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# Surface photoconductivity of organosilicate glass dielectrics induced by vacuum-ultraviolet radiation

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The temporary increase in the electrical surface conductivity of low-k organosilicate glass (SiCOH) during exposure to vacuum-ultraviolet radiation (VUV) is investigated. To measure the photoconductivity, patterned "comb structures" are deposited on dielectric films and exposed to synchrotron radiation in the range of 8-25 eV, which is in the energy range of most plasma vacuum-ultraviolet radiation. The change in photo surface conductivity induced by VUV radiation may be beneficial in limiting charging damage of dielectrics by depleting the plasma-deposited charge. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4817427]

#### I. INTRODUCTION AND BACKGROUND

Plasma processing is widely used in the manufacturing of VLSI/ULSI devices. However, electrical charging during processing can cause degradation of gate oxides as well as to interlayer insulation in MOS devices and is a leading cause of damage to semiconductor devices.<sup>1–4</sup> Therefore, searching for a proper method to limit and deplete charging damage for low-k dielectric material (SiCOH) has received great interest. We hypothesize that vacuum-ultraviolet radiation (VUV) with photon energies between 8–25 eV can induce surface photoconductivity, which can often deplete process induced charge<sup>1–3</sup> including electron shading.<sup>5,6</sup>

To measure the photo-induced surface conductivity of SiO<sub>2</sub> accurately, a patterned "comb structure" was deposited on the dielectric films. The films were then exposed to synchrotron radiation in the wavelength range of 50-150 nm (8-25 eV) which is in the energy range of most emitted plasma vacuum-ultraviolet radiation.<sup>1</sup> By utilizing Labview software to measure the I-V characteristics of the comb test structures under controlled fluxes of VUV light, it was determined that the measured current per unit photonflux intensity in SiO<sub>2</sub> varies linearly with applied electric field up to a saturation value that is VUV flux limited.<sup>1</sup> This feature permits the surface photoconductivity to be calculated.<sup>1</sup>

Low dielectric constant (low-k) materials can increase the speed of integrated circuits by exhibiting low capacitance and are therefore used mainly as insulators for interconnects. Specific types of organosilicate glass (SiCOH) with dielectric constants below k = 2 can be produced and these have received wide interest for semiconductor fabrication techniques.<sup>7–11</sup> The purpose of this work is to make a set of surface-conductivity measurements on one of these dielectrics, SiCOH, to determine its VUV-induced surface photoconductivity and whether it follows a similar pattern to that previously obtained for SiO<sub>2</sub>.<sup>1</sup>

#### **II. TEST STRUCTURE AND EXPERIMENTAL SETUP**

#### A. SiCOH and comb structure

A titanium "comb structure" was deposited on the SiCOH dielectric to investigate the effect of VUV radiation on the surface conductivity of low-k dielectric films. Figure 1 shows the structure. Several variations of this design were built to have different separation distances between the metal "fingers" of the comb structure of 5, 7, and 25  $\mu$ m, respectively. The thickness of the titanium comb structure is 100 nm.

#### B. Synchrotron radiation system

The exposure of the test structures was made at the University of Wisconsin-Madison Synchrotron Radiation Center (SRC). The synchrotron-radiation exposure setup, shown in Figure 2, was inserted in a vacuum chamber at a distance of 5 feet from the exit slit of a normal-incidence Wadsworth Monochromator attached to the synchrotron. The synchrotron can easily generate photon energies between 8 and 25 eV. During the measurements, the chamber was



FIG. 1. Ti-SiCOH-Si comb structures.



FIG. 2. Synchrotron VUV-exposure System.

evacuated to pressures in the  $10^{-8}$  Torr range. For measurements of the VUV-induced current along the surface of the dielectric layer between the metal fingers, electrical connections were made from the test structure to outside circuitry through vacuum feedthroughs. The test structures were connected to a Keithley 486 Picoammeter with a resolution of 10 fA and a variable-voltage dc power supply with a maximum voltage of 25 V. The VUV radiation was focused on the test structure with a spot dimension of  $0.5 \times 1.5$  mm (also shown in Figure 1). The photon flux was  $5.6 \times 10^{12}$  photons/s at a photon energy of 15 eV. This flux is similar to that emitted by most high-density processing plasmas.<sup>1</sup>

#### **III. RESULTS AND ANALYSIS**

#### A. SiCOH VUV exposures

Since the thickness of the SiCOH for our test structure is approximately 500 nm, VUV photons can penetrate through the SiCOH dielectric layer and increase the photoinjection current from the substrate significantly.<sup>1</sup> Therefore, if the VUV-induced surface conductivity is to be calculated accurately, the effect of photoinjection is a significant issue. Fortunately, by comparing the IV characteristics of the SiCOH sample with VUV radiation under low applied electric fields (0-1100 V/cm) with the IV characteristics of the SiCOH sample without VUV radiation present, we find that the photoinjection (leakage) current is at least one order of magnitude less than the measured VUV-induced surface current and thus we can neglect it. However, at higher bias voltages, the surface current is much smaller than the photoinjection current from the substrate and thus it dominates the measured VUV-induced current. Hence, to obtain the surface photoconductivity of SiCOH, it is only possible to do so when using low (<1100 V/cm) applied electric field. Figure 3 shows the current between the finger electrodes as a function of applied electric field from  $0-10^{5}$  V/cm, while irradiating the test structure with 15 eV monochromatic synchrotron light at a constant photon flux.

The dominant dielectric conduction mechanisms as a function of electric field are Schottky emission, Poole-Frenkel emission and Fowler-Nordheim tunneling.<sup>12</sup> The energy ranges where they are valid<sup>13</sup> are as follows: (1)



FIG. 3. Electric current across the SiCOH layer measured between electrodes per unit photon flux density for a photon energy of 15 eV, as a function of applied electric field.

Schottky emission (with the applied electric field varying from 1100 to 4400 V/cm), (2) Poole-Frenkel emission (4400 to 7000 V/cm), and (3) Fowler-Nordheim tunneling (>7000 V/cm). Although this work is centered on SiCOH, a similar model can also be utilized for other dielectric materials and has also been shown to be valid for the analysis of the conduction mechanisms in TiO<sub>2</sub>.<sup>11</sup>

In the experiments reported here, these three leakagecurrent models showed a good fit to the results.

Schottky emission is expressed as follows:

$$J = AT^2 \exp\left[\frac{-q(\varphi - \sqrt{qE/4\pi\varepsilon})}{kT}\right],$$
 (1)

where *J* denotes the current density, *A* is the Richardson constant,<sup>10</sup> *T* is the absolute temperature, *q* is the electronic charge,  $\varphi$  is the potential barrier at the metal/dielectric interface, *E* is the electric field in the dielectric,  $\varepsilon$  is the dielectric constant, and *k* is the Boltzmann constant. By plotting ln (*J*) as a function of  $E^{1/2} (V/cm)^{1/2}$ , as in Figure 4, a linear relation should be seen when the conduction mechanism is Schottky emission. Figure 4 shows the experimental results. It can be seen that they indeed fit well to the Schottky emission model for applied electric fields from 1100 to 4400V/cm. However, for an applied electric field between 4400 and 7000 V/cm (Figure 5), the current is dominated by Poole-Frenkel conduction<sup>10</sup> described as

$$J \sim E \exp\left[\frac{-q(\varphi - \sqrt{qE/4\pi\varepsilon})}{kT}\right].$$
 (2)

By plotting ln (J/E) as a function of  $E^{1/2}$   $(V/cm)^{1/2}$ , a linear relation is seen (in Figure 5), which shows that the measured IV curve fits the Poole-Frenkel emission model when the applied electric fields are in the range of 4400–7000 V/cm.

Similarly, for applied electric fields above 7000 V/cm (Figure 6), Fowler-Nordheim tunneling is the dominant conduction mechanism and it is described as<sup>10</sup>



FIG. 4.  $\ln(J)$  as a function of  $E^{1/2}$  with applied electric field below 7000 V/cm, showing good fit with Schottky emission model from 1100 V/cm to 4400 V/cm.

$$J \sim E^2 \exp\left[-\frac{4\sqrt{2m^*}(q\varphi)^{3/2}}{3q\hbar E}\right],\tag{3}$$

where  $m^*$  is the effective mass and  $\hbar$  is the reduced Planck's constant. By plotting ln  $(J/E^2)$  as a function of  $E^{-1}$  (cm/V), a linear relation between ln  $(J/E^2)$  and  $E^{-1}$  is seen for applied fields larger than 7000 V/cm, which satisfies the assumption that Fowler-Nordheim tunneling is the dominant conduction mechanism in this range.

Thus, under high applied electric fields, high leakage currents are induced and dominate the measured current. However, with low applied electric fields, the effects of the leakage currents are at least one order of magnitude lower than the VUV-induced surface current and can be neglected. The reason for this is that photoinjected electrons under high electric fields can gain sufficient energy to overcome the Si-SiCOH interface barrier and easily get injected into the dielectric, while many fewer electrons contribute to the photoinjection current under low applied electric fields.



FIG. 5.  $\ln(J/E)$  as a function of  $E^{1/2}$  with applied electric field below 7000 V/cm, showing Poole-Frenkel emission from 4400 V/cm to 7000 V/cm.



FIG. 6.  $\ln(J/E^2)$  as a function of 1/E with applied electric field over 7000 V/cm, showing Fowler-Nordheim tunneling beyond 7000 V/cm.

Figure 7 shows the surface current across the SiCOH layer per unit photon-flux density for a photon energy of 15 eV, in the low electric field region (0–1100 V/cm). It can be seen in the figure that there is a linear relation between the surface current and the applied electric field under VUV irradiation, which points to a linear model for surface photoconductivity<sup>14</sup> (shown in Figure 8).<sup>1</sup>

The photocurrent induced by the absorption of the incident radiation can be expressed as

$$I = eY\tau\mu\Phi\frac{V}{L^2},\tag{4}$$

where *I* is the measured surface current in amperes. The surface current density is defined by dividing the surface current *I* by the length of the comb electrodes (*L*) that are irradiated by the VUV beam. *e* is the electronic charge, *Y* is the absolute electron-hole yield of SiCOH (electron-hole pairs/ absorbed photon), and  $\tau$  and  $\mu$  are the hole lifetime and mobility.  $\Phi$  is the incident photon flux in number of photons per

10<sup>-22</sup> Current/Flux density @15eV(A s cm2/ph) -lighlighted Re 4000 6000 Electric Field (V/cm) Current per Flux density @15 eV Fitting curve 3∟ 400 500 600 700 800 900 1000 1100 1200 Electric Field (V/cm)

FIG. 7. Electric current across the SiCOH layer measured between electrodes per unit photon flux density for a photon energy of 15 eV, as a function of applied electric field from 0 V/cm to 1100 V/cm.



FIG. 8. Photoconductor model.

second, and V is the applied voltage. Equation (4) relates the photocurrent to the incident flux and the Y factor in Eq. (4) corrects for the fact that not all incident photons create electron-hole pairs.

For the specific comb-structure test samples used here, Figure 9 shows the arrangement of electrodes to be utilized in the calculations. In this diagram,  $d_{ox}$  refers to the distance between the comb electrodes along the surface of the oxide layer, and *L* is the length of the electrodes that are irradiated as described above. Following Ref. 1, the surface current between the measuring electrodes is given by the expression,

$$I_{ox}^{s} = eY\tau\mu\Phi\frac{V_{ox}}{d_{ox}^{2}}.$$
(5)

The photon flux is  $\Phi = \varphi L d_{ox}$ , where  $\varphi$  is the photon flux density impinging on the oxide surface, *L* is the irradiated length of the comb electrodes,  $L d_{ox}$  is the area exposed to the photons, and, as before, *Y* is the absolute electron-hole yield of SiCOH

$$I_{ox}^{s} = eY\tau\mu\varphi L\frac{V_{ox}}{d_{ox}}.$$
(6)

The surface-current density  $J_{ox}^s$  is defined by dividing the current  $I_{ox}^s$  by L



FIG. 9. Surface conductivity model.

$$J_{ox}^{s} = eY\tau\mu\varphi\frac{V_{ox}}{d_{ox}}.$$
(7)

If a fitting parameter  $C^s$  is utilized which is equal to  $eY\tau\mu$ , and the electric field is  $E = V_{ox}/d_{ox}$ , the surface-current density and the dielectric surface conductivity can be expressed as

$$J_{or}^s = C^s \varphi E, \tag{8}$$

$$\sigma_{\alpha x}^{s} = C^{s} \varphi, \tag{9}$$

respectively. The VUV-induced surface currents in SiCOH are expected to be proportional to the number of electronhole pairs generated per second by the incident photons strike the dielectric surface. We then expect that the surface current will be linear with respect to the applied electric field up to a saturation value, when all the generated carriers are collected at the electrodes. Thus, it is possible to fit the experimental data to this surface-current model and find the value of the fitting parameter  $C^{s}$ . Using the fitting parameter  $C^{s}$ , in Eq. (9), the corresponding surface conductivity for SiCOH sample was calculated to be  $4.67 \times 10^{-10} \,\Omega^{-1}$ . This is significantly larger under VUV exposure to 15 eV photons from the surface conductivity measured under zero photon exposure. 15 eV photons were chosen for irradiation since this energy is higher than the bandgaps of SiCOH and SiO<sub>2</sub>. It is expected that photons, as long as they have higher energies than the bandgap of the dielectric, will show a similar effect.

## B. Comparison of the experimental results between SiCOH and SiO<sub>2</sub> test samples

To compare the different effects of VUV radiation on traditional semiconductor materials and emerging low-k dielectric materials, measurement of the VUV-induced electric currents across the surface of  $SiO_2$  as a function of the applied electric field was also made with the same experimental setup. Figure 10 shows the comparison of the IV curves for a  $SiO_2$  sample with a SiCOH sample that were both irradiated with 15 eV VUV radiation as the applied electric field was varied from 0 to 10 000 V/cm. For  $SiO_2$  samples, the measured surface current per unit photon-flux density was linear with the applied electric field up to a saturation value of about 2000 V/cm. The measurements were repeated several times to show that the results were consistent.

The shape of the measured VUV-induced current as a function of applied electric field differs for SiO<sub>2</sub> and SiCOH because of the significant difference in the thickness of the dielectric films. Since the thickness of the thermally grown SiO<sub>2</sub> layer is 1  $\mu$ m, and is thicker than the SiCOH dielectric layer, the current flow from the comb electrodes to the Si substrate can easily be neglected. This means that for SiO<sub>2</sub>, the induced leakage current is too small to affect the surface current. Thus, we can easily utilize a linear model to calculate the surface conductivity of SiO<sub>2</sub>. However, since the SiCOH unless the bias is low, because of the significant photoinjection current



FIG. 10. Comparison of measured surface electric currents between electrodes per unit photon flux density across the  $SiO_2$  and SiCOH surfaces as a function of applied electric field. The photon energy was 15 eV.

coming from the substrate. Based on Eq. (9) and the experimental data for the SiO<sub>2</sub> samples, the surface conductivity for SiO<sub>2</sub> under 15eV VUV radiation was found to be 1.12  $\times 10^{-10} \Omega^{-1}$  while the surface conductivity for the SiCOH sample under 15 eV radiation was 4.67  $\times 10^{-10} \Omega^{-1}$ . For comparison, the intrinsic surface conductivities for SiCOH and SiO<sub>2</sub> are 2.16  $\times 10^{-12} \Omega^{-1}$  and  $1 \times 10^{-14} \Omega^{-1}$ , respectively. All these results are listed in Table I.

TABLE I. Surface conductivity	as a function of p	photon energy.
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	Pristine SiO <sub>2</sub>	SiO <sub>2</sub> after VUV irradiation (8 eV)	Pristine SiCOH	SiCOH after VUV irradiation (8 eV)		
Surface						
conductivity						
$(\Omega^{-1})$	$1 \times 10^{-14}$	$6.67 \times 10^{-12}$	$2.16 \times 10^{-12}$	$5.11 \times 10^{-11}$		
Surface conductivity $(\Omega^{-1})$						
Photon energy	y (eV)	_	$SiO_2$	SiCOH		
0 (as-deposite	ed)		$1 \times 10^{-14}$	$2.16 \times 10^{-12}$		
8		6	$.67 \times 10^{-12}$	$5.11 \times 10^{-11}$		
9		4	$.33 \times 10^{-11}$	$1.82  imes 10^{-10}$		
10		5	$.56 \times 10^{-11}$	$1.26  imes 10^{-10}$		
11		3	$.16 \times 10^{-11}$	$1.33  imes 10^{-10}$		
12		1	$.11 \times 10^{-11}$	$8.51\times10^{-11}$		
13		2	$.22 \times 10^{-11}$	$9.34  imes 10^{-11}$		
14		$3.70 imes10^{-11}$		$2.83  imes 10^{-10}$		
15		$1.12  imes 10^{-10}$		$4.67  imes 10^{-10}$		
16		1	$.56  imes 10^{-10}$	$1.19  imes 10^{-09}$		
17		2	$.38 \times 10^{-10}$	$9.99  imes 10^{-10}$		
18		3	$.67 \times 10^{-10}$	$9.81  imes 10^{-10}$		
19		5	$.56  imes 10^{-10}$	$2.13  imes 10^{-09}$		
20		5	$.08 \times 10^{-10}$	$4.26  imes 10^{-09}$		
21		4	$.39 \times 10^{-10}$	$1.84  imes 10^{-09}$		
22		2	$.78 \times 10^{-10}$	$2.13  imes 10^{-09}$		
23		2	$.06 \times 10^{-10}$	$1.64  imes 10^{-09}$		
24		2	$.16 \times 10^{-10}$	$1.65  imes 10^{-09}$		
25		2	$.67 \times 10^{-10}$	$2.04 \times 10^{-09}$		



FIG. 11. VUV induced SiCOH and SiO<sub>2</sub> surface conductivity as a function of photon energy.

To investigate the effect of VUV radiation with photon energies other than 15 eV, the induced surface conductivities of SiO<sub>2</sub> and SiCOH were also measured over an energy range from 8 to 25 eV. Figure 11 shows the VUV-induced surface conductivities of the SiCOH and SiO<sub>2</sub> samples over this range of photon energies in steps of 1 eV. The lowest conductivity of SiO<sub>2</sub> was found at 8 eV with a value of  $6.67 \times 10^{-12} \Omega^{-1}$ , while the highest conductivity of SiO<sub>2</sub> was found at 19 eV, with a value of  $5.56 \times 10^{-10} \Omega^{-1}$ . This shows that the surface conductivity increased at least two orders of magnitude compared with the intrinsic surface conductivity of SiO<sub>2</sub> with no VUV radiation.

The surface conductivity as a function of photon energy for SiCOH is similar to that for SiO<sub>2</sub> for the same range of photon energies. The minimum surface conductivity of SiCOH also occurs at 8 eV photon energy and is  $5.11 \times 10^{-11} \Omega^{-1}$ . The maximum VUV-induced surface conductivity for SiCOH is  $4.26 \times 10^{-9} \Omega^{-1}$  which was reached at 20 eV. These results are also shown in Table I as well as in Figure 11.

#### **IV. CONCLUSIONS**

The surface conductivity of SiCOH can be increased under VUV radiation, which has been shown to be beneficial in limiting charging damage to dielectrics by depleting processing-induced charge.<sup>1</sup> The surface-current density and the applied electric field are linearly proportional and, by utilizing an appropriate model, the surface conductivity can be found. This shows that the photon-induced increase in VUV-induced surface conductivity is nearly two orders of magnitude higher than for an as-deposited sample. Both SiO<sub>2</sub> and SiCOH surface conductivities exhibit similar trends as a function of photon energy.

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