Comparison of the vacuum-ultraviolet radiation response of HfO$_2$/SiO$_2$/Si dielectric stacks with SiO$_2$/Si

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Vacuum ultraviolet (vuv) emitted during plasma processing degrades dielectrics by generating electron-hole pairs. VUV-induced charging of SiO$_2$/p-Si and HfO$_2$/SiO$_2$/p-Si dielectric stacks are compared. For SiO$_2$/p-Si, charging is observed for photon energies >15 eV by ionization of dielectric atoms from photoinjected electrons. In HfO$_2$/SiO$_2$/p-Si, charging is observed for photon >10 eV and is due to ionization by photoinjected electrons and by H$^+$ trapping in the HfO$_2$/SiO$_2$ bulk. Hydrogen appears during annealing at the Si–SiO$_2$ interface forming Si–H, which, during irradiation, is depassivated by photoinjected electrons. The authors conclude that dielectric charging in thin oxides (<10 nm) occurs more easily in HfO$_2$/SiO$_2$ than in SiO$_2$. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2591371]

Processing plasmas emit vacuum-ultraviolet radiation (vuv) with energies from 10 to 20 eV.[1] vuv photons generate electron-hole pairs that degrade dielectrics by trapping charge carriers and introducing additional interface states.[2,3] Little is known about the vuv response of high-dielectric-constant (high-K) materials such as hafnium oxide. HfO$_2$ is typically deposited on a layer of SiO$_2$ with a conduction-band offset of ~4 eV with Si.[4] Previous work has studied growth, thermal stability, electrical characteristics, interface defects, and the radiation response of HfO$_2$.[5–10] It is believed that HfO$_2$ is more likely to be susceptible to damage than SiO$_2$ because of its higher density and imperfect growth techniques.[11,12]

To assess this, vuv-induced surface potentials and photoemission and substrate currents during irradiation of a thin (10 nm) HfO$_2$/SiO$_2$ dielectric stack are compared with 10-nm-thick SiO$_2$. The currents and potentials, along with the photon-transmission percentage into the Si substrate as a function of photon energy (10–20 eV), allow identification of the charge-producing processes. Since the vuv response of SiO$_2$ measured in this way is in good agreement with existing models,[13] this leads to confidence in similar measurements for the vuv response of HfO$_2$/SiO$_2$.

For thin dielectric layers (≤10 nm), at the vuv energies studied here, more than 50% of the photons reach the Si substrate[14] and excite electrons from the Si valence band to the Si conduction band. Some electrons overcome the conduction-band offset and are injected into the dielectric, forming a photoinjection current. For thin layers, both photoemission and photoinjection currents are significant.

The dielectrics were grown on p-type silicon with an additional 1 nm intermediate layer of SiO$_2$ for HfO$_2$/SiO$_2$. Thermal growth and atomic-layer deposition were used to grow the SiO$_2$ and HfO$_2$/SiO$_2$, respectively.[15]

vuv exposure is provided by a synchrotron beam of area ~3 cm^2 on the dielectric surfaces. The flux was ~2.1×10^{11} photons/s for 10 min. Surface potentials for both dielectrics were measured with a Kelvin probe.[16] Before vuv exposure, the potentials ranged from −0.3 to −0.5 V for both dielectrics.

The photoemission (I_{p1}) and substrate (I_{sub}) currents were measured with the circuit in Fig. 1. The aluminum plate was biased to +48 V to collect I_{p1}, which is returned to the substrate via I_{sub}. Photoemitted electrons *not* collected by the Al plate (I_{p2}) are also returned to the Si substrate through the ground. Thus, $I_{sub}=I_{p1}+I_{p2}$. The dark currents in the absence of vuv were ~10^{-11} A.

Photoemission of *photoinjected* electrons into vacuum does not charge the dielectric, because these electrons are returned to the substrate via I_{p1} or I_{p2}. Possible mechanisms for surface-potential generation are (1) impact ionization of the oxide atoms by the photoinjected electrons, (2) photoemission of electrons produced by photon absorption in the dielectric, and (3) impurity ion trapping in the bulk oxide.

I_{sub}, I_{p1}, and the estimated photon transmission[14] through both dielectrics are shown as a function of photon energy in Fig. 2. I_{sub} and I_{p1} do not change with time during exposure.
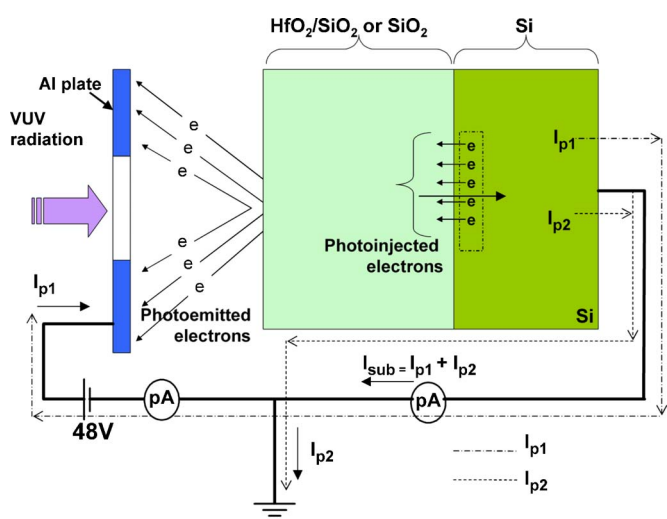

FIG. 1. (Color online) Experimental setup for the vuv exposure of dielectric materials. The figure shows the photoemission and photoinjection current paths. This figure is not to scale and the dielectric layer is shown to be thicker than the substrate for illustration purposes.
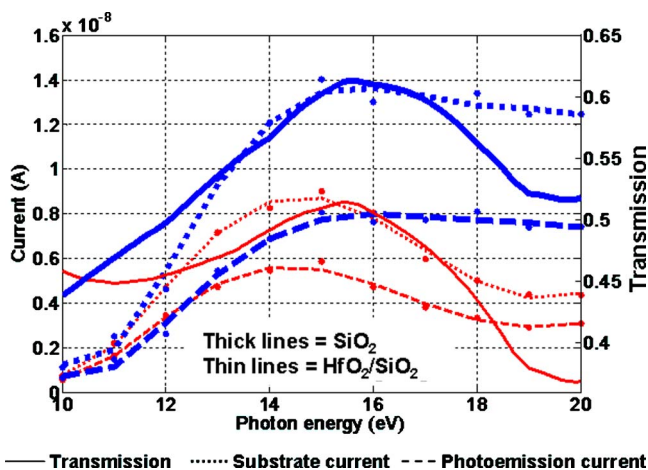
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FIG. 2. (Color online) Measured substrate (dotted lines) and photoemission currents (dashed lines) through both a 10-nm-thick SiO_2 layer (thick solid line) and a 10-nm-thick HfO_2/SiO_2 dielectric stack (thin solid line) as a function of photon energy. The normalized photon-transmission coefficients for both dielectrics are the solid lines.

The peak surface potentials are plotted in Fig. 3 for both dielectrics.

We first discuss the SiO_2 results. Here, both I_{sub} and I_{p1} follow the photon transmission as a function of photon energy. It is unlikely that these currents are caused by the photoemission of electrons produced *within* the dielectric, because, for a 10 eV photon, the electron energy after excitation from the SiO_2 valence band to the conduction band is ~1 eV. Since an electron loses energy before reaching the dielectric-vacuum interface, its energy is too low to overcome the vacuum barrier (~1 eV for SiO_2) and be photoemitted. Hence, I_{sub} and I_{p1} are from emission of photoinjected electrons that travel from the Si substrate through the dielectric and into vacuum.

For a 10 eV photon, an electron excited into the Si conduction band will have an energy of 8.9 eV (Si band gap 1.1 eV). The energy is dissipated by phonon emission and impact ionization.[13] However, some of these electrons can be injected into the oxide. Since an electron loses ~3 eV in overcoming the Si–SiO_2 conduction-band offset, it will be left with ~5.9 eV in the oxide. By using the continuous-slowing-down approximation[17] (CSDA) and the experimentally determined energy relaxation rate $[(1/E)(dE/dt)]$,[13] we
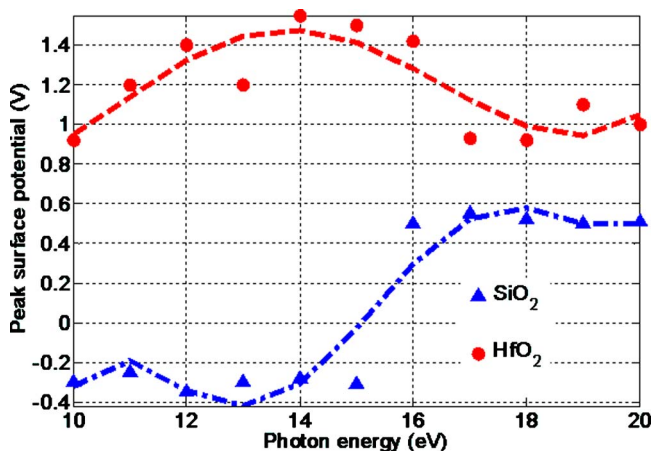

FIG. 3. (Color online) Peak surface potential measured with a Kelvin probe after vuv irradiation for both the SiO_2 and the HfO_2/SiO_2 dielectric stack.

estimate that a 5.9 eV electron in SiO_2 must travel ~400 nm before losing its energy. This distance increases with electron energy.[13] Since the SiO_2 is only 10 nm thick, a large number of the photoinjected electrons can be photoemitted.

The increase in I_{p1} and I_{sub} at higher photon energies (from 11 to 15 eV), as shown in Fig. 2, is due to two possible effects. They are (1) an increase in the number of photoinjected electrons because more photons reach the silicon at higher energies and (2) higher-energy electrons generated by photon absorption in the dielectric.

From Monte-Carlo simulation,[18] for all photon energies considered here, photoemission of photoinjected electrons dominates over photoemission from electrons produced in the dielectric. Even for 20 eV photons in SiO_2, the simulation indicates that the photoemission yield (the number of photoemitted electrons divided by the total number of incident photons) is ~0.02. From experiment, the photoemission yield is obtained by dividing I_{sub} by $q\Gamma$, where q is the electron charge and Γ is the photon flux. The experimental yield was ~0.36 which is significantly larger than the simulation-estimated value. Since the simulation accounts only for photoemitted electrons produced by photon absorption in the dielectric, the difference between the simulation results and the experimentally measured value must be due to the emission of photoinjected electrons from Si into vacuum. Therefore, photoemission from photons absorbed in the SiO_2 can be neglected. In Fig. 2, the decrease of I_{p1} and I_{sub} with energy for photon energies between 15 and 20 eV correlates with the decrease in photon transmission to the substrate and matches the decrease in photoinjection current.

For photon energies between 10 and 15 eV, photons that reach the silicon generate photoinjected electrons with energies $<\sim9$ eV after they are injected into SiO_2. However, for energies >15 eV, the photoinjected electron energy is >9 eV (SiO_2 band gap). These electrons can produce impact ionization of the dielectric atoms.

The energy relaxation rate of these electrons increases with energy ($>10^{14}$ s^{-1}).[13] Using CSDA, it was determined that these electrons dissipate all their kinetic energy within a depth of ~2 nm from the SiO_2–Si interface by breaking chemical bonds and generating secondary electron-hole pairs.[13] It is these secondary electrons, when they are photoemitted, which generate a net positive charge in the dielectric. This is confirmed, as shown in Fig. 3 for SiO_2, by a surface potential of approximately +0.5 V for energies >15 eV. There is no positive surface potential for photon energies between 10 and 15 eV.

We now turn to HfO_2/SiO_2. From Fig. 2, for photon energies between 10 and 12 eV, the photon transmission through HfO_2/SiO_2 is approximately equal to that for SiO_2. For energies >12 eV the transmission is smaller than that for SiO_2. The substrate and photoemission currents of $HfO_2/SiO_2/Si$ also track the photon transmission as a function of energy and show a strong dependence on photoinjection current. For photon energies ≤12 eV, the photon transmission into the silicon is ~45% and I_{sub} is 0.8×10^{-9} A. Thus, for both dielectrics, the photoemission and substrate currents are from emission of photoinjected electrons from Si traveling through the dielectric and into vacuum for energies ≤12 eV.

The Monte-Carlo simulation for 20 eV exposure of HfO_2/SiO_2 reveals that the photoemission yield from photons absorbed in the dielectric is 0.008 while the experimen-

tal value is 0.12. A comparison of simulation results and experimental data for all vuv energies considered here indicates that photoemission due to photons absorbed in HfO_2 is small, again showing that the photoinjected electrons dominate the photoemission. As shown in Fig. 2, the photoemission and substrate-current dependence of HfO_2/SiO_2 on photon transmission is identical to the SiO_2 case.

However, in sharp contrast to SiO_2, where a positive (+0.5 V) surface potential with respect to the background was measured for photon energies >15 eV, for HfO_2/SiO_2 the surface potential was 0.9 V, as shown in Fig. 3, even for vuv energies of 10 eV. Although for SiO_2 the positive-charge accumulation was determined to be from impact ionization, it is unlikely that this applies to low energy (10–11 eV) exposure of HfO_2/SiO_2.

Furthermore, once in the HfO_2 conduction band, the electron energy falls to 6 eV which is only marginally larger than the HfO_2 band gap (5.9 eV). Since this is not large enough to cause impact ionization, another process must be responsible for the charge accumulation.

We propose that this charging (<12 eV) is induced by hydrogen trapping in deep-trap states in HfO_2/SiO_2.[19] The hydrogen is introduced during annealing after dielectric deposition to passivate trivalent Si dangling bonds at the Si–SiO_2 interface.[19] However, photoinjected electrons from the Si depassivate the Si–H bonds and release a positively charged hydrogen ion which is trapped in the HfO_2/SiO_2 bulk causing a net positive-charge buildup in the dielectric.

From the surface-potential data for HfO_2/SiO_2 in Fig. 3, it can be seen that the potential follows the photon-transmission curve (Fig. 2) as a function of energy beyond the threshold for impact ionization (~12 eV). Although for SiO_2 the threshold for impact ionization is larger (~15 eV), the surface-potential data follow the photon-transmission curve (Fig. 2) for energies >15 eV. An increase in the trapped-charge density corresponding to an increase in photoinjection suggests that, although impact ionization in HfO_2/SiO_2 due to photoinjected electrons is unlikely at low photon energies (<12 eV), it must be included when higher energies are considered.

This is consistent with other measurements where a rapid positive-charge buildup that is resistant to neutralization by hot electrons injected from silicon was observed in HfO_2 during negative-bias temperature instability stressing of a positive channel metal-oxide semiconductor transistor.[20]

From the perspective of damage to high-K gate oxides, it is significant that positive-charge accumulation in HfO_2/SiO_2 occurs for photon energies as low as 10 eV. It is likely that hydrogen introduced in the oxide during annealing plays an important role in the positive-charge buildup at low photon energies (<12 eV). However, for photon energies ≥12 eV, net positive-charge accumulation in HfO_2/SiO_2 is produced by photoinjected-electron-impact ionization of the oxide atoms. The smaller band gap of HfO_2, as compared

with SiO_2 facilitates electron-hole-pair creation in HfO_2 by lower-energy photoinjected electrons (≥7 eV) from the silicon substrate.

We conclude that the vuv-radiation response of 10-nm-thick SiO_2/Si and $HfO_2/SiO_2/Si$ dielectric stacks show that the photoemission and substrate currents follow the photon-transmission curve as a function of energy in both dielectrics, thereby indicating photoemission of photoinjected electrons in 10-nm-thick dielectric layers. Surface-potential data indicate that positive-charge buildup in SiO_2 occurs only for photon energies greater than 15 eV and is attributed to impact ionization of the oxide atoms by photoinjected electrons. For HfO_2/SiO_2, positive charging is induced for photon energies greater than 10 eV and is attributed to impact ionization plus H^+ trapping in the HfO_2/SiO_2 bulk. This suggests that HfO_2/SiO_2 is more susceptible to plasma-induced radiation damage than SiO_2.

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