LETTERS

Effect of vacuum ultraviolet and ultraviolet irradiation on mobile charges in the bandgap of low-*k*-porous organosilicate dielectrics

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Capacitance-voltage (*C-V*) measurements are used to determine the effect of vacuum ultraviolet (VUV) and ultraviolet irradiation on mobile charges in porous low-*k* organosilicate (SiCOH) dielectrics. Hysteresis in the *C-V* characteristics shows that VUV irradiation increases the number of mobile charges in the dielectric. This is because VUV photons excite the trapped electrons from defect states to make them mobile carriers. Conversely UV reverses this effect by reducing the mobile charges through photoemission of free electrons and repopulation of trap states. Thus UV irradiation can be used to improve the electrical properties of plasma-processed dielectrics that are subjected to VUV irradiation. © *2011 American Vacuum Society.* [DOI: 10.1116/1.3520433]

I. INTRODUCTION

In solid-state device fabrication, dielectrics undergo plasma processing during which vacuum ultraviolet (VUV) and UV irradiation of the dielectric often takes place.[1,2] It has been shown that the capacitance-voltage (*C-V*) characteristics can be used as a tool to analyze the effect of VUV/UV on the low-*k* dielectrics.[3,4] The *C-V* characteristics provide information on changes in fixed charge, mobile charge, and interface charge.[5,6] The effects of VUV/UV on fixed trapped electrons are known.[7,8] In this paper, we report the effect of VUV and UV irradiation on mobile charges in low-*k* organosilicate glass (SiCOH). The mobile charges move under the influence of electric fields. Hence, depending on the applied voltage bias, the electrical properties of the dielectric can vary. It should be pointed out that self-consistent electric fields, generated by the charges themselves, can be neglected when the dielectric is biased. We show here that VUV and UV irradiation affects the hysteresis of the *C-V* characteristics. The level of hysteresis of the *C-V* characteristics is related explicitly to the number of mobile charges in the dielectric. Hysteresis can also be caused due to dielectric-substrate interfacial defect states. However, by using a suitable sample that has minimal interfacial defect states, it is possible to analyze the effect of VUV/UV on mobile charges.

II. THEORY

External electric fields in dielectrics cause motion of mobile charges. The location of these mobile charges in the dielectric affects the capacitance.[5] When a positive bias with respect to the substrate is applied to the dielectric, the mobile

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electrons drift away from the dielectric-substrate interface. This causes a positive shift in the flat-band voltage.[5] With the application of a negative bias, there should be a negative shift in the flat-band voltage. The measured flat-band voltage will depend on whether the *C-V* characteristics are made by sweeping voltage from a positive to a negative bias or *vice versa*. This will result in a hysteresis loop. The width of the hysteresis loop is proportional to the number of mobile charges in the dielectric.[9]

Interfacial (dielectric-silicon) defect states can also cause hysteresis in the *C-V* characteristics.[5,10] On application of an electric field, the interface states are populated or depopulated with electrons.[12] When a positive bias is applied on the dielectric with respect to the substrate, electrons from the substrate fill the interface defect states. This results in a decrease in the amount of trapped positive charge at the interface. Conversely, an applied negative bias on the dielectric with respect to the substrate increases the amount of interface-trapped positive charge at the interface. Thus, changing the bias during *C-V* characteristic measurements can increase or decrease the level of trapped positive charge in the dielectric. These changes cause a lateral shift in the *C-V* characteristics, the direction of which depends on whether the measurement starts at a high positive or a high negative bias.[3,4]

The interface defects exist because of the dangling bonds created due to termination of the silicon lattice.[11,12] However, growth of a thermal oxide reduces the number of dangling bonds and hence the interfacial defect states.[13] Thus the hysteresis-loop width produced by the interfacial defect states varies depending on whether a low-*k* dielectric is deposited on silicon or on silicon with thermally grown oxide. By analyzing two sets of samples, (1) a low-*k* dielectric deposited on silicon and (2) a low-*k* dielectric deposited on a thin layer of thermally grown oxide, we can eliminate the hysteresis caused by interfacial defect states. Thus, any additional hysteresis must be produced by the effect of VUV/UV irradiation on mobile charges in these dielectrics.

VUV irradiation is known to depopulate trapped electrons from defect states in the dielectric.[3,4] When depopulation of electrons from the defect states occurs due to VUV irradiation, the electrons can be photoemitted or excited into the conduction band.[14] Photoemission will generate fixed trapped positive charge. However, for photoemission to occur, an electron must be able to overcome the bandgap and the electron affinity energy barriers. It is possible that an electron in the bulk of dielectric may not be photoemitted after overcoming the bandgap and electron affinity energy barriers. Instead, these electrons act as mobile charges and participate in conduction.[2] Thus, after VUV irradiation, the number of mobile charges can increase and can move from one state to another at the same energy level. These charges have been found to exist in SiCOH for days. It has been reported from surface-potential measurements that neutralization of trapped charges in SiCOH is a slow process.[15] The self-induced electric fields, as a result of trapped charges, however, can reduce the dielectric lifetime by time dependent dielectric breakdown.[16]

On the other hand, UV irradiation of dielectrics can reduce the number of mobile charges that were created as a result of VUV irradiation. Two separate processes can occur during UV irradiation that result in reduced mobile charges.

The first process is photoinjection of electrons from the substrate to the dielectric.[3,4] During photoinjection, the electrons overcome the silicon-dielectric interface energy barrier. After crossing the energy barrier, the electrons do not have enough energy to be excited into the conduction band. These electrons end up filling the defect states and neutralizing the trapped positive charge. This also reduces the number of states available for conduction of the mobile charges.

The second process is photoemission because UV photons can supply energy to the mobile electrons in the dielectric that is sufficient to overcome the electron affinity and be photoemitted. Thus, after UV irradiation, the number of mobile charges in the dielectric reduces. The decrease in the number of mobile charges causes decrease in the width of the hysteresis loop.

III. EXPERIMENTAL APPARATUS

Four dielectric samples were used to analyze the effect of VUV and UV irradiation. They are (1) 266 nm low-*k* porous SiCOH ($k=2.65$), (2) 250 nm SiCN, (3) a stacked layer of 15 nm SiCN/175 nm low-*k* porous SiCOH ($k=2.4$)/15 nm SiCN deposited on silicon by plasma-enhanced chemical-vapor deposition, and (4) the same stacked layer of SiCN/SiCOH/SiCN deposited on silicon with a 5 nm layer of thermally grown oxide. Sample (4) was fabricated because, as discussed above, it was expected that the presence of the oxide layer would reduce the number of interface defect states.[12]

The defect states in SiCOH are located 0.5 eV above the valence band.[4] Hence, we chose 8 eV VUV photons for VUV irradiation. 8 eV photons can cause photoemission of electrons trapped in the defect states. The VUV photon dose ($\sim 10^{14}-10^{15}$ photons/cm^2) was chosen so that it is comparable to photon doses received during plasma processing. Furthermore, these doses result in a steady-state photoemission/substrate current along with a steady surface potential showing that no additional trapped charges are generated in the dielectric for these doses. 4.9 eV photons were chosen for UV radiation. These photons can cause photoinjection of electrons across the SiCOH–Si interface energy barrier, which is known to be 3.5–4.5 eV.[17] Also the UV photon energy is greater than the electron affinity, allowing photoemission of any free electrons.

The UW-Madison synchrotron was used as the source of VUV photons.[18] A mercury pen lamp with an energy peak at 4.9 eV was used as a source of the UV photons. The mercury drop contact area has a diameter of approximately 760 μm. The *C-V* characteristics at 100 kHz were measured with a mercury probe (MDC-862) and an *LCR* meter (SR-720). The *C-V* measurements were made by sweeping the bias from positive to negative and vice versa. The *C-V* measurements

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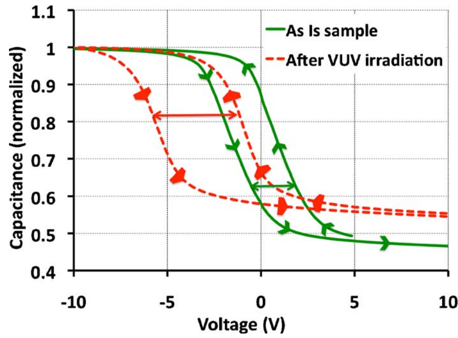

FIG. 1. (Color online) *C-V* characteristic curve for as-is and VUV irradiated SiCOH (k=2.65). The voltage was swept from positive to negative and vice versa.

were made for each of the dielectric under the following three conditions: (1) as is, (2) after 8 eV VUV, and (3) after 8 eV VUV exposure followed by 4.9 eV UV exposure.

IV. RESULTS

Figure 1 shows the *C-V* characteristics for the as-is and the VUV irradiated 266 nm SiCOH samples. It is seen that a hysteresis loop is present in the as-is sample. This hysteresis loop is caused by the interfacial defect states present at the SiCOH–Si interface. After VUV irradiation at the synchrotron, widening of the hysteresis loop was observed which occurs due to the increase in the number of mobile charges.

Figure 2 compares the hysteresis effect on the 266 nm SiCOH sample irradiated with VUV to the sample irradiated with VUV followed by UV. The hysteresis-loop width reduces after UV irradiation. We believe that this occurs due to a reduction in mobile charges. Quantitatively similar results were obtained for SiCN and for the stacked layer of SiCN/SiCOH/SiCN samples.

No hysteresis was observed in the *C-V* measurement for the as-is SiCN/SiCOH/SiCN stack deposited on silicon with thermally grown oxide. This is shown in Fig. 3. Because the oxide layer is thermally grown on silicon, interface traps are greatly reduced. Hence, negligible hysteresis was observed. The positive-to-negative sweep *C-V* curve almost overlaps with the *C-V* curve for the reverse-bias sweep. However,

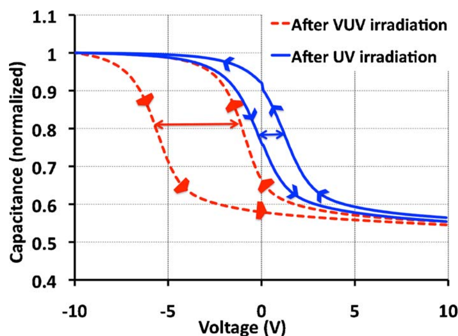

FIG. 2. (Color online) *C-V* characteristic curve for VUV irradiated and UV irradiated SiCOH (k=2.65). The voltage was swept from positive to negative and vice versa.

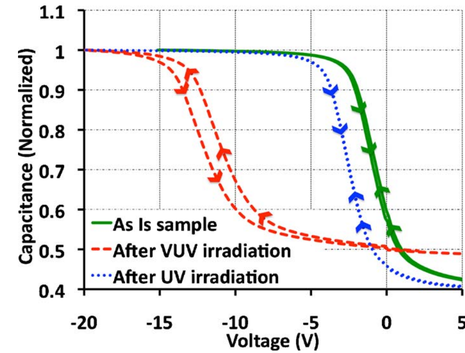

FIG. 3. (Color online) *C-V* characteristic curve for as-is, VUV irradiated, and UV irradiated SiCN/SiCOH/SiCN deposited on silicon with thermally grown oxide. The voltage was swept from positive to negative and vice versa.

after VUV irradiation, hysteresis is observed. Since negligible interfacial defect states are present, the observed hysteresis is likely to be caused by mobile charges. After UV irradiation of VUV irradiated dielectric stack deposited on the thermal oxide the hysteresis in the *C-V* characteristics becomes negligible, just as it was for the as-is sample. Hence it is likely that UV irradiation reduces mobile charges.

V. CONCLUSION

To conclude, both mobile charges and interfacial defect states were found to cause hysteresis in the *C-V* characteristics. The thermally grown oxide eliminates hysteresis due to interface charges present in defect states. Hence, for the dielectric stack deposited on thermal oxide grown on silicon, since there are no interfacial defect charges, the observed hysteresis depends only on the mobile charges in the SiCOH. These mobile charges can be produced during VUV irradiation. This is evidenced by an increase in the width of the hysteresis loop in the *C-V* characteristic. As a result, since UV irradiation at 4.9 eV reduces the amount of mobile charges in the dielectric, by adjusting the UV to a suitable dose during processing with plasma systems, it should be possible to reduce hysteresis and hence improve the electrical properties of the dielectric.

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