# Plasma and vacuum ultraviolet induced charging of SiO<sub>2</sub> and HfO<sub>2</sub> patterned structures

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The authors compare the effects of plasma charging and vacuum ultraviolet (VUV) irradiation on oxidized patterned Si structures with and without atomic-layer-deposited HfO<sub>2</sub>. It was found that, unlike planar oxidized Si wafers, oxidized patterned Si wafers charge up significantly after exposure in an electron-cyclotron resonance plasma. The charging is dependent on the aspect ratio of the patterned structures. This is attributed to electron and/or ion shading during plasma exposure. The addition of a 10 nm thick HfO<sub>2</sub> layer deposited on top of the oxidized silicon structures increases the photoemission yield during VUV irradiation, resulting in more trapped positive charge compared to patterns without the HfO<sub>2</sub> dielectric. © 2012 American Vacuum Society. [DOI: 10.1116/1.3654012]

# I. INTRODUCTION

Processing-induced charging damage can occur to dielectrics during plasma exposure from bombardment by energetic electrons, ions, and/or photons.<sup>1,2</sup> These cause damage by creating defects within dielectrics that can trap charge.<sup>3–5</sup> Three mechanisms of plasma-induced charging damage have been identified. These are (i) plasma nonuniformities,<sup>6</sup> (ii) nonuniformities that naturally appear in the patterning of the wafer (topography-dependent charging),<sup>6</sup> and (iii) plasma irradiation.<sup>7</sup> Plasma radiation includes both ultraviolet (UV) and vacuum ultraviolet (VUV) radiation.<sup>8</sup>

In particular, during plasma processing of semiconductor wafers with high-aspect-ratio features, differential charging occurs inside a high-aspect-ratio pit or trench due to the differences in the angular distribution of velocities between the ions and electrons reaching the pit bottom from the plasma.<sup>9</sup> This can lead to the charging of surfaces exposed to the plasma. as well as unexposed locations in the microstructure.<sup>10</sup> In particular, during plasma etching, charging of the bottom or top edges of high-aspect-ratio (depth/diameter) trenches<sup>11</sup> can alter the trajectories of the ions impinging on the material, resulting in more trapped positive charge within the patterned structure, and etch the bottom corners of a pit/trench/hole (undercutting), thereby physically weakening the structure.<sup>12</sup>

Consequently, the overall yield, as well as the reliability, of semiconductor devices can be adversely affected.<sup>13</sup> As a result, finding a way to control and mediate plasma-processinduced charging damage has become a crucial issue in assuring high process yields.

Metal-oxide-semiconductor trench-capacitors are critical in several areas of microelectronic applications that require a high density of capacitors.<sup>14</sup> The use of high-k dielectrics for both stacked and trench capacitors is required for the scaling of memory density and for increasing the capacity per unit area.<sup>15,16</sup> Hafnium-based oxides are currently leading candidates for high-k dielectrics in gate insulators and dynamic random access memory capacitors.<sup>16</sup> However, a wellknown issue is the existence of intrinsic traps within the HfO<sub>2</sub>/SiO<sub>2</sub> dielectric stack.<sup>17</sup> Several studies have explored the effects of radiation-induced charge trapping and leakage currents within planar HfO<sub>2</sub>/SiO<sub>2</sub> dielectric stacks.<sup>18</sup> The goal of this work is to determine the effects of radiation on HfO<sub>2</sub>/SiO<sub>2</sub> within *patterned* structures. The work will show that not only ion bombardment but also VUV irradiation can cause significant charge trapping in HfO<sub>2</sub>/SiO<sub>2</sub>.

# **II. BACKGROUND**

In this work, the effect of the aspect ratio on the charging of oxidized Si structures after plasma exposure is determined by measuring the surface potential over the patterned regions of the wafer with a Kelvin probe. In addition, the effects of VUV radiation on oxidized patterned Si structures with and without a 10 nm thick HfO<sub>2</sub> layer is investigated. The HfO<sub>2</sub> layer increases the photoemission yield (photoemitted electrons per incident photon) during VUV irradiation, as compared with SiO<sub>2</sub> alone, resulting in more trapped positive charge within the patterned structure.

VUV photons can create/inject electrons and/or holes in the dielectric layer that become trapped by the defects.<sup>19–21</sup> When a VUV photon is incident on a dielectric surface, there are several processes that can occur depending on the thickness of the dielectric layer and the energy of the VUV photon. If the photon has an energy greater than the bandgap of the dielectric  $(E_g = 9.0 \text{ eV} \text{ for } \text{SiO}_2 \text{ and } E_g = 6.0 \text{ eV} \text{ for}$ HfO<sub>2</sub>), then it can create electron-hole pairs within the dielectric layer. The location of the electron-hole pairs that are generated within the dielectric depends on the penetration depth of the VUV photons ( $\sim 10 \text{ nm for SiO}_2$ ).<sup>20</sup> Electrons excited into the conduction band (if they are near the vacuum-dielectric interface) that have energies greater than the electron affinity  $(E_{aff})$  of the dielectric material can be photoemitted into the vacuum. We thus express the threshold for photoemission as  $E_{PE} = E_g + E_{aff}$ . The threshold for photoemission is reduced if the electron in trapped in defect states in the bandgap of the dielectric, as the energy required in order for an electron to be excited from the valence to the conductance band will be less than  $E_g$ . Both free electrons and holes within the dielectric layer are able to move throughout the layer, which results in its becoming a photoconductor.<sup>22</sup> If there is an electric field within the dielectric layer, the free electrons and holes can move in response to the electric field until they become trapped, recombine, or leave the dielectric.

Photons with energies less than the bandgap of the dielectric can travel through the dielectric layer and excite electrons from defect states located within the dielectric bandgap into the conduction band. In addition, those VUV photons that penetrate to the substrate can cause electrons or holes to be photoinjected into the dielectric layer from the underlying substrate. All four processes (photoemission, photoconductivity, trap liberation, and photoinjection) can result in current flowing through the dielectric layer during VUV irradiation that can significantly affect the amount of trapped charge within the dielectric layer.

## III. TEST STRUCTURES

The patterned-dielectric test structures that were used in this work were designed and fabricated at the Stanford Nanofabrication Facility. Conventional methods of fabricating high-aspect-ratio dielectric structures involve direct plasma etching into the dielectric. However, during plasma etching, the dielectric quality is often adversely affected due to charged-particle and photon bombardment from the plasma. Because the purpose of this work is to study the response of patterned dielectrics to plasma and VUV irradiation, it is imperative that the oxide on the structures not be exposed to plasma during any fabrication step. Thus, a novel process recipe that obviates the exposure of the oxide to plasma was used and is described as follows.

Unoxidized Si wafers were covered with a photoresist using a spin coater. Circular pits  $1 \mu m$  in diameter were defined on the photoresist using optical lithography. After the photoresist was developed, the wafer was exposed to an HBr plasma to define a set of high-aspect-ratio patterns on the Si wafer. Once the pits in the Si had been etched, an oxide layer was thermally grown on the wafer via wet oxidation at 1000 °C. This temperature was selected to allow the oxidation to proceed in the surface-reaction-controlled regime so as to ensure uniform coverage of the etched Si





FIG. 1. (Color online) (a) Schematic of the 100 mm patterned wafer with 22 individual dice, each with dimensions of  $(8 \times 8)$  mm<sup>2</sup>. (b) SEM image of the cross section of a sample patterned wafer with an aspect ratio of ~2.5:1.

substrate by the oxide, even inside the high-aspect-ratio pits. Because the oxide was grown after the wafer was etched, the oxide quality is intact and can be used for plasma and radiation-response studies. Figure 1 shows an SEM image of the cross-section of the test structures before HfO<sub>2</sub> deposition. In order to determine the difference between HfO<sub>2</sub>-coated oxidized patterned Si structures and structures without the HfO<sub>2</sub>, the oxidized patterned Si wafers were cleaved in half, and a 10 nm thick HfO<sub>2</sub> layer was conformally deposited via atomic layer deposition used HfCl<sub>4</sub> and H<sub>2</sub>O precursors. One hundred cycles of deposition were done, and each atomic layer was  $\sim 0.1$  nm in thickness.

Each patterned die consists of holes that have a diameter of  $0.8 \,\mu\text{m}$  with a hole spacing (pitch) of approximately  $1.6 \,\mu\text{m}$ . Holes were created with depths that varied from 1 to  $11 \,\mu\text{m}$ , while keeping the hole diameter fixed, in order to study charging as a function of the hole aspect ratio. The hole shown in Fig. 1(b) has a depth of  $2 \,\mu\text{m}$ .

# **IV. EXPERIMENT**

An electron cyclotron resonance (ECR) plasma was used to charge the patterned oxide-coated wafers. A helium ECR discharge at 20 mTorr was generated with 100 W of 2.45 GHz microwave radiation. The VUV spectrum for helium plasma in this reactor has been reported previously,<sup>7</sup> with dominant VUV energy peaks at 10.2 eV and 21.2 eV. Samples with various aspect ratios were exposed to the plasma simultaneously for approximately 30 s. The wafer substrates were secured to the wafer chuck with conductive silver paint and grounded to the chamber through conductive carbon tape. Spatially resolved Kelvin probe measurements of the surface potential of the wafers before and after plasma exposure were made in order to assess the effects of the aspect ratio on plasma charging.

The experimental arrangement for VUV irradiation is shown in Fig. 2. It was constructed to allow for the simultaneous measurement of the photoemission current and the current flowing though a bare unmetalized dielectric layer during VUV exposure. The samples were inserted in a vacuum chamber at a distance of 1.5 m from the exit slit of a normal-incidence Seya-Namioka VUV monochromator at the University of Wisconsin Synchrotron Research Center. The monochromator has an output energy range of between 4 and 30 eV and a bandpass of 0.3 nm. The vacuum chamber was evacuated to  $10^{-8}$  Torr, after which the samples could be exposed to the VUV photon beam. At the location of the wafer, the photon beam was elliptical and measured to be roughly  $25 \text{ mm} \times 10 \text{ mm}$  on the wafer surface. The photoemission current was measured during VUV irradiation by placing an aluminum plate 3.5 cm in front of, but electrically insulated from, the wafer, as shown in Fig. 2. The aluminum plate has a hole in it that allows the VUV photons to be normally incident upon the dielectric-coated wafer. A dc bias voltage of +48 V was placed on the aluminum plate with respect to ground to ensure that most of the photoemitted electrons would be collected. Both the substrate and photoemission currents were measured with a Keithley 486 picoammeter. In measuring the current to the substrate, care was taken to shield it from any source of current not flowing through the sample.

After plasma or VUV exposure, the samples were taken out of the vacuum chamber and the surface potential was measured with a Kelvin probe.<sup>23,24</sup> The Kelvin probe is essentially a vibrating capacitor that can be used to measure the surface potential of a charged dielectric on a conducting



FIG. 2. (Color online) Experimental arrangement for VUV irradiation.

(or semiconducting) substrate.<sup>3,25</sup> The tip of the Kelvin probe was 1.5 mm in diameter and was scanned over the surface of the patterned wafer with the surface potential measured every 2.5 mm, thus creating a surface-potential map of the wafer surface.

# **V. RESULTS**

The results given here are split into two parts: (1) plasmainduced charging of patterned structures and (2) VUVinduced charging of patterned structures. In part (1), the effect of the aspect ratio on the charging of oxidized patterned Si structures is investigated. In part (2), the effect that the 10 nm thick  $HfO_2$  layer has on the VUV-induced charging of oxidized patterned Si structures is examined.

## A. Plasma-induced charging of patterned structures

As a first set of experiments, the surface potential of an unpatterned oxidized Si wafer after ECR plasma exposure was measured. Surprisingly, no measurable change in the surface potential was observed for an unpatterned wafer after plasma exposure. This indicates that the ion and electron fluxes remained approximately equal at the outset over the unpatterned wafer surface. However, for patterned wafers, a spatially averaged potential  $V_{av}$  was significantly larger than the surface potential of the unpatterned wafer and appeared at all locations on the wafer, even on the flat unpatterned surfaces between the pits. It should be noted that the resolution of the Kelvin probe is larger than the pattern features.<sup>9</sup>

To illustrate how the patterned structures charge up in the plasma and how the Kelvin-probe system is able to resolve the charging of individual dice on the surface of the wafer, the entire patterned wafer without cleaving was exposed to a dc N<sub>2</sub> plasma discharge at 60 mTorr.<sup>10</sup> The VUV spectrum for nitrogen plasma in this reactor was reported previously,<sup>7</sup> with dominant VUV energy peaks at 8.3 eV and 10.3 eV. The dc plasma was generated by applying 400 V on the cathode, which was separated by 3 cm from the grounded anode. The patterned wafer was placed on the cathode and exposed to the plasma for 6 s. Surface-potential measurements of the patterned wafer after plasma exposure show that the patterned regions of the wafer charged up to a higher voltage than the area surrounding the dice, as shown in Fig. 3.

Over the dice, the surface potential is in the range of 10-15 V. However, around the dice, the surface potential is in the 0-5 V range. This shows that the average surface potential over an individual die can be resolved with the Kelvin probe. Furthermore, we determined that the surface potential increases with the aspect ratio of the holes in the patterned wafer as shown in Fig. 4, which is consistent with the electron-shading theory.

The dependence of  $V_{av}$  on the aspect ratio (depth/diameter of the pit) of the structures is shown in Fig. 4. An aspect ratio of zero in Fig. 1 corresponds to an unpatterned wafer. As seen in Fig. 4,  $V_{av}$  increases with aspect ratio for aspect ratios up to a value of 4:1. For aspect ratios greater than 4:1, the change in  $V_{av}$  as a function of aspect ratio is negligible. We believe this might be due to ion shading within the

#### JVST A - Vacuum, Surfaces, and Films



FIG. 3. (Color online) Surface potential map measured after plasma exposure. The regions of the dice appear as square regions with a larger surface potential than the unpatterned regions surrounding the dice.

structures, in that the ions never reach the bottom of the pitch with an aspect ratio greater than 4:1. As a result, there is only a slight increase in the surface potential for aspect ratios greater than 4:1. This trend is consistent with the findings by Matsui *et al.*, which showed that with increasing aspect ratio the surface potential increases until it reaches a maximum value for high aspect ratios.<sup>26</sup>

## B. VUV-induced charging of patterned structures

Figure 5 shows the current drawn by the substrate during VUV irradiation of uncharged oxidized Si structures with and without a 10 nm thick HfO<sub>2</sub> layer deposited on top of the SiO<sub>2</sub> layer within the pits and surrounding area on the wafer surface. The pits were 3  $\mu$ m deep with an aspect ratio of about 3 and a pitch of 1.5  $\mu$ m. The VUV photons had an energy of 11 eV, and the total exposure time was 600 s.

The photon-flux density incident on the wafer surface was the same for both the  $SiO_2$ - and  $HfO_2$ -coated structures. As can be seen in Fig. 5, the initial current drawn by the substrate is higher for the  $HfO_2$ -coated structures than the  $SiO_2$ structures. Given that the photon flux density is the same for



Fig. 4. (Color online) Dependence of the spatially averaged surface potential as a function of the aspect ratio of the pits.



Fig. 5. (Color online) Current drawn by the oxidized patterned Si wafers with and without a 10 nm thick  $HfO_2$  layer deposited on the SiO<sub>2</sub> layer.

both exposures, this implies that the photoemission yield (photoemitted electrons per incident photon) is larger for the structures with the 10 nm thick HfO<sub>2</sub> surface layer. In addition, the current drawn by the HfO2-coated structures decreases more rapidly as a function of time. Typically, for unpatterned wafers during VUV irradiation, the rate of decrease of the current drawn by the substrate is inversely proportional to the increase in the surface potential. This is because the difference between the total photoemission current and the steady-state current (i.e., the photoinjection current) as a function of time is proportional to the number of trapped charges generated.<sup>25</sup> This suggests that the patterned structures with the HfO<sub>2</sub> layer are charging up more during VUV irradiation than the structures without the HfO<sub>2</sub> layer. This is most likely due to the higher photoemission yield of the HfO<sub>2</sub> layer.<sup>27</sup> It has been reported that in HfO<sub>2</sub> the oxygen interstitial defects (OIDs) are responsible for the defect states between 5.5 and 6.0 eV.<sup>27</sup> Therefore, VUV irradiation can excite an electron from the energy level created by the OIDs in  $HfO_2$  into the conduction band of the  $HfO_2$ . Note that the steady-state currents for SiO<sub>2</sub>- and HfO<sub>2</sub>-coated SiO<sub>2</sub> samples are not the same. This is because the steadystate current (i.e., the photoinjection current) depends on the interface energy barriers, which are different for the two samples.<sup>28</sup>

Figure 6 shows two surface-potential maps measured across an oxidized wafer (without the  $HfO_2$  coating). Figure 6(a) is before VUV irradiation with 11 eV photons, and Fig. 6(b) is after VUV irradiation. The figure also shows that before VUV irradiation, the surface potential is nearly constant across the surface of the wafer, even over the patterned regions. However, after VUV irradiation, the surface potential increases by about 1 to 2 V over both the patterned and unpatterned regions.

Figure 7 shows two surface-potential maps measured (a) before VUV irradiation and (b) after VUV irradiation of the same structures shown in Fig. 1, but with the 10 nm thick HfO<sub>2</sub> layer deposited conformally on top of the SiO<sub>2</sub> layer within the 3  $\mu$ m deep pits and the surrounding area on the

# J. Vac. Sci. Technol. A, Vol. 30, No. 1, Jan/Feb 2012



Fig. 6. (Color online) Surface-potential maps of oxidized Si structures taken (a) before VUV irradiation and (b) after VUV irradiation with 11 eV photons.

wafer surface. By comparing the surface potential measured after VUV irradiation in Figs. 6 and 7, we see that the surface potential is 4 to 6 V higher on the wafers with the HfO<sub>2</sub> layer than on those without. This fact is consistent with the current measurements shown in Fig. 5. That is, the current drawn by the HfO<sub>2</sub> layer decays more rapidly during



FIG. 7. (Color online) Surface-potential maps of oxidized Si structures with 10 nm of HfO<sub>2</sub> taken (a) before VUV irradiation and (b) after VUV irradiation with 11 eV photons.

irradiation than the current drawn by the  $SiO_2$  layer. This is likely is due to the higher surface potential on the HfO<sub>2</sub> layer. The higher potential is produced by a greater accumulation of trapped positive charge that is likely to be produced because the HfO<sub>2</sub> layer has a higher photoemission yield than the SiO<sub>2</sub> layer.

# **VI. CONCLUSIONS**

The charging effects from plasma and VUV exposure on oxidized patterned Si structures with and without atomiclayer-deposited HfO<sub>2</sub> were compared. Unlike unpatterned oxidized Si wafers, oxidized *patterned* Si wafers charge up significantly after plasma irradiation. The charging is dependent on the aspect ratio of the patterned structures and is likely due to electron and/or ion shading during plasma exposure. Finally, the addition of a 10 nm thick HfO<sub>2</sub> layer deposited on top of the oxidized structures results in an increase in the photoemission yield during VUV irradiation, resulting in a greater trapped positive charge compared with the patterns without the HfO<sub>2</sub> dielectric layer.

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#### JVST A - Vacuum, Surfaces, and Films

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