

# Effect of thermal annealing on charge exchange between oxygen interstitial defects within HfO<sub>2</sub> and oxygen-deficient silicon centers within the SiO<sub>2</sub>/Si interface

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We compare the charging response of rapid thermally annealed (800 and 1000 °C) 4 nm thick HfO<sub>2</sub> to as-deposited HfO<sub>2</sub> on Si by measuring the surface potential of the HfO<sub>2</sub> layers after vacuum ultraviolet (VUV) irradiation with 11.6 eV photons. From VUV spectroscopy, we determined all HfO<sub>2</sub> layers show the presence of oxygen-interstitial defects (OIDs). The electronic states of OID in HfO<sub>2</sub> line up in energy with oxygen-deficient Si centers within the SiO<sub>2</sub> interfacial layer. This implies charge exchange between OIDs within HfO<sub>2</sub> and the O-deficient silicon centers within the SiO<sub>2</sub> interfacial layer are very important for controlling the radiation-induced trapped charge in HfO<sub>2</sub> dielectric stacks. © 2009 American Institute of Physics. [DOI: 10.1063/1.3122925]

Leakage currents and trapped charge within high-*k* gate dielectrics significantly contribute to threshold voltage shifts<sup>1,2</sup> and can cause Coulomb scattering<sup>2</sup> of electrons in channels of metal-oxide-semiconductor transistors.<sup>3</sup> The chemistry of the “SiO<sub>2</sub>-like” interface layer (IL) between HfO<sub>2</sub> and the Si substrate has been shown to dominate the radiation response of the HfO<sub>2</sub>/Si interface.<sup>4,5</sup> Recent studies<sup>6</sup> show that deep-level defects related to oxygen (O)-deficient silicon are responsible for trapping charge in the SiO<sub>2</sub> IL.<sup>7-9</sup> However, what is not understood is how defects within HfO<sub>2</sub> may interact, both electrically and chemically, with defects within the SiO<sub>2</sub> IL.<sup>10</sup>

Processing plasmas produce significant vacuum ultraviolet (VUV) radiation<sup>11-13</sup> which creates electron-hole pairs within dielectrics. VUV changes the conductivity of dielectrics during processing which either contributes to<sup>14-17</sup> or mitigates<sup>18-20</sup> trapped charge. In this letter, we use a Kelvin probe<sup>21,22</sup> to measure surface potentials<sup>23</sup> of atomic-layer-deposited 4 nm thick HfO<sub>2</sub> dielectrics on ⟨111⟩ *p*-type Si wafers (1000 Ω cm) after VUV irradiation with 11.6 eV photons which are often emitted from Ar processing plasmas.<sup>11,13</sup> We compare rapid thermal annealing (RTA) of HfO<sub>2</sub> at 800 and 1000 °C to that of as-deposited HfO<sub>2</sub> on the radiation-induced trapped charge.

By comparing VUV-spectroscopic measurements of HfO<sub>2</sub> to density of state (DOS) calculations<sup>24-26</sup> for HfO<sub>2</sub> we identify several states due to oxygen interstitial defects (OIDs) within the HfO<sub>2</sub> layer. In addition, comparing the defect states of HfO<sub>2</sub> to that of SiO<sub>2</sub>, we find the defects related to OID within HfO<sub>2</sub> create states that closely line up (in energy) to O-deficient silicon centers within the SiO<sub>2</sub> layer. We hypothesize that the charged state of OIDs within HfO<sub>2</sub> affects the density of holes trapped within the SiO<sub>2</sub> IL after VUV irradiation. This is supported by surface-potential measurements taken after VUV irradiation, which show a lower surface potential on HfO<sub>2</sub> layers that have negatively charged OIDs (OID<sup>-</sup>) compared with an HfO<sub>2</sub> layer that has neutral (OID<sup>0</sup>) or positively charged OIDs (OID<sup>+</sup>).

The procedure to expose wafers to synchrotron-VUV radiation has been described elsewhere.<sup>27</sup> The wafers were mounted in a chamber evacuated to a pressure of 10<sup>-8</sup> torr. At the wafer, the VUV beam was elliptical and measured to be roughly 25 × 10 mm<sup>2</sup>. Surface-potential measurements were made 1 h after VUV irradiation. VUV spectroscopy was accomplished by measuring the substrate current with a picoammeter while photon energy was scanned between 5 and 30 eV.

Figure 1 shows a comparison of surface potential on 4 nm of HfO<sub>2</sub> after irradiation by 11.6 eV photons as a function of photon dose for as deposited and RTAs of 800 and 1000 °C. The error bars shown in Fig. 1 represent (one standard deviation)/2 in the average surface potential measured in the VUV irradiated region. In addition, Fig. 1 shows the surface potential for 4 nm of SiO<sub>2</sub>, rapid thermally annealed at 800 °C, under the same conditions as the HfO<sub>2</sub>. The potential is positive for the as deposited and 800 °C-HfO<sub>2</sub> dielectrics as well as the SiO<sub>2</sub> layer, indicating trapped holes. The as-deposited HfO<sub>2</sub> samples have the largest surface potential while the HfO<sub>2</sub> samples RTAd at 1000 C show no indication of charging for all photon doses.

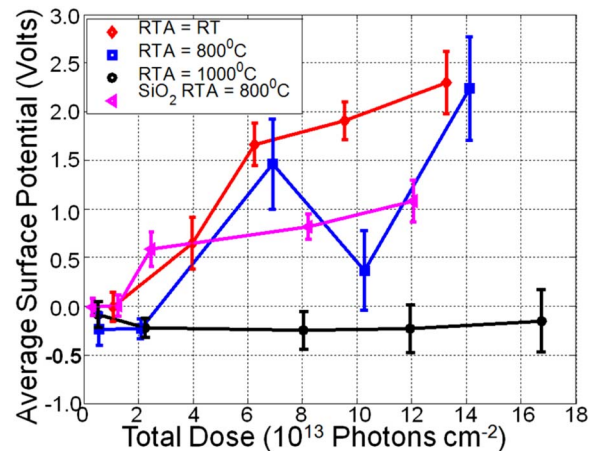


FIG. 1. (Color online) Average surface potential on 4 nm of SiO<sub>2</sub> and HfO<sub>2</sub> RTA at RT, 800 and 1000 °C as a function of total photon dose of 11.6 eV photons.

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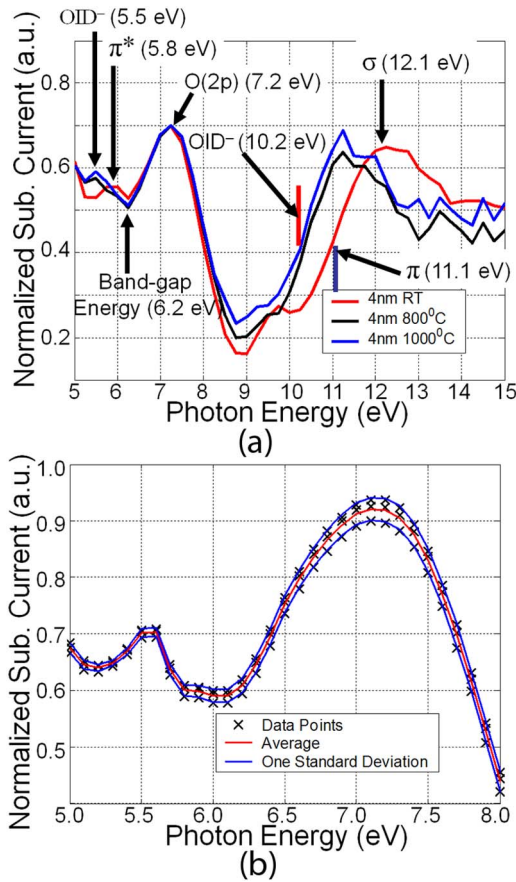


FIG. 2. (Color online) (a) Normalized substrate current during the irradiation of 4 nm of HfO<sub>2</sub> annealed at RT, 800 °C and 1000 °C as a function of photon energy. (b) Normalized substrate current for three consecutive scans at the same location of the surface of a 4 nm HfO<sub>2</sub> layer which was rapid thermally annealed at 1000 °C.

Figure 2(a) shows the normalized substrate current during irradiation of 4 nm of HfO<sub>2</sub>, for several annealing temperatures, with photon energies between 5 and 15 eV. To illustrate the reproducibility of the measurements, three consecutive scans were performed at the same location on the surface of a 4 nm HfO<sub>2</sub> layer which was rapid thermally annealed at 1000 °C with photon energies between 5 and 8 eV, as shown in Fig. 2(b). The raw data points as well as the average between the scans and  $\pm$  one standard deviation (SD) between the consecutive scans are shown Fig. 2(b). It can be seen that all three scans fall within one SD of the average for all data points with photon energies between 5 and 8 eV. The peaks in the current as a function of photon energy are due to the excitation of electrons from specific states within the HfO<sub>2</sub>-dielectric stack. This results in current due to one or more of the following processes depending on the photon energy: photoemission,<sup>20</sup> photoconduction,<sup>23</sup> photoinjection,<sup>27</sup> and liberation of trapped charge.<sup>37,38</sup>

Comparing the peaks in the substrate current shown in Fig. 2 with DOS calculations<sup>24–26</sup> for HfO<sub>2</sub> allows us to determine the source of the electronic transitions. We attribute the broad peak centered at 7.2 eV to be due to O (2p) states<sup>28,29</sup> from oxygen atoms within the HfO<sub>2</sub> lattice<sup>30,31</sup> as well as O-deficient Si centers within the SiO<sub>2</sub> IL. The O (2p) states define the upper-valence band of HfO<sub>2</sub> layer<sup>30–32</sup> and the O-deficient Si centers are often excited by 7.6 eV photons.<sup>36,37</sup> The broad peak at 7.2 eV is at the same energy for all three curves regardless of annealing temperature.

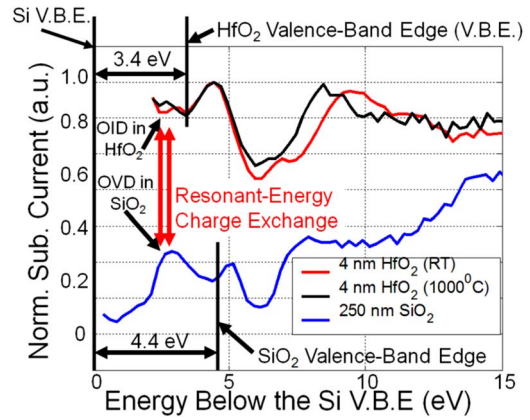


FIG. 3. (Color online) Comparison of normalized substrate current between 4 nm of HfO<sub>2</sub> (top curves) and 250 nm of SiO<sub>2</sub> (bottom curve) with the band-gap edges shifted in energy with respect to Si.

Thus, as shown in Fig. 2, all HfO<sub>2</sub> layers have the same bandgap energy of 6.2 eV.

In Fig. 2, the as-deposited HfO<sub>2</sub> shows an OI<sup>D</sup> or an OI<sup>D+</sup> due to the electronic states located just ( $<1$  eV) above<sup>33</sup> the HfO<sub>2</sub> valence band as well as states located 5–10 eV below the HfO<sub>2</sub> valence-band edge (VBE).<sup>25</sup> We attribute the electronic states located at 5.8, 11.1, and 12.1 eV to  $\pi^*$ -antibonding,  $\pi$ -bonding, and  $\sigma$ -bonding states,<sup>24,25</sup> respectively, from OI<sup>D</sup> or OI<sup>D+</sup> within the as-deposited HfO<sub>2</sub> layer. Also shown in Fig. 2, the electronic states due to the OI<sup>D</sup>s in the HfO<sub>2</sub> layers rapid thermally annealed at 800 and 1000 °C shift to lower energies, compared to the as-deposited HfO<sub>2</sub> layer. By comparing these electronic states to DOS calculations,<sup>25</sup> we find the states located at 5.5 and 10.2 eV are likely due to OI<sup>D-</sup> within the HfO<sub>2</sub> layer. This suggests that some of the OI<sup>D</sup> in the as-deposited HfO<sub>2</sub> are transformed into OI<sup>D-</sup> after RTA temperatures of 800 and 1000 °C. This transformation may be due to changes in the crystalline structure of the HfO<sub>2</sub> layer after RTA.<sup>34</sup>

Alignment of electronic states between two dielectrics can significantly affect the leakage currents and trapped charge within the dielectric stack. Hole transport within HfO<sub>2</sub> dielectrics occurs through the electronic states associated with the OI<sup>D</sup>s (Ref. 25) just above the VBE. Therefore, alignment of OI<sup>D</sup> states within HfO<sub>2</sub> (in energy) with O-deficient Si centers within the SiO<sub>2</sub> IL can have a significant effect on the density of radiation-induced trapped holes after VUV irradiation. Thus, we compare the electronic structure of HfO<sub>2</sub> to SiO<sub>2</sub>.

From VUV-spectroscopic measurements of 250 nm thick SiO<sub>2</sub> on Si, we determined the bandgap energy of SiO<sub>2</sub> to be 9 eV along with a threshold for photoemission of 9.8 eV. In addition, 7.6 eV photons excite electrons from oxygen-deficient Si centers, located near the SiO<sub>2</sub>/Si interface, into the SiO<sub>2</sub> conduction band<sup>36,37</sup> Figure 3 compares the electronic structure of HfO<sub>2</sub> and SiO<sub>2</sub> as measured with VUV spectroscopy. To facilitate comparison between the electronic structure of HfO<sub>2</sub> and SiO<sub>2</sub>, we positioned their VBE against the VBE of Si.<sup>25</sup> From the literature,<sup>35</sup> we know the VBEs of SiO<sub>2</sub> and HfO<sub>2</sub> are 4.4 and 3.4 eV below the VBE of Si,<sup>35</sup> respectively. In Fig. 3, the Si VBE is set at 0 eV. It can clearly be seen in Fig. 3 that the states due to the OI<sup>D</sup>s in HfO<sub>2</sub> layer line up closely (in energy) to the O-deficient silicon centers in SiO<sub>2</sub>. This strongly suggests resonant-

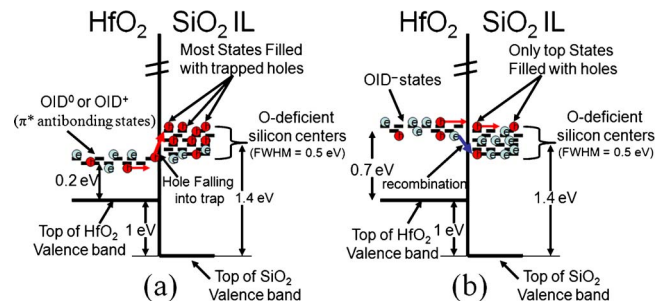


FIG. 4. (Color online) Simplified electron band diagrams for the bottom half of the band-gap of at the interface between a HfO<sub>2</sub> layer and a SiO<sub>2</sub> IL with (a) OID<sup>0</sup> or OID<sup>+</sup> in the HfO<sub>2</sub> layer and (b) OID<sup>-</sup> within the HfO<sub>2</sub> layer (not to scale).

energy charge exchange can occur between OIDs in HfO<sub>2</sub> with O-deficient Si centers in the SiO<sub>2</sub> IL.

To illustrate how charge exchange between OIDs in HfO<sub>2</sub> with O-deficient Si centers in the SiO<sub>2</sub> IL can affect the radiation-induced trapped holes after VUV irradiation, we create the electron energy-band diagrams shown in Fig. 4. The diagram for a HfO<sub>2</sub> layer with OID<sup>0</sup>s or OID<sup>+</sup>s is shown in Fig. 4(a) and for an HfO<sub>2</sub> layer with OID<sup>-</sup>s in Fig. 4(b). For ease of illustrating the charge exchange mechanism between HfO<sub>2</sub> and the SiO<sub>2</sub> IL, we neglect the effects of band bending due to space-charge accumulation in the electron diagrams shown in Fig. 4. The O-deficient silicon centers within the SiO<sub>2</sub> IL shown in Fig. 4 are about 1.4 eV above the VBE of SiO<sub>2</sub> and have a full width at half maximum of 0.5 eV.<sup>36–38</sup>

We see from Fig. 4(a), the  $\pi^*$  states of the OID<sup>0</sup> or OID<sup>+</sup> are 0.2 eV above<sup>25,26</sup> the top of the VBE in HfO<sub>2</sub>. Since the valence-band offset between HfO<sub>2</sub> and SiO<sub>2</sub> is 1 eV, the  $\pi^*$  states line up just below the O-deficient silicon centers. As a result, holes within the  $\pi^*$  states in HfO<sub>2</sub> can fall into a large density of states (with higher electron energy) created by the O-deficient Si centers within the SiO<sub>2</sub> IL.

From Fig. 4(b) we see the OID<sup>-</sup> states are 0.7 eV above<sup>39</sup> the VBE of HfO<sub>2</sub>. This places the OID<sup>-</sup> states near the top of the O-deficient silicon centers in the SiO<sub>2</sub> IL. As a result, only O-deficient Si centers with states that have energies equal to or greater than the OID<sup>-</sup> states in HfO<sub>2</sub> are filled with holes. This is because electrons in the OID<sup>-</sup> states of HfO<sub>2</sub> can neutralize holes that become trapped in O-deficient Si centers that have a lower electron energy, as shown in Fig. 4(b). This suggests that HfO<sub>2</sub> layers with OID<sup>-</sup> present (i.e., HfO<sub>2</sub> RTA at 1000 °C) will have fewer trapped holes within the SiO<sub>2</sub> IL after VUV irradiation than an HfO<sub>2</sub> layer with OID<sup>0</sup> or OID<sup>+</sup> states (i.e., as-deposited HfO<sub>2</sub>). This is consistent with the surface-potential measurements shown in Fig. 1. That is, the as-deposited HfO<sub>2</sub> has a higher surface potential than the HfO<sub>2</sub> layer RTA at 1000 °C due to the presence of a higher density of holes trapped by O-deficient Si centers in the SiO<sub>2</sub> IL.

We conclude that charge exchange between defect states within HfO<sub>2</sub> and the SiO<sub>2</sub> interfacial layer is very important for controlling the radiation-induced trapped charge in HfO<sub>2</sub> dielectric stacks and may well be responsible for leakage currents in these dielectrics. As a result, controlling the density, charged state, and location of OIDs in HfO<sub>2</sub> is a critical step in processing these materials.

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