

Effects of vacuum ultraviolet radiation on deposited and ultraviolet-cured low-*k* porous organosilicate glass

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The authors compare the effects of vacuum ultraviolet (VUV) irradiation on pristine and UV-cured low-*k* porous organosilicate glass (SiCOH). The authors find that during VUV irradiation, more trapped charges are generated in UV-cured SiCOH as compared to pristine SiCOH. VUV is also used as a tool to investigate effects of UV curing. From comparison of VUV spectroscopy and photoinjection current of the two samples, the authors find that UV curing reduces the number of defect states in SiCOH. The authors also find that UV-cured SiCOH has higher photoconductivity and intrinsic conductivity from VUV spectroscopy and trapped-charge decay rate, respectively. © 2011 American Vacuum Society. [DOI: 10.1116/1.3570818]

I. INTRODUCTION

In device fabrication, chemical-vapor deposited low-*k*-porous organosilicate (SiCOH) glass is often cured with ultraviolet (UV) irradiation.¹ UV curing is advantageous, yielding the benefits of improved hardness and corrosive strength of the dielectric.^{2,3} After UV curing, these dielectrics are subjected to plasma processing during which charged-particle bombardment and vacuum ultraviolet (VUV) irradiation occur.^{4–6} In this article, we compare the effects of VUV radiation on pristine SiCOH and UV-cured SiCOH. We can eliminate charged-particle bombardment in our analysis by the use of a synchrotron as the source of VUV photons. Photoemission/substrate and photoinjection currents during VUV irradiation and VUV spectroscopy are used as the analysis tools. Using these tools, we determine the number of trapped positive charges generated in each dielectric during VUV irradiation. We find that more trapped positive charges are generated in UV-cured SiCOH compared to pristine SiCOH. We also find that UV curing reduces the number of defect states but increases both the intrinsic and photoconductivities of SiCOH. This can result in higher leakage current, reducing the isolation in between metal lines in devices.^{7,8}

II. BACKGROUND

VUV irradiation causes photoconduction, photoemission, and photoinjection in the dielectric.^{9–12} VUV photons pro-

duce electron-hole pairs in the dielectric and the underlying silicon substrate. Electron photoemission from the dielectric will occur if the energy transferred to the electrons from the photons is greater than the photoemission energy barrier.¹³ During VUV irradiation electrons can be depopulated from the defect states and then photoemitted to create trapped positive charge. The electrons produced in the substrate by the VUV photons can be injected into the dielectric (photoinjection). The photoinjected electrons can repopulate the defect states and hence reduce the amount of trapped positive charge.

With increasing VUV photon dose, more trapped charges are created in the dielectric. As a result, a self-consistent electric field is produced which, in turn, reduces the photoemission flux.^{10,14} However, the photoinjection current of electrons, from the substrate into the dielectric, can be approximated to be a constant during VUV irradiation as it primarily depends on the dielectric-substrate interface barrier energy and the photon flux per unit time.¹⁵

It is plausible that photoinjected electrons conduct from the substrate-dielectric interface to the dielectric-vacuum interface and are photoemitted.^{11,14} Thus, at any given time during VUV irradiation, photoemitted electrons will consist of (1) depopulated electrons from the defect states and (2) photoinjected electrons. Trapped charges due to depopulation of defect states will continue to be created until a steady state is achieved.¹⁰ At steady state no more trapped charges will be generated in the dielectric and the photoemitted electron flux will equal the flux of photoinjected electrons. In order to

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have a complete circuit, charge conservation dictates that when the substrate is connected to ground, the photoemitted electrons are returned to the substrate. Thus, the photoemission current is equal to the substrate current.

We propose that, during VUV irradiation, by subtracting the photoinjected electron current from the photoemission/substrate electron current we can find the rate of increase of trapped positive charges stored in the dielectric. Integrating these data over the irradiation time until a steady state is achieved can be used to determine the total number of trapped charges generated by VUV irradiation in the dielectric.¹⁶

In steady state, the photoemission/substrate current can be used to obtain the defect density and photoconductivity of the dielectric as follows. First, when the VUV photon energies are less than the band gap energy, the following three processes can occur. (1) If the photon energy is greater than the energy difference between a defect state in the band gap and the vacuum, electrons trapped in these defect states can be photoemitted.¹⁰ (2) If the photon energy is less than the energy difference between the defect state in the band gap and the vacuum, electrons can be excited into higher-energy defect states and then be photoemitted.¹⁰ (3) The VUV photons can excite electrons from the valence band into the defect states if the photon energy is greater than the energy difference between the defect state and the valence band. Thus, if we sum up the three processes, we can expect that the photoemitted electrons originate in valence band and travel through the defect states before being photoemitted. Note that in this case the photon energy is less than the band gap energy; hence, direct photoemission from the valence band is not possible. Thus, for VUV photon energy less than the band gap, the number of defect states is the limiting factor for the electron photoemission/substrate current. Hence, for photon energies less than the band gap energy, the photoemission/substrate current in steady state will be proportional to the defect-state density.

On the other hand, VUV photons of energies greater than the band gap energy can be used to determine the sum of the intrinsic conductivity and photoconductivity as follows. First, these photons cause direct photoemission of electrons from *both* the valence band and defect states in the band gap. The density of states of electrons in the valence band is much greater than the defect-state density in the band gap.^{15,17} Thus, photoemitted electrons will constitute primarily of electrons directly photoemitted from the valence band. Hence, for VUV photon energies greater than the band gap energy, the defect states are not the determining factor for the photoemission/substrate current.

As mentioned earlier, the photoemitted electrons are collected and returned to the grounded substrate and subsequently reinjected into the dielectric. These electrons then again conduct through the dielectric before being photoemitted again and this process continues as long as the irradiation takes place.¹⁴ Under these circumstances, the dielectric and the substrate provide the resistance to current flow. Since a dielectric has resistance that is much higher than the resis-

tance of the silicon substrate, the current flow will be dependent on the intrinsic resistance and any decrease in resistance due to the photon flux (photoconductivity) of the dielectric.^{18,19} Thus, for VUV irradiation with photons of energy greater than the band gap, the photoemission/substrate current will be proportional to the sum of the intrinsic conductivity and the photoconductivity.

The intrinsic conductivity can be computed from the trapped-charge decay rate after VUV irradiation as follows.^{20,21} The trapped positive charges recombine with free electrons under influence of a self-consistent electric field.²² In the absence of VUV photons, the drift motion of electrons under the self-consistent electric field in the dielectric is determined by the intrinsic conductivity. Since the surface potential is a measure of the amount of trapped charge in the dielectric, then, from the decay rate of the surface potential, the intrinsic conductivity of both pristine SiCOH and UV-cured SiCOH can be determined and compared.²³

III. EXPERIMENT

To investigate these effects, 640 nm of low-*k* porous SiCOH dielectric was deposited by plasma-enhanced chemical-vapor deposition (PECVD) on two Si wafers.^{24,25} On the Si wafer, approximately 1-nm-thick native oxide was present. The deposition process took place in a capacitively coupled PECVD reactor with a radiofrequency source of 13.56 MHz in the presence of various inert and reactive gases. An organosilane precursor was used in the deposition process. It should be pointed out that a structure forming and porogen molecule approach was not used. One sample was kept pristine while the other sample was UV cured with a Novellus System SOLA™ ultraviolet thermal processing system. Photons with energies between 3.1 and 6.2 eV were used in the UV-curing process. The total UV-curing fluence was approximately 1×10^{16} photons/s cm². After UV curing, the dielectric thickness was measured to be 500 nm. The dielectric constant of the cured material was measured to be 2.55. From X-ray reflectivity measurements the density was found to be 1.24 g/cm³ and was verified by Rutherford backscattering spectroscopy. The porosity was measured to be 15%–20% by ellipsometric porosimetry.

The sum of the band gap energy and electron affinity for SiCOH is 8.5 eV.^{9,10} This is the minimum energy required for photoemission from the valence band. Thus, for photon energies less than 8.5 eV, photoemission can occur only from the defect states in the band gap. Hence, we chose 8 eV photons for irradiation. However, these photons can also cause photoinjection of electrons across the SiCOH–Si interface energy barrier, which is known to be 3.5–4.5 eV.¹⁵

The UW-Madison synchrotron was used as the source of VUV photons. A picoammeter (Keithley-486) was used for photoemission/substrate current measurements. The following measurements were made on pristine SiCOH and UV-cured SiCOH: (1) VUV spectroscopy, in which photoemission/substrate current is measured as a function of incident photon energy, between 4.5 and 12 eV—a low pho-

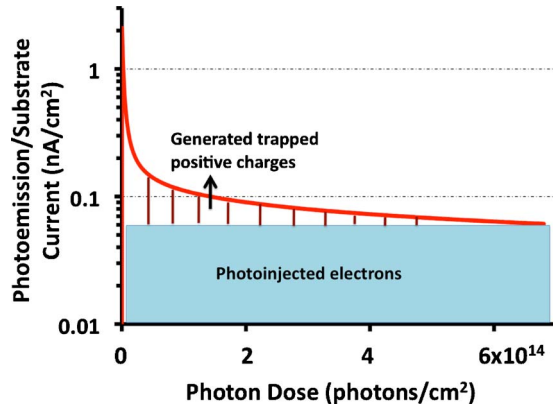


FIG. 1. (Color online) Photoemission flux of pristine SiCOH as a function of increasing dose of 8 eV VUV photons.

ton flux is used in VUV spectroscopy to determine the spectrum without generating appreciable trapped charges in the dielectric—and (2) single VUV photon energy at higher flux. In this case, the photon energy was 8 eV. The 8 eV photon dose was adjusted so as to achieve steady state. The photoemission/substrate current was measured as a function of time/dose during irradiation. The surface potential map was measured with a Kelvin probe to observe the decay in trapped charges. Finally, the VUV spectroscopy was repeated after the 8 eV VUV irradiation.

IV. RESULTS AND DISCUSSION

Figure 1 shows the photoemission/substrate current density as a function of the 8 eV VUV photon dose per unit area for the pristine sample. After reaching steady state, from the photoemission/substrate current measured for pristine SiCOH and UV-cured SiCOH, we calculate the number of trapped positive charges generated per unit area of VUV irradiation. It was repeatably found that the UV-cured dielectric has approximately 5.6% more trapped positive charge in comparison to the pristine dielectric. Furthermore, it was also found that the photoinjection current in the UV-cured sample was approximately 7.9% less as compared with the pristine SiCOH sample. These results are shown in Table I.

To understand this effect, note that the UV-cured SiCOH has fewer defect states than the pristine SiCOH. However, the UV-cured SiCOH has a smaller photoinjection current than the pristine SiCOH. Hence, the photoinjection current does not neutralize as many of the trapped positive charges in UV-cured SiCOH.

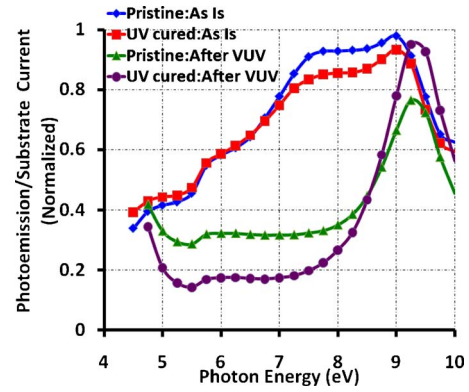


FIG. 2. (Color online) VUV spectroscopy at 4.5–10 eV for pristine and UV-cured SiCOH before and after 8 eV VUV irradiation.

Then, by comparing the surface potential as a function of time after irradiation for both samples, we find that trapped charges in the UV-cured sample decay faster. The surface potential in the UV-cured sample decayed to the preirradiation potential in 23 h after VUV irradiation. In comparison, it took 75 h for the pristine SiCOH. As presented above, the UV-cured sample had 5.6% more trapped charges after VUV irradiation. However, the time taken for the trapped charges in the UV-cured SiCOH to decay was one-third of that for the pristine SiCOH. Thus, we can infer that UV-cured dielectrics have higher intrinsic conductivity.

Figure 2 shows VUV spectroscopy for pristine and UV-cured SiCOH before and after 8 eV VUV irradiation. Before VUV irradiation, the spectroscopy measurements for pristine and UV-cured SiCOH overlap. However, after VUV irradiation, the spectroscopy showed two important differences.

First, for photon energies less than 8.5 eV, the photoemission/substrate current in steady state for pristine SiCOH is larger than the steady-state photoemission/substrate current for the UV-cured SiCOH. This occurs because, for photon energies less than 8.5 eV, photoemission can occur only from the defect states in the band gap. Since the photoemission current will be proportional to the number of defect states, we can conclude that pristine SiCOH has more defect states in the band gap as compared to UV-cured SiCOH. On the other hand, for photon energies higher than 8.5 eV, the photoemission current for in UV-cured SiCOH is larger than in pristine SiCOH. This is because for energies greater than 8.5 eV, photoemission can occur directly from the valence band in addition to the photoemission from the defect states. Thus, the photoconductivity of the dielectric

TABLE I. Comparison of trapped charges generated by 8 eV VUV photons, trapped-charge decay time, and photoinjection flux for pristine and UV-cured SiCOH.

	Pristine SiCOH (640 nm)	UV-cured SiCOH (500 nm)
Trapped charges (No./cm ²)	8.03×10^{11}	8.48×10^{11}
Photoinjection current (pA/cm ²)	60.95	54.16
Trapped charged decay time (h)	75	23

determines the photoemission/substrate current. Hence, we can conclude that UV-cured SiCOH is higher photoconductivity than pristine SiCOH.

V. SUMMARY AND CONCLUSIONS

In conclusion, more trapped charges are generated in UV-cured SiCOH than in pristine SiCOH during VUV irradiation. In addition, both the intrinsic and photoconductivities of SiCOH increase after UV curing. This shows that although there are advantages of UV curing, there are also some deleterious effects that are of importance in plasma processing of low- k SiCOH.

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