Bandgap measurements of low-k porous organosilicate dielectrics using vacuum ultraviolet irradiation

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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. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4865407]

Plasma processing is widely used in the manufacturing of ULSI devices. However, during fabrication of these devices, dielectrics are exposed to numerous processing steps in which vacuum ultraviolet irradiation (VUV) takes place. Since charge accumulation during plasma processing is a leading cause of damage to semiconductor devices, the effects of vacuum ultraviolet irradiation on charge accumulation, especially for low-k porous organosilicate dielectrics (e.g., SiCOH) are of great concern. This Letter shows that the effects of VUV radiation depend on the energy of VUV photons. This dependence can be resolved with vacuum ultraviolet photoemission spectroscopy. In addition, the band-gap plus the electron affinity of VUV-exposed SiCOH films can also be easily found.

VUV irradiation of dielectrics can cause electron-hole pair generation, photoconduction, photoemission, and photo-injection of electrons from the substrate into the dielectric.[1,2] 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 defect states within the dielectric. 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.[3] 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 dielectric.[2] Photoemission can take place by electrons ejected from either the valence band or the defect states present in the dielectric.[4,5] Electron photoemission leads to depopulation of electrons within the dielectric and after photoemission, the dielectric develops a net positive charge.

Previous work on charge accumulation in dielectrics caused by VUV irradiation has been investigated deeply using two techniques: (1) capacitance versus voltage characteristics obtained with a mercury probe[1,5,6] and (2) surface-potential measurements obtained with a Kelvin probe.[1,5,6]

These references showed that charge accumulation can be caused by VUV irradiation over a range of photon energies.[1,5,6] In this work, it is shown that VUV photoemission spectroscopy is an effective method to measure the band-gap plus vacuum affinity of low-k dielectrics. Moreover, it is also shown by VUV photoemission spectroscopy that VUV irradiation *over a different range* of photon energies can deplete charge accumulation and can be utilized in semiconductor fabrication to decrease processing-induced charging damage.

To investigate the effect of VUV irradiation on charge accumulation in SiCOH, charged porous SiCOH/Si wafers (k = 3.05) were irradiated with monochromatic VUV synchrotron radiation at the University of Wisconsin-Synchrotron Radiation Center (SRC) using the experimental setup shown in Figure 1. The advantage of a synchrotron is that it generates pure radiation (no charged particles) and can
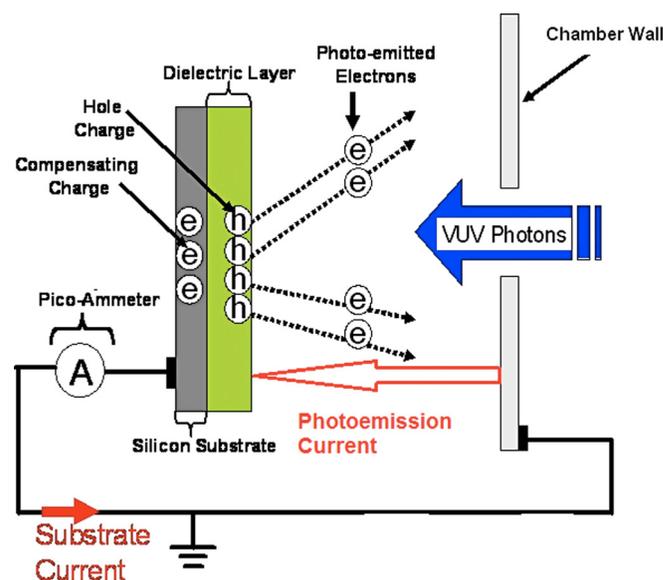

FIG. 1. Synchrotron VUV-exposure system.

be varied over a continuum of photon energies. The photon-energy range was chosen to be between 6–15 eV. This range is typical of processing plasmas.

As shown in Figure 1, VUV photons were normally incident on the surface of a 150-nm thick porous SiCOH sample at a pressure of 10^{-8} Torr. A picoammeter was connected to the silicon substrate of the wafer to monitor charge transfer into and out of the dielectric so as to measure the photoemission current during VUV irradiation. The VUV beam on the surface of the wafer had a cross-sectional area of 3 $\times$ 0.1 cm^2. The maximum photon flux was 1.5×10^{12} photons/s at a photon energy of 12 eV. This value was chosen because the synchrotron photon flux was large at this energy and also because this energy is substantially above the bandgap plus electron affinity energy level.[5,7]

To monitor the repopulation and depopulation of charges within the dielectric layer caused by VUV irradiation, VUV photoemission spectra were measured before and after VUV irradiation. This was done by rapidly scanning the exposed SiCOH sample over a range of energies and recording the photoemission current from the sample as a function of photon energy. 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. This further emphasizes the need for a rapid scan. In these experiments, the low-k dielectric sample was not moved during VUV irradiation and photoemission spectroscopy. In addition, the photon flux was approximately two orders of magnitude smaller for VUV photoemission spectroscopy than for monochromatic VUV irradiation and did not affect the measured intrinsic characteristics of the dielectric layer.

In this experiment, VUV spectra were recorded before and after 12 eV monochromatic photon irradiation. Since dielectric materials often have bandgaps in the 7–9 eV range,[8] and the electron vacuum affinity is around 1 eV,[6] a photon energy of 12 eV was chosen since it is likely to be greater than the sum of the band gap energy and the electron affinity of SiCOH. Thus, photons of this energy should produce photoemission of a large number of electrons from the valence band and defect states of SiCOH sample after sufficient irradiation fluence.

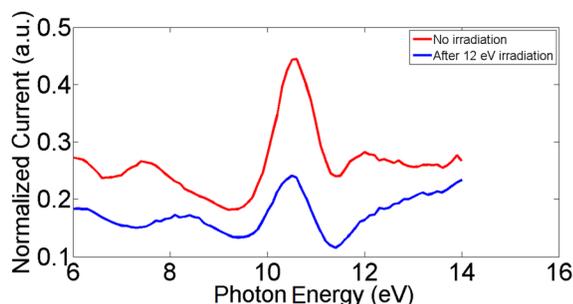Figure 2 shows a comparison of VUV photoemission spectroscopic measurements of a SiCOH dielectric film before and after irradiation with 12 eV photons. The photon dose for 12 eV irradiation was 3.5×10^{15} photons/cm^2, which was large enough to make sure that a significant number of the electrons from the valence band and from defect states in the dielectric layer were photoemitted. The electron photoemission results in a net positive charge after irradiation.

In Figure 2, two significant peaks were observed before monochromatic VUV irradiation in the VUV photoemission spectrum at energies of 7.4 and 10.6 eV. The peak at 7.4 eV is from oxygen-deficient Si centers[5,9] and the peak at 10.6 eV is from O 2p states.[10–12] After the dielectric was irradiated with 12 eV photons, the follow-on VUV photoemission spectrum shows that the photoemission decreased to a steady-state value indicating that most of the electrons that can be photoemitted from the dielectric have done so. The steady-state current is formed from those electrons photoinjected from the substrate into the dielectric.[2,4,5,7] In Figure 2, the photoemission current was normalized by dividing the measured photoemission current by the incoming VUV photon flux. In addition, the peak at 7.4 eV decreased significantly after 12 eV irradiation, which suggests that 7.4 eV is a defect center for SiCOH,[4,10] since these defect states were depopulated after the 12 eV exposure. As a result, there are few electrons within the defect states available to be excited when the VUV photoemission spectroscopic measurements were made *after* VUV irradiation. It must be mentioned that the electrons within the defect states play a critical role in the leakage currents in low-k dielectrics[13] and some unpopulated traps could also contribute to the defect state at 7.4 eV.[14] 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.[5]

To investigate the effect of photon energy on the accumulated charge within the 12-eV irradiated SiCOH samples, they were re-exposed to other VUV photon energies from 8.9 to 10.7 eV in steps of 0.1 eV and were again followed by VUV photoemission spectroscopy. All VUV exposures had a fluence of 3.5×10^{15} photons/cm^2 in order to compare these results with the previous ones described above. Figures 3 and 4 show a comparison of photoemission spectroscopic measurements after photon irradiation over a range between 8.9 and 10.7 eV. It must be mentioned that the VUV photoemission spectroscopy spectra are not shown after separate VUV exposures between 9.0 and 10.4 eV in steps of 0.1 eV because they are nearly identical to those produced by VUV photoemission after 10.5 eV irradiation shown in Figure 3.
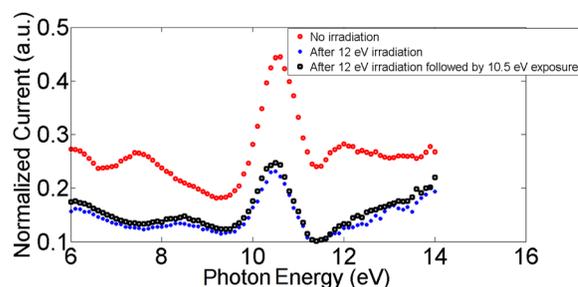

FIG. 2. VUV photoemission spectroscopic measurements on 150 nm SiCOH before and after 12 eV VUV irradiation with 3.5×10^{15} photons/cm^2 fluence.

FIG. 3. VUV photoemission spectroscopic measurements on 150 nm SiCOH before and after 12 eV followed by 10.5 eV VUV irradiation with 3.5×10^{15} photons/cm^2 fluence.
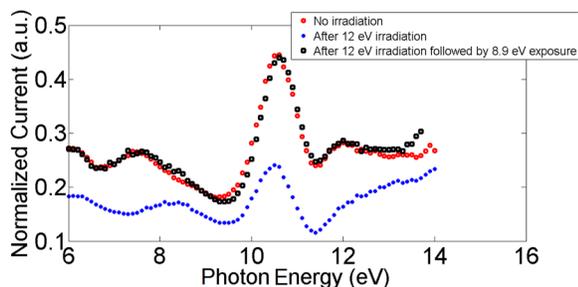
FIG. 4. VUV photoemission spectroscopic measurements on 150 nm SiCOH before and after 12 eV followed by 8.9 eV VUV irradiation with 3.5×10^{15} photons/cm^2 fluence.

Based on these results, it was found that additional VUV irradiation above 9.0 eV did not change the amount of accumulated charge compared with the charge after 12 eV photon irradiation. That is, VUV photoemission spectroscopy did not show significant changes after VUV irradiation with photon energies higher than 9.0 eV. This means that the number of photoemitted electrons was not changed by VUV radiation with photon energies higher than 9.0 eV.

In Figure 4, VUV photoemission spectroscopy measurements were made after monochromatic irradiation with two photon energies. They are 12 eV followed by 8.9 eV. It was observed that the VUV photoemission spectra for pristine SiCOH and the VUV spectrum after 12 eV + 8.9 eV irradiation are nearly identical. Moreover, the peak at 7.4 eV as seen in the pristine VUV photoemission spectrum, shows the location of defect states within the dielectric layer reappears *after* 12 eV exposure followed by 8.9 eV exposure. This means that photon radiation with energies of 8.9 eV likely repopulates the electrons in defect states and therefore lowers the net positive charge caused by 12 eV exposure. For VUV exposure with photon energies higher than 9.0 eV, no beneficial effect on the charge depletion was detected.

These experimental results can be explained by considering the two dominant VUV radiation-induced processes in the dielectric: (a) *photoemission* of electrons from the dielectric into the vacuum and (b) *photoinjection* of electrons from the Si substrate into the dielectric layer.

As described above, photoemission can occur when the photon energy is greater than the sum of the band-gap energy and the electron affinity. However, photoinjection can also result in a net current. Photoinjection of electrons from the substrate to the dielectric can occur if a VUV photon is not absorbed by the dielectric layer and passes into the substrate.

Based on the relation between the wavelength of the VUV photons and their penetration depth in low-k dielectrics,[15] photons that are not absorbed in SiCOH can penetrate through the dielectric layer and directly impinge on the Si substrate. These VUV 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,[5] some of the electrons that are formed with higher energies 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 plus the electron affinity of the dielectric layer to be emitted into vacuum, they may neutralize the positive net charge and thus deplete the charge accumulation. Therefore, if photoinjection depletes the net

charge in the dielectric by repopulating the traps, photons whose energies are lower than the sum of the bandgap and electron affinity energies can produce this result. Photoinjected electrons that are indeed photoemitted cannot neutralize the trapped charge.

To summarize, during after 12 eV photon exposure, the photoemission current decreased and reached a steady state.[2,5,7,8] This steady-state current is caused by photoinjected electrons that are not trapped in the dielectric layer and are thus able to contribute to the photoemission current. For VUV photons with energies higher than 9.0 eV, since these photons cannot repopulate the traps, it is likely that photoinjection might not be the dominant process. However, VUV radiation with photon energies less than 9 eV can deplete the charge accumulation by repopulating the traps. This shows that the band gap of SiCOH plus the electron affinity energy should be less than 9.0 eV. In this case, electrons from electron-hole pairs that are generated by photons do not have sufficient energies to overcome the dielectric-vacuum barrier (band gap of SiCOH plus electron affinity) to be emitted into vacuum space and some of the photons can penetrate into the Si substrate and have the potential to produce photoinjection current. Therefore, if the photons that penetrate into the substrate have energies larger than the Si-SiCOH interface barrier (4.2 eV), some of the electrons formed in the Si substrate could be produced with enough energy to be injected into the SiCOH dielectric layers and repopulate the traps in the dielectric that were depopulated during the 12 eV exposure. As the photon energies increase, more electrons can be injected into the dielectric layer to deplete the charge accumulation. Finally, VUV photoemission spectroscopic measurements after 8.9 eV irradiation and the VUV spectrum for intrinsic SiCOH samples were identical, which shows that the net positive charge was depleted by 8.9 eV irradiation.

Based on the experimental results presented here, it was determined that photon energies between 4.2 and 9.0 eV are able to deplete accumulated charge in low-k porous organosilicate dielectric wafers. Energy of 4.2 eV is the lowest photon energy needed to overcome the Si/SiCOH interface barrier and be injected into the dielectric layer. For SiCOH, a photon energy of 8.9 eV was found to be the most efficient for depletion of accumulated charge. This implies the bandgap plus the electron affinity of the exposed SiCOH sample is 8.9 eV. Since the electron affinity is around 1 eV,[5,6,8] the band-gap for the exposed porous SiCOH should be approximately 7.9 eV. In addition, VUV spectroscopy was also used to make band-gap measurements of low-k *nonporous* SiCOH samples with dielectric thicknesses of both 50 (k = 3.25) and 100 nm (k = 3.1). For these samples, the measured band-gap was 8.2 eV. These results match previous work on band-gap measurements of low-k dielectric material.[14,16] Thus, VUV exposure followed by VUV photoemission spectroscopy has the potential to find the bandgap of dielectric materials simply and efficiently.[17,18]

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