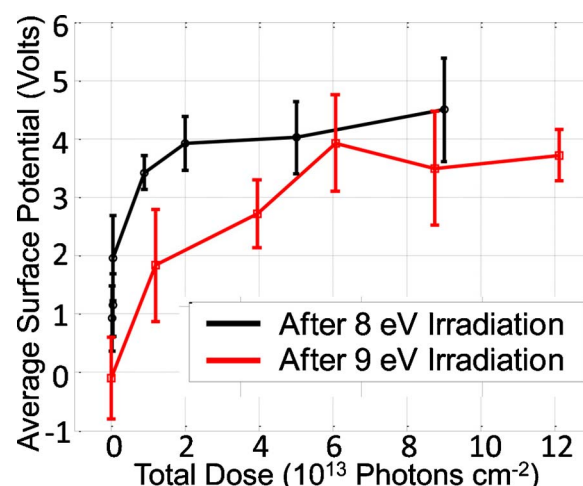
Figure 3 shows the  $C$ - $V$  characteristics for no irradiation, for only VUV irradiation, and for VUV followed by UV irradiation on 266 nm of SiCOH ( $k = 2.65$ ). The energy of the VUV photons for all exposures was 8 eV with a total VUV photon density of  $1.1 \times 10^{15}$  photons  $\text{cm}^{-2}$ . The VUV-irradiated region was then exposed to the HgAr pen lamp for 1 min. In Fig. 3, the FB voltages for the three curves are labeled as  $V_{\text{FB0}}$ ,  $V_{\text{FB1}}$ , and  $V_{\text{FB2}}$ , which represent the FB voltage for no VUV irradiation, after VUV irradiation, and after VUV and follow-on UV radiation, respectively. Similar to Fig. 2,  $V_{\text{FB0}}$  is about  $-2$  V due to the residual trapped charge within the dielectric. After VUV irradiation,  $V_{\text{FB1}}$  reached a saturation voltage of  $-6$  V. However, if we irradiate the same sample with VUV followed by UV irradiation, we find that the FB voltage  $V_{\text{FB2}}$  has shifted to lower negative voltages that are very close to the ideal case of 0 V. This suggests that the UV light not only neutralizes the positive trapped charge created by the VUV irradiation, but it also neutralizes the residual trapped charge within the dielectric produced during deposition. The neutralization takes place with electrons that are photoinjected into the SiCOH layer from the Si substrate during UV irradiation.

We also observe an increase in the capacitance of the dielectric after UV irradiation. As shown in Fig. 3, the  $C$ - $V$  curve after UV irradiation shifts upward as compared to the  $C$ - $V$  curve for no irradiation and VUV irradiation. After UV irradiation, we observed a 15% increase in capacitance for 266 nm SiCOH ( $k = 2.65$ ). For thicker samples (444 nm,  $k = 2.65$  and 458 nm,  $k = 2.75$ ) we observed an approximate 11% increase in capacitance.

From a plasma processing point of view, the neutralization of trapped positive charge from VUV irradiation with UV photons is very important. Because plasmas often emit significant amounts of both UV and VUV irradiation, the processes of positive-charge accumulation due to VUV irradiation and charge neutralization with UV radiation are competing factors. Therefore, it is important to verify these results with another technique and hopefully gain insight into the charge-neutralization process. Thus, we repeated the same VUV and UV exposures and evaluated the accumulation and neutralization effects with a Kelvin probe. This is described in the following section.

#### Surface-Potential Measurements

To verify the results of trapped charge accumulation and neutralization reported in the previous section, we used a Kelvin probe to measure the surface potential after VUV and UV irradiation. First, we measured the accumulation of trapped positive charge under



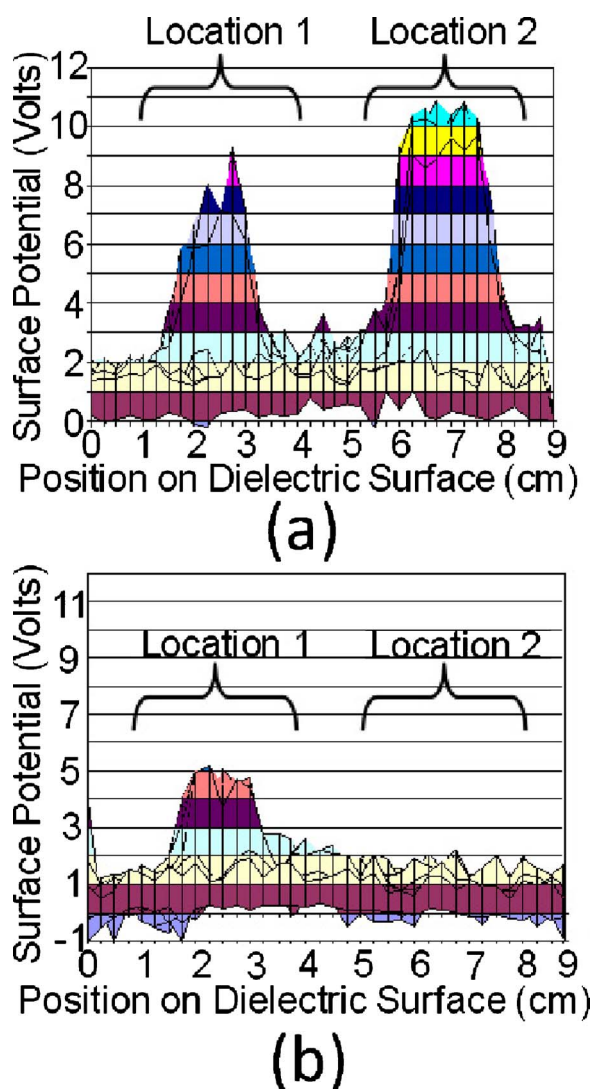
**Figure 4.** (Color online) Average surface potential as a function of total photon dose on porous SiCOH ( $k = 2.55$ ) after irradiation with 8 and 9 eV photons.

VUV irradiation alone as a function of total photon dose. Then, we verified the effect of trapped-charge accumulation and neutralization by measuring the surface potential after VUV followed by UV irradiation.

Figure 4 shows a comparison of the average surface potential measured on 251 nm of SiCOH ( $k = 2.55$ ) as a function of photon dose for 8 and 9 eV photons. These energies were chosen because they are just above and below the bandgap energy of SiCOH (in the next section, we show the bandgap for SiCOH to be 8.5 eV). The error bars shown in Fig. 4 represent one standard deviation of the average surface potential measured inside the VUV-irradiated region. In Fig. 4, the surface potential saturates at 4 V for both 8 and 9 eV photon irradiation. However, the surface potential reaches saturation at lower photon doses for 8 eV photons ( $3 \times 10^{13}$  photons  $\text{cm}^{-2}$ ) than with 9 eV photons ( $6 \times 10^{13}$  photons  $\text{cm}^{-2}$ ). This implies that 8 eV photons are more efficient in inducing a net positive charge on SiCOH dielectrics than 9 eV photons. This is an interesting fact because 8 eV photons are smaller than the bandgap of SiCOH and, thus, they should not be absorbed by the SiCOH layer. However, as will be shown in the following section, there are trap states located within the bandgap of the dielectric layer that absorb 8 eV photons.

There is a difference between the photon dose at which the FB voltage shift of the  $C$ - $V$  characteristics saturates (see Fig. 2) and the photon dose at which the surface potential saturates after an 8 eV photon irradiation. We attribute this to a difference in the thickness of the dielectric layer. The  $C$ - $V$  characteristics were measured on a 266 nm SiCOH ( $k = 2.65$ ) layer, while the surface-potential measurements were measured on a 231 nm thick SiCOH ( $k = 2.55$ ) layer. In general, thicker dielectrics tend to need higher photon doses to reach saturation. For example, if the traps are uniformly located throughout the bulk of the dielectric layer, a thicker dielectric has more traps to fill than a thinner dielectric. Unfortunately,  $C$ - $V$  and surface potential measurements could not be performed on the same dielectric thickness and  $k$  value because of lack of samples.

To determine the effect that UV has on the VUV-induced positive charge, the surface potentials (1) after VUV and (2) after VUV followed by UV irradiation were measured. Figure 4a shows a surface-potential map measured across the surface of a 500 nm thick SiCOH dielectric after being irradiated with VUV at two locations with slightly different photon doses. The two VUV-irradiated regions on the wafer surface can clearly be seen in Fig. 4a as two peaks in surface potential. The surface potential shown in Fig. 4a is

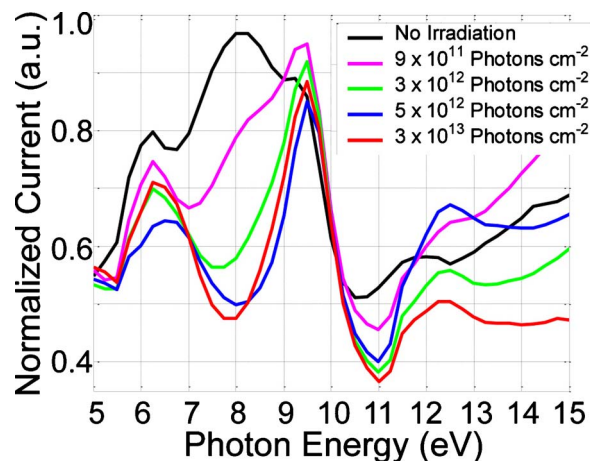


**Figure 5.** (Color online) Surface potential maps measured (a) after VUV irradiation at two locations on the surface of 500 nm of SiCOH ( $k = 2.55$ ) and (b) surface potential map measured on the same dielectric layer shown in (a) immediately after location 2 was irradiated with UV light from a HgAr pen lamp.

larger than the average surface potential shown in Fig. 1 because, for these measurements, the SiCOH dielectric is more than twice as thick.

After the surface-potential map was obtained, the VUV-irradiated region under location 1 in Fig. 4a was covered with a UV-absorbent material, while location 2 was irradiated with follow-on UV radiation from the HgAr pen lamp for 2 min. The surface-potential map measured immediately after UV irradiation is shown in Fig. 4b. The surface potential measured under location 2 reduces to the same voltage as the area around the VUV-irradiated regions, while the surface potential under location 1 is only slightly reduced in magnitude. Thus, the UV light must have neutralized the trapped positive charge.

These results verify the  $C$ - $V$  characteristics shown in Fig. 3. That is, the trapped positive charge created during VUV irradiation is neutralized by photoinjected electrons during UV irradiation. In addition, the surface potential did not become negative from the photoinjection of electrons into the porous SiCOH dielectric, just like the FB voltage of the  $C$ - $V$  characteristic did not become positive after UV irradiation. This suggests that there are a few negatively charged traps within the SiCOH dielectric. Alternatively, if there are



**Figure 6.** (Color online) VUV spectroscopic measurements on 231 nm of SiCOH ( $k = 2.55$ ) after VUV irradiation by several doses of 8 eV photons.

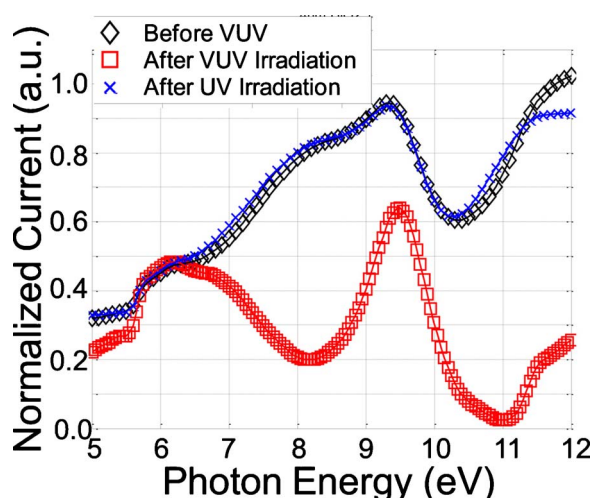
negatively charged trap states, they quickly decay before the  $C$ - $V$  and surface-potential measurements are measured. These results prove that the accumulation of trapped positive charge due to VUV irradiation of the SiOCH dielectric can be successfully neutralized with UV radiation. However, an important issue is the determination of the location where the charges are located within the bandgap. We address this issue in the next section using VUV spectroscopy to determine the energy distribution of the trap states within the bandgap of the SiOCH dielectric layer.

#### VUV Spectroscopy

In the previous sections, we have shown that SiCOH dielectrics accumulate positive charge after VUV irradiation and that UV radiation can neutralize the trapped positive charge. From a device performance perspective, it is very important to know the energy distribution of the trap states within the bandgap of SiOCH. For example, if the trap states line up in energy with electronic states that are in adjacent dielectrics or conductors, resonant energy charge exchange can occur between the two materials.<sup>6</sup> Charge exchange with SiCOH and other materials can result in larger leakage currents and thus reduce the performance of microprocessors.<sup>9,11</sup>

To determine the bandgap energy of SiCOH and the location of the trap states within the bandgap, VUV spectroscopic measurements were made on several low- $k$  porous SiCOH dielectrics. As previously mentioned, VUV spectroscopic measurements are made by measuring the currents drawn by the substrate and the Al plate as the photon energy is scanned at a low flux rate, for example, between 5 and 15 eV. This results in peaks in the measured substrate and Al plate currents at various photon energies due to the excitation of electrons from specific electronic states to an energy above the conduction band of the dielectric layer. By comparing the photon energy at which the electronic states are excited with the energy levels calculated by first-principles studies<sup>29</sup> reported,<sup>30</sup> we can determine the energy levels from which the electrons were excited.<sup>31</sup> However, because there are very few first-principles studies reported for porous SiCOH, we compare the VUV spectroscopic results with SiO<sub>2</sub>. This is justifiable because the chemical structures of SiOCH and SiO<sub>2</sub> are similar and, as will be shown, we measured electronic states that absorb photons at nearly identical energies for the two dielectrics.

Figure 6 shows four VUV spectroscopic measurements between 5 and 15 eV taken after irradiating the SiCOH dielectric with four different doses of 8 eV photons. These are  $9 \times 10^{11}$ ,  $3 \times 10^{12}$ ,  $5 \times 10^{12}$ , and  $3 \times 10^{13}$  photons  $\text{cm}^{-2}$ . Zero photon dose (no irradiation) is also shown for comparison. In Fig. 6, three distinct peaks are observed for photon energies of 6.2, 8.0, and 9.6 eV before VUV irradiation. VUV spectroscopic measurements on SiO<sub>2</sub> (not shown)



**Figure 7.** (Color online) VUV spectroscopic measurements on 231 nm of SiCOH ( $k = 2.55$ ) before VUV irradiation, after VUV irradiation with 8 eV photons, and after UV irradiation.

show very similar peaks at 8.0 and 9.6 eV. According to the literature, the peak at 8.0 eV in SiO<sub>2</sub> is due to oxygen-deficient Si centers.<sup>30,32,33</sup> This suggests that there may be a similar defect center in SiCOH. The peak at 9.6 eV in SiO<sub>2</sub> is due to O 2p states, and these states define the upper valence band of SiO<sub>2</sub>.<sup>34</sup> Because SiO<sub>2</sub> and SiCOH have similar chemical structures, the peak at 9.6 eV is also due to O 2p states in SiCOH. Thus, SiCOH has the same band-gap energy as SiO<sub>2</sub> of about 9.0 eV. In addition, for SiO<sub>2</sub>, the peak at 8.0 eV is due to oxygen-deficient Si centers.<sup>32,33</sup> This suggests that there may be a similar defect center in SiCOH. From UV spectroscopic ellipsometry, Eslava et al.<sup>35</sup> attributed the peak at 6.2 eV to the presence of CH<sub>x</sub> organic porogens within the SiCOH dielectric.

If the SiCOH dielectric is irradiated with 8 eV photons before VUV spectroscopy, then the peak due to defect states at 8 eV, as shown in Fig. 6, reduces in magnitude relative to the other peaks at 6.2 and 9.6 eV, as the 8 eV photon dose is increased. The magnitude of the peak at 8.0 eV eventually saturates (stops decreasing) for photon doses higher than  $3 \times 10^{13}$  photons cm<sup>-2</sup>. This is caused by the depletion of electrons from the defect states. That is, before VUV irradiation, the defect states are filled with electrons. During VUV irradiation, the electrons are excited from the defect states to energies above the conduction band where they are either photo-emitted, trapped, or collected by the substrate. As a result, there are fewer electrons within the defect states available to be excited when a VUV spectroscopic measurement is made after VUV irradiation. Thus, because the defects have been depleted of electrons, the magnitude of the current drawn is lower when the photon energy is scanned over the energy range where the defect states are located.

The surface potential measured after 8 eV irradiation, shown in Fig. 5, also saturates at a total photon dose of about  $3 \times 10^{13}$  photons cm<sup>-2</sup>. Thus, there appears to be a direct correlation between the minimum height of the peak due to defect states at 8 eV shown in Fig. 6 and the accumulation of trapped positive charge shown in Fig. 5.

To determine the effects of both UV and VUV on SiCOH, a single sample was irradiated as follows. First, VUV spectroscopy was performed before irradiation, as shown in Fig. 7. After irradiation with 8 eV photons with a total dose of  $15 \times 10^{12}$  photons cm<sup>-2</sup>, a second VUV spectroscopic scan was made to verify that the defect states were depleted of electrons. Next, after the wafer was removed from the vacuum chamber, the VUV-exposed region was irradiated with UV with the HgAr pen lamp for 5 min. Then the sample was placed back into the vacuum chamber, and a third VUV spectroscopic scan was made at the same location on the wafer surface. Figure 7 shows the results from the three VUV

spectroscopic measurements taken (1) before VUV, (2) after VUV, and (3) after follow-on UV exposure. Similar to Fig. 5, the peak at 8 eV decays after VUV irradiation because the traps are depleted of electrons. However, after the follow-on UV irradiation, the peak at 8 eV reappears. In fact, Fig. 7 shows that the curves before VUV and after UV irradiation are nearly identical. This proves that the defect states can become repopulated with electrons due to photoinjection of electrons from the underlying Si substrate into the SiCOH layer.

## Conclusions

Porous SiCOH dielectrics accumulate a net positive charge after VUV irradiation, but the positive charge can be neutralized with UV radiation from a HgAr pen lamp. The trapped positive charge is due to the depletion of electrons by VUV irradiation from trap states 1 eV above the top of the valence-band edge of SiCOH. Under UV irradiation, electrons are photoinjected from the Si substrate and into the SiCOH where they can be captured by the positively charged defect states, thus neutralizing the trapped positive charge accumulated during VUV irradiation. These observations are very similar to how an oxygen-deficient Si center would behave under similar conditions, i.e., the center is positive when depleted of electrons, electrically neutral (uncharged) when filled with an electron, and then can absorb photons that have an energy of around 8.0 eV. This suggests that the dangling silicon bond within low- $k$  porous SiCOH may be responsible for the charge trapping. However, further work is necessary to verify this hypothesis.

The results shown in this work are very important for plasma processing because plasmas often emit significant amounts of both UV and VUV irradiation. We conclude that the processes of positive-charge accumulation due to VUV irradiation and charge neutralization with UV radiation are competing factors. By suitably optimizing and supplementing the beneficial spectrum (UV) of the emitted radiation, it may be possible to significantly reduce the amount of trapped charge within dielectrics, while minimizing any increase in capacitance, thus improving process yields of microelectronic devices.

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