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Effect of vacuum ultraviolet and ultraviolet Irradiation on capacitance-voltage characteristics of low-k-porous organosilicate dielectrics

H. Sinha,[1] J. L. Lauer,[1] M. T. Nichols,[1] G. A. Antonelli,[2] Y. Nishi,[3] and J. L. Shohet[1,a)]
[1]*Department of Electrical and Computer Engineering and Plasma Processing and Technology Laboratory, University of Wisconsin–Madison, Madison, Wisconsin 53706, USA*
[2]*Novellus Systems, Tualatin, Oregon 97062, USA*
[3]*Stanford University, Stanford, California 94305, USA*

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High frequency capacitance-voltage (C-V) measurements are used to determine the effects of vacuum ultraviolet (VUV) and ultraviolet (UV) irradiation on defect states in porous low-k organosilicate (SiCOH) dielectrics. The characteristics show that VUV photons depopulate trapped electrons from defect states within the dielectric creating trapped positive charge. This is evidenced by a negative shift in the flat-band voltage of the C-V characteristic. UV irradiation reverses this effect by repopulating the defect states with electrons photoinjected from the silicon substrate. Thus, UV reduces the number of trapped positive charges in the dielectric and can effectively repair processing-induced damage. © *2010 American Institute of Physics*. [doi:10.1063/1.3306729]

During manufacturing of solid-state devices, dielectrics are exposed to numerous plasma-processing steps in which vacuum ultraviolet (VUV) and ultraviolet (UV) irradiation takes place. This irradiation often produces charge embedded within dielectrics, which can lead to dielectric damage.[1,2] Typically, the capacitance versus voltage relationship (C-V) gives us details on the deviation of dielectrics from ideal behavior.[3] This letter shows the relationship between C-V characteristics and the induced charge in organosilicate SiCOH deposited on silicon after VUV/UV irradiation.

VUV/UV irradiation of dielectrics can cause electron-hole pair generation, photoconduction, photoemission, and photoinjection of electrons from the substrate into the dielectric.[4] 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.[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 dielectric.[4,6] Photoemission can take place by electrons ejected from either the valence band or the defect states present in the dielectric.[5] Photoemission from the defect states leads to depopulation of electrons within the dielectric. Thus, after photoemission, the dielectric develops a net positive charge.

For photoinjection to occur, the substrate-dielectric interface energy barrier should be less than the energy of the electrons. The Si-SiCOH interface has an energy barrier of 4 ± 0.5 eV.[6] As a result, only electrons in silicon with energies greater than 4.5 eV can be injected into SiCOH. The photoinjection is further enhanced by the presence of trapped charges in SiCOH at the interface. The trapped charges reduce the interface energy barrier by acting as low-energy conduction pathways.[6] Photoinjected electrons from silicon can travel in the dielectric and recombine with positive trapped charges there. Thus, photoinjection can repopulate the defect states with electrons resulting in depletion of the trapped positive charges. The repopulation will affect the characteristics of the dielectric. In addition, depending on their energy, some of the photoinjected electrons can be photoemitted from the dielectric.[7] However, the amount of charge in the dielectric is unchanged as the photoemitted electrons were photoinjected from Si. Thus there will no effect on characteristics of the dielectric due to photoemission of the photoinjected electrons.

The changes in the trapped charges due to depopulation or population of electrons within the dielectric, can be monitored by examining the C-V characteristics.[8] The C-V characteristics as well as the flat-band voltage shift as a function of the number of trapped charges in the dielectric. An increase in the number of positive trapped charges is evidenced by a negative shift in the flat-band voltage. Repopulation of defect states with electrons (decreasing positive charges) produces a positive shift in the flat-band voltage. The flat-band voltage shift is always directly proportional to the change in the number of trapped charges.[8] For an ideal dielectric, there should be no trapped charges and as a result the flat-band voltage should be zero.[8]

The trapped charges also affect the surface potential of the dielectric.[4] The trapped positive charge after VUV irradiation often results in a positive surface potential. The surface potential decreases after repopulation of defect states with electrons.[4] For an ideal dielectric, we should measure zero surface potential since there are no defect states or trapped charges.[8] By monitoring the shifts in the flat-band voltage and the surface potential, we can determine the effect of irradiation of varying energies (such as VUV and UV radiation) on the defect states in the dielectrics.

To investigate the effect of VUV/UV, SiCOH samples of various dielectric constants and thicknesses were deposited on p-type silicon using plasma enhanced chemical vapor

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[a)] Electronic mail: shohet@engr.wisc.edu.

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deposition (PECVD). It is well known that plasma deposition can induce defect states.[9] Thus, PECVD SiCOH dielectrics can exhibit nonideal C-V characteristics. If no charged defect states are present, then the samples should have zero flat-band voltage shift as well as zero surface potential. For the samples, the flat-band voltage indicated process-induced positive charges. To determine the flat-band voltage, the transition point from accumulation to depletion was found from the C-V characteristics. The voltage at which the capacitance starts decreasing from its maximum value is defined as the flat-band voltage. A flat-band voltage of −2 V was observed for 266-nm SiCOH (K=2.65). For thicker samples, (444-nm SiCOH K=2.65) and (458-nm SiCOH K=2.75) the flat-band voltage was −4 V. The surface potential was a low positive value (~1 volt) that also indicated process-induced positive charge.

C-V characteristics at 100 kHz were measured using a Mercury Probe (MDC 862) and an LCR meter (SR 720). The surface-potential measurements were made with a Kelvin Probe.[10,11] Before exposure of the samples to VUV/UV irradiation, C-V and surface-potential measurements were obtained for reference. The samples were then irradiated with VUV photons at the Synchrotron Radiation Center at UW-Madison. The energy of the VUV photons was chosen based on the defect states present in SiCOH. By examining the level of depopulation of the defect states as a function of photon energy, the location of these states above the valence band can be determined. It was found that photon energy of 8 eV maximizes the depopulation of electrons from the defect states by photoemission. For SiCOH, the sum of band-gap energy and electron affinity is 8.5 eV and therefore the majority of the defect states are located 0.5 eV above the valence band.[4] Following this exposure, the same C-V and surface potential measurements were made.

The samples were then exposed to UV irradiation from HgAr pen lamp for 1 min. The energy peak of the UV irradiation was 4.9 eV. The UV photons did not have enough energy to cause photoemission from either the valence band or the defect states of SiCOH. However, the UV photon energy was greater than the interface energy barrier of 4 ± 0.5 eV. Thus, the dominant process at this energy is photoinjection of electrons from the silicon substrate into the SiCOH. UV irradiation also reduces the porosity of SiCOH dielectrics, which then decreases the dielectric thickness and increases the dielectric constant of the sample.[12] These will result in an increase in the capacitance of the SiCOH sample. After UV irradiation, the C-V characteristic and surface-potential measurements were repeated.

We now compare the C-V and surface potential measurements after irradiation. For VUV irradiation of 8 eV photons at a dose of 5.5×10^{14} photons/cm^2 incident on 266-nm thick SiCOH (K=2.65) we observed the flat-band voltage shifted to −4 V. This is shown in Fig. 1 as V_{FB1}. The negative shift shows that the defect states have been depopulated by the VUV resulting in more trapped positive charges.

As photon dose increased, the flat-band voltage shifted more negatively until the flat-band voltage saturated at a maximum value of −6 V at a dose of 1.1×10^{15} photons/cm^2. This saturation flat-band voltage V_{FB2}, is shown in Fig. 1.

The surface potential also increased as the magnitude of the flat-band voltage increased. We found, that for the same photon dose (1.1×10^{15} photons/cm^2) that results in flat-band voltage saturation, the surface potential also saturated at +4 V. This also implies that with increasing doses of VUV, more defect states were depleted of electrons. The maximum values of flat-band voltage and surface potential occur when all the defect states are depleted of electrons.

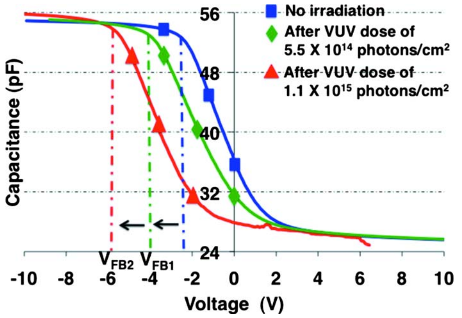

FIG. 1. (Color online) Shifts in C-V characteristic curve for SiCOH (K=2.65) with varying VUV dose.

After subsequent UV irradiation, we observed a positive shift in the flat-band voltage of the C-V characteristics. As shown in Fig. 2, after UV irradiation, we observed a +6 V shift in the flat-band voltage. This implies that UV irradiation has caused repopulation of the defect states and reduces the number trapped charges in the dielectric. The C-V characteristics indicate that UV irradiation reverses the effect of VUV irradiation. We believe that photoinjection of electrons from the silicon substrate is the major contributor of electrons for repopulation of the defect states. The energy supplied by the UV photons is greater than the band gap of silicon, and thus photoinjection is feasible. Similar measurements were made for 458-nm thick SiCOH (K=2.75), which are shown in Fig. 3. However, for the same dose of UV irradiation we observed a reduced positive shift in the flat-band voltage as compared to SiCOH (K=2.65) of same thickness. We believe this change is due to the higher density of the K=2.75 SiCOH sample.

Comparison of the magnitude of the change in the flat-band voltage shift after VUV and UV irradiation shows that UV irradiation causes a larger shift. For 266-nm SiCOH (K=2.65), VUV caused a −4.5 V change in flat-band voltage where as UV caused a +6 V change. As the magnitude of the change in flat-band voltage is proportional to the change in the amount of trapped charges, we conclude that UV repopulated more defects states than the ones depopulated by VUV irradiation. Therefore, the amount of positive charge in the dielectric has reduced. We believe that the ad-

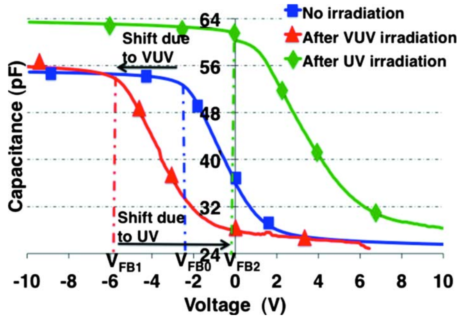

FIG. 2. (Color online) C-V characteristics for 266-nm SiCOH (K=2.65) for no irradiation, after VUV irradiation and after UV irradiation.

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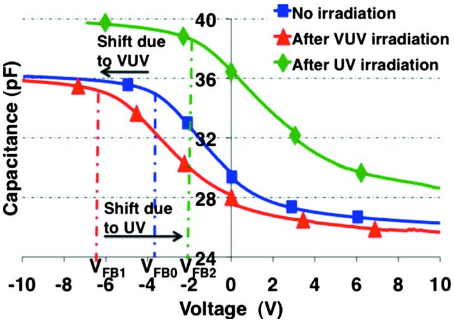

FIG. 3. (Color online) C-V characteristics for 458-nm SiCOH (K=2.75) for no irradiation, after VUV irradiation and after UV irradiation.

ditional 1.5 V shift in flat-band voltage due to UV irradiation is caused by repopulation of processing-induced defect states. These defect states were created during PECVD of SiCOH and thus were present in the dielectric before VUV irradiation. The flat-band voltage measured after UV irradiation was −0.5 V, which is closer to the ideal than the flat-band voltage on the unirradiated samples. In addition, the surface potential also reduced to a level that was comparable to the background noise. Thus, in addition to reversing the effects of VUV, UV irradiation can also deplete the processing-induced trapped charges and thus reduce the damage to the dielectrics.

After UV irradiation of the samples, we observed the expected increase in the capacitance. This was consistently observed for various dielectric constants and thicknesses. As shown in Figs. 2 and 3, the C-V characteristic curves after UV irradiation were shifted upwards as compared to the C-V characteristic curve for samples with no irradiation and/or after VUV irradiation, For 266-nm SiCOH (K=2.65), we observed an approximate 15% increase in capacitance after UV irradiation. For thicker samples (444-nm SiCOH K=2.65) and (458-nm SiCOH K=2.75) we observed an approximate 11% increase in capacitance.

By analyzing the changes of the C-V characteristics, we found that VUV irradiation depopulates defect states whereas UV irradiation can repopulate these defect states. Observed shifts in the flat-band voltage toward zero volts after UV irradiation indicate that positive trapped charges created during processing of the dielectrics can be neutralized. Thus, UV irradiation decreases the defects while also increasing the capacitance. The results were substantiated and directly correlate with the changes in surface potential. However, we believe that by adjusting the UV dose, we can minimize both the defects and the increase in capacitance. Thus, by suitably optimizing and/or supplementing the spectrum of the emitted radiation, it is possible to reduce the amount of trapped charge significantly and thus minimize damage to the dielectric.

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