Journal of Applied Physics

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Citation: J. Appl. Phys. **114**, 104107 (2013); doi: 10.1063/1.4821065
View online: http://dx.doi.org/10.1063/1.4821065
View Table of Contents: http://jap.aip.org/resource/1/JAPIAU/v114/i10
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The effects of plasma exposure and vacuum ultraviolet irradiation on photopatternable low-k dielectric materials

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(Received 14 June 2013; accepted 27 August 2013; published online 12 September 2013)

The effects of plasma exposure and vacuum-ultraviolet (VUV) irradiation on photopatternable low-k (PPLK) dielectric materials are investigated. In order to examine these effects, current-voltage measurements were made on PPLK materials before and after exposure to a variety of inert plasma-exposure conditions. In order to examine the effects of photon irradiation alone, PPLK samples were also exposed to monochromatic synchrotron radiation with 10 eV photon energy. It was found that plasma exposure causes significant degradation in electrical characteristics, resulting in increased leakage-currents and decreased breakdown voltage. X-ray photoelectron spectroscopy measurements also show appreciable carbon loss near the sample surface after plasma exposure. Conversely, VUV exposure was found to increase breakdown voltage and reduce leakage-current magnitudes. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4821065]

I. INTRODUCTION

Silsesquioxane-based photopatternable low-k (PPLK) dielectric materials are emerging as promising future alternatives to existing low-k dielectrics due to their potential for significant reduction of back-end-of-line (BEOL) integration complexity and dramatically reduced exposure of low-k materials to damaging plasma.[1,2] A patternable low-k dielectric material combines the functions of a traditional photoresist and an inter-metal-layer dielectric material into one single material. It acts as a traditional resist during patterning and is subsequently converted to a low-k dielectric material during a post-patterning curing process while maintaining its pattern integrity. No sacrificial materials (separate photoresists or hardmasks) and their related deposition, pattern transfer (etch), and removal (strip) are required to form dual-damascene BEOL patterns.

While PPLK materials have been successfully integrated into single-damascene and dual-damascene copper BEOL with minimal plasma processing, the effects of charged-particle bombardment and photon irradiation (particularly in the vacuum ultraviolet (VUV) range)[3] have not been be fully elucidated.

In this work, the effects of processing-induced damage on PPLK materials are investigated. The combined effects of charged-particle and photon bombardment are examined by exposing PPLK materials to an inert plasma using a variety of biasing conditions. Synchrotron radiation is used to isolate the effects of VUV photon bombardment. Ramped-voltage I-V measurements made before and after each exposure reveal an increase in the magnitude of leakage currents as well as a reduction in breakdown voltage. Conversely, VUV photon bombardment is found to *reduce* the magnitude of leakage currents and *increase* the maximum breakdown voltage. X-ray photoelectron spectroscopy (XPS) measurements are used to examine the mechanism behind these changes. Chemical shifts and reduction in the C 1s peak after plasma exposure indicate that a damaged surface layer is responsible for the degradation in electrical characteristics.

II. BACKGROUND

It is well understood that plasma reactors used in semiconductor processing can expose dielectric materials to energetic charged particles, gas-phase radicals, and potentially large fluxes of energetic photons.[4] Previous work on porous low-k materials has demonstrated that plasma exposure can adversely affect the capacitance, breakdown voltage, and leakage currents of these dielectrics,[5,6] and can also significantly reduce time-dependent dielectric breakdown (TDDB) lifetimes.[7] In particular, the slope of the IV characteristics has been found to be related to the Weibull statistics slope of TDDB characteristics in low-k dielectrics.[8,9]

Additionally, photons of sufficient energy, particularly in the VUV range, have been shown to cause a number of unwanted effects, including differential charging of patterned structures[10] and the creation of bulk and interfacial trap states that contribute to damage induced by leakage currents.[11]

III. EXPERIMENT

Photopatternable low-k samples were prepared by spin-coating a PPLK precursor on 200 mm p-type Si wafers. The films were baked at 110 °C for 60 s. Some samples (as-deposited films) were further baked at 200 °C for 120 s as controls. The remaining films were UV-cured by exposure to a broadband ultraviolet light source at 400 °C under a nitrogen ambient for approximately 10 min. The as-deposited films were found to have a k-value of approximately 3.5, whereas the UV-cured films had a k-value of 2.7. Film thicknesses and optical constants were measured before and after UV exposure using a Filmetrics F-20 optical reflectometer. A summary of the types of samples used in this work is shown in

0021-8979/2013/114(10)/104107/6/$30.00

TABLE I. Details of the samples used in this work.

Sample	Exposure	Thickness (nm)	Index of refraction (at 632.8 nm)
As-deposited	None	410.4	1.7
As-deposited	10 eV	401.2	1.68
UV-cured	None	326.2	1.61
UV-cured	Plasma no bias	323.6	1.59
UV-cured	Plasma −100 V bias	321	1.59

Table I. Although the films used in this work do not contain any sacrificial porogens, as with any silsesquioxane-based material, some porosity is naturally present in the films.

Metal-insulator-semiconductor (MIS) structures were fabricated by e-beam evaporating 1000-nm thick, 80 μm diameter titanium electrodes through a stencil mask. Electrical measurements were performed using a probe station (Signatone) in a dark box kept at 300 K. The MIS structures were biased such that the Si substrate was at a negative potential relative to the contact. Ramped-voltage measurements were performed by stepping a variable voltage source in 0.125 V increments to provide an effective voltage-ramp rate of 0.5 V/s. This rate was found to provide the most reproducible results, and the leakage current was measured at each data point after a settling time of 250 ms. Using this procedure, I-V measurements were found to be highly repeatable, and the observed trends were found to be consistent across multiple samples.

Plasma exposures were made in a 2.45 GHz electron cyclotron resonance (ECR) reactor at 5 mTorr neutral argon pressure and with 300 W microwave power. The wafer chuck was biased using a 100 W radiofrequency (RF) source and coupled to the plasma through an L-type matching network. The plasma exposure apparatus used in this work is shown in Figure 1. Control of the ion-impact energy was accomplished by varying the RF power to obtain a DC bias on the wafer in the range of 0 to −100 V. It has been previously established that ion bombardment plays an important role in plasma-induced damage to low-k dielectrics, resulting in surface densification and increased dielectric constant.[12] As a result, inert plasma exposure conditions in this work were specifically chosen to investigate the effects of charged-particle bombardment and photon irradiation without introducing chemically reactive species.

Monochromatic radiation exposures were made at the UW-Madison Synchrotron Radiation facility using an apparatus described previously.[13] Photon bombardment energies were specifically selected to mimic those emitted by processing plasmas; specifically, photons of 10 eV energy (120 nm wavelength) were used to mimic the strong emission lines due to hydrogen in a CHF_3 discharge typically used for dielectric etch.[14] Photon flux was monitored *in-situ* using a photodiode (AXUV100) to ensure samples were irradiated with approximately 10^{14} photons/cm^2.

IV. RESULTS

Initial leakage-current versus time measurements were made to compare UV-cured and as-deposited PPLK films. Comparison of the leakage currents for 326-nm thick UV-cured (k = 2.75) with 410-nm thick as-deposited (k ~ 3.1) PPLK films are shown in Figure 2. For lower electric fields (i.e., between 0 and 2.5 MV/cm), both UV-cured and as-deposited samples have roughly comparable leakage currents. However, at higher fields, e.g., >3 MV/cm, as-deposited films exhibit increased leakage currents relative to UV-cured samples. Reduced leakage currents in the UV-cured films are likely due to UV-induced elimination of silanol groups via a condensation reaction to form Si-O-Si bonds in these materials.[17] This behavior is consistent with results observed by Choi *et al.*,[15] where the leakage current density was observed to decrease for UV-cured SiCOH samples with increasing UV-curing time. As-deposited films also showed reduced breakdown voltages compared to UV-cured films (10 MV/cm versus 13 MV/cm, respectively).

Over a wide range of electric fields (from 2.25 MV/cm to 8.25 MV/cm), the unexposed UV-cured samples were found to exhibit a remarkably constant slope, indicating that a single conduction mechanism is likely to be dominant over a large range of applied fields. This region is highlighted in Figure 3, with the upper (green) curve corresponding to the measured data. To determine whether Schottky emission (S-E) or Poole-Frenkel (P-F) conduction was responsible for

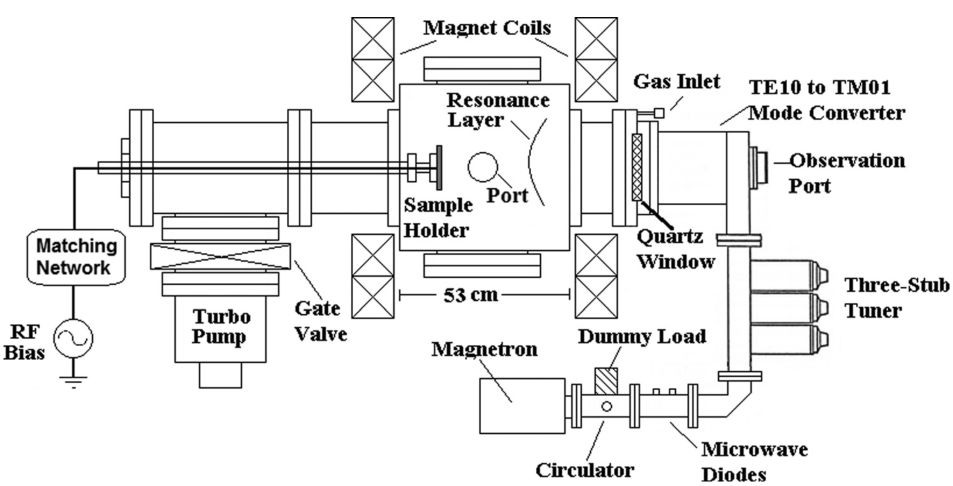

FIG. 1. Schematic of the electron cyclotron resonance plasma exposure apparatus used in this work.

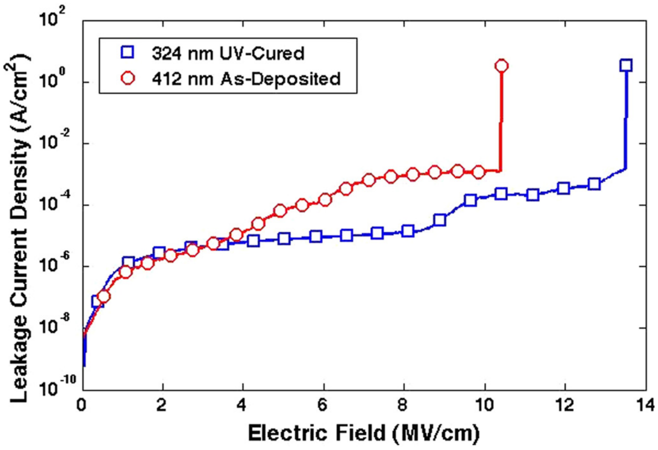

FIG. 2. Comparison of current-voltage characteristics for unexposed UV-cured and as-deposited samples.

the observed leakage current, the measured data, plotted in the upper (green) graph of Figure 3, includes the experimentally observed slope of the I-V characteristic. This was compared with the theoretically expected slopes for S-E and P-F mechanisms, given by β_{SE}/k_BT and β_{PF}/k_BT, respectively, where $\beta_{SE} = \sqrt{\frac{q^3}{4\pi\epsilon_r\epsilon_0}}$ and $\beta_{PF} = \sqrt{\frac{q^3}{\pi\epsilon_r\epsilon_0}}$.[16] For S-E, the experimental data were compared with a least-squares fit of the form $\ln(J)$vs $\sqrt{E}$, shown as the dashed line in the graph of the figure. For P-F conduction, the data were compared with a least-squares fit of the form $\ln(\frac{J}{E})$vs $\sqrt{E}$, shown in lower (blue) graph of the figure. In both the upper and lower plots, the measured data would appear as a straight line when plotted as shown if S-E or P-F mechanisms were dominant, respectively.[17]

Because the permittivities of the UV-cured and as-deposited samples are k = 2.75 and k = 3.1, respectively, the expected slopes corresponding to P-F conduction and S-E currents were calculated to be $\beta_{SE} = 3.67 \times 10^{-24}$ and $\beta_{PF} = 7.34 \times 10^{-24}$, respectively. The calculated slope of the least-squares fit for the upper curve of Figure 3 is equal to 2.27×10^{-24}, shown as the dashed line in the upper graph, which is closer in agreement with Schottky emission. However, as expected, the least-squares fit line does not fit the entire region. Instead, the upper graph only exhibits this linear slope for field values between 2.8 and 8.2 MV/cm. To see if the P-F mechanism resulted in a better fit, the measured data were replotted as ln (J/E) versus the square root of the electric field and are shown in the lower (blue) graph in Figure 3. As can be observed, the data do not appear to be linear over a wider range than the S-E data, and hence P-F conduction is unlikely. In fact, if there is any significant linear region, the slope is much smaller than either the SE or PF theoretical slopes.

Aside from this specific region, no dominant conduction mechanisms were identifiable. Based on this analysis, it is likely that Schottky emission is one of the primary mechanisms causing leakage currents, but competing mechanisms are of comparable importance at both higher and lower fields.

To investigate the effects of processing-induced damage on the leakage currents in PPLK films, selected 1 cm^2 samples of the k = 2.75 UV-cured PPLK material were exposed to various plasma conditions. These exposures were performed using the electron-cyclotron resonance plasma reactor in a “downstream” configuration using a single magnet coil closest to the microwave transmission window. The microwave power was set to produce 300 W net power (forward minus reflected) at 5 mTorr argon neutral pressure, and the applied DC bias was varied from 0 volts (i.e., floating) to -100 V_{DC} using the RF power supply. The sample chuck was located approximately 30-cm downstream from the

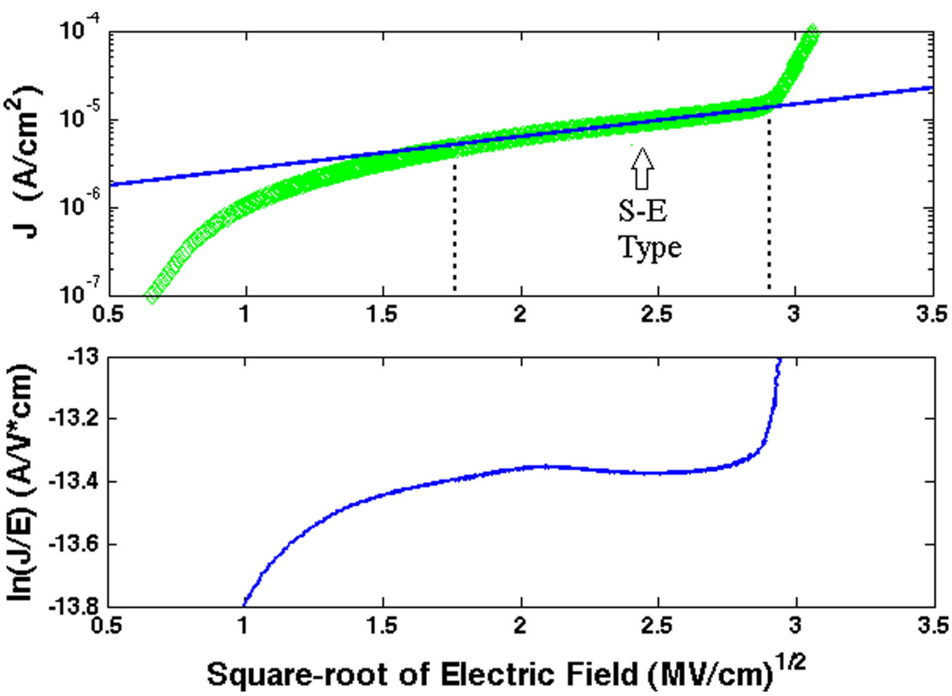

FIG. 3. Identification of Schottky emission in PPLK films. The upper graph shows a good fit to the Schottky emission conduction mechanism. The lower graph shows a poor fit to the Poole-Frenkel conduction mechanism. Note that the vertical axes of both graphs are logarithmic. The upper graph is proportional to the log of the leakage current density while the upper graph is proportional to the log of the ratio of the leakage current to the electric field. The horizontal axes are identical.

resonant layer for all exposures. The exposure time for each sample was 5 min and was measured from the time that the microwave power was switched on. After exposure, the samples were immediately taken to the deposition chamber to deposit electrical contacts.

The results of these exposures on the leakage currents are shown in Fig. 4. Three distinct cases (1-3) are shown. (1) The first, corresponding to the solid red curve, shows the current-voltage behavior for an unexposed sample. (2) The blue diamond markers correspond to samples exposed to the ECR plasma with no applied RF bias. (3) The black open circles correspond to samples exposed to the same plasma conditions with a RF-induced $-100\ V_{DC}$ bias applied to the wafer chuck. Because all of the other plasma parameters remain unchanged, and because the RF bias does not draw a net DC current from the plasma, variation of the wafer bias should only change the energy of ions impinging on the surface of the sample.

Plasma-exposed UV-cured PPLK materials were not found to exhibit increased leakage currents over all measured electric fields. Instead, samples corresponding to the unbiased and the $-100\ V_{DC}$ bias cases exhibit qualitative differences in their leakage-current profiles compared with the unexposed samples. At low fields, between 0 and 2 MV/cm, both exposure conditions resulted in lower leakage currents. At higher fields, both exposures resulted in 1-2 orders of magnitude higher leakage currents, with the $-100\ V_{DC}$ exposed sample exhibiting the highest leakage current of the three samples. Additionally, both plasma-exposure conditions resulted in significantly reduced breakdown strength, with 9 MV/cm breakdown for the 0 V bias case and 7 MV/cm breakdown field for the -100 V bias case.

To understand the observed results from the effects of plasma exposure, better, monochromatic synchrotron VUV exposures were made on both UV-cured and as-deposited PPLK samples. The latter were also investigated to determine whether VUV irradiation could be used to approximate the UV-curing process. Photon-bombardment energies were specifically selected to mimic those emitted by processing plasmas; specifically, photons of 10 eV energy (120 nm wavelength) were used to mimic the strong emission lines due to hydrogen in a CHF_3 discharge typically used for dielectric etch.[14] Exposure times for every exposure were chosen so that the total photon fluence impinging on the sample was approximately 1×10^{14} photons/cm^2. This fluence is comparable to the total VUV photon fluence emitted during a typical plasma process ($\sim 3 \times 10^{14}$ photons/cm^2 10 eV photons).[4]

The effects of VUV radiation on the leakage currents in as-deposited PPLK are shown in Figure 5. The leakage currents for unexposed samples are shown as blue diamond, and the current measured from the 10-eV exposed sample is indicated by red open circles. What is significant about this data is that the 10 eV exposure appears to *reduce* the magnitude of the leakage currents in the as-deposited films for electric fields larger than 0.75 MV/cm. Additionally, the slope of the current density seems to decrease after exposure compared with the unexposed case. Both of these effects show similar differences as in Figure 2 where the comparison was made between as-deposited and UV-cured films. Based on these data, it appears that exposure to 10 eV photons may accomplish (to a less extent) a similar effect as the commercial UV-curing process. This can be advantageous because a separate UV curing system may not be necessary to accomplish this.

XPS core-level spectra measured before and after plasma exposure are shown in Fig. 6. The number of electrons collected is plotted on the y-axis (proportional to the density of states N(E)), and the corresponding binding energy is plotted on the x-axis. The solid lines correspond to the unexposed samples, and open circles correspond to samples exposed to the ECR plasma conditions detailed above with a $-100\ V_{DC}$ bias applied. A Lorentzian lineshape was fit to each of the core lines and a Shirley background was subtracted from the spectra.[18,19] The resulting data points were exported and plotted in MATLAB for analysis.

A significant change in the relative concentration of oxygen atoms and considerable carbon loss after plasma exposure is evident, indicating the formation of an oxide-like layer near the film surface. In the case of PPLK films, this effect is not entirely deleterious; the addition of an oxide-like surface layer after plasma exposure and subsequent exposure to atmosphere may explain the observed reduced leakage-current magnitudes at lower electric fields. However, this oxide-like layer may be more susceptible to

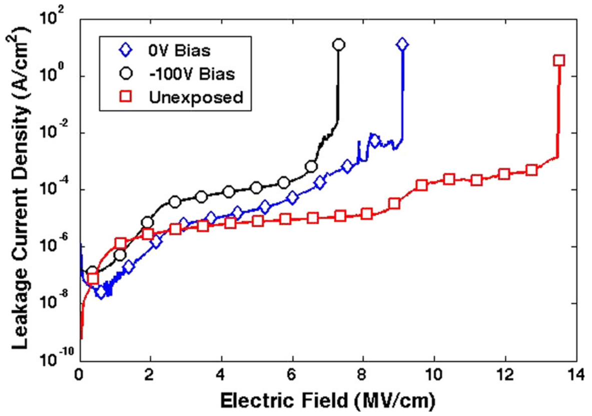

FIG. 4. Effect of argon plasma exposure on current-voltage characteristics of UV-cured PPLK.

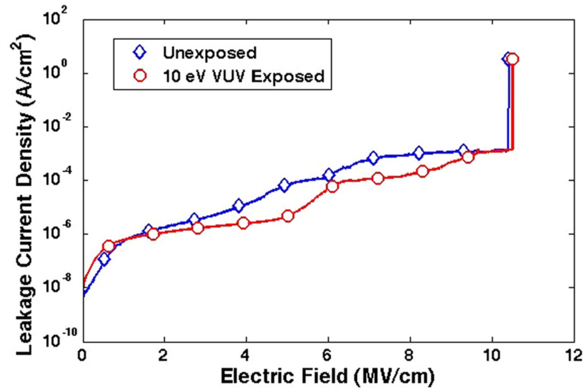

FIG. 5. Effect of 10 eV VUV exposure on current-voltage characteristics of as-deposited PPLK material.

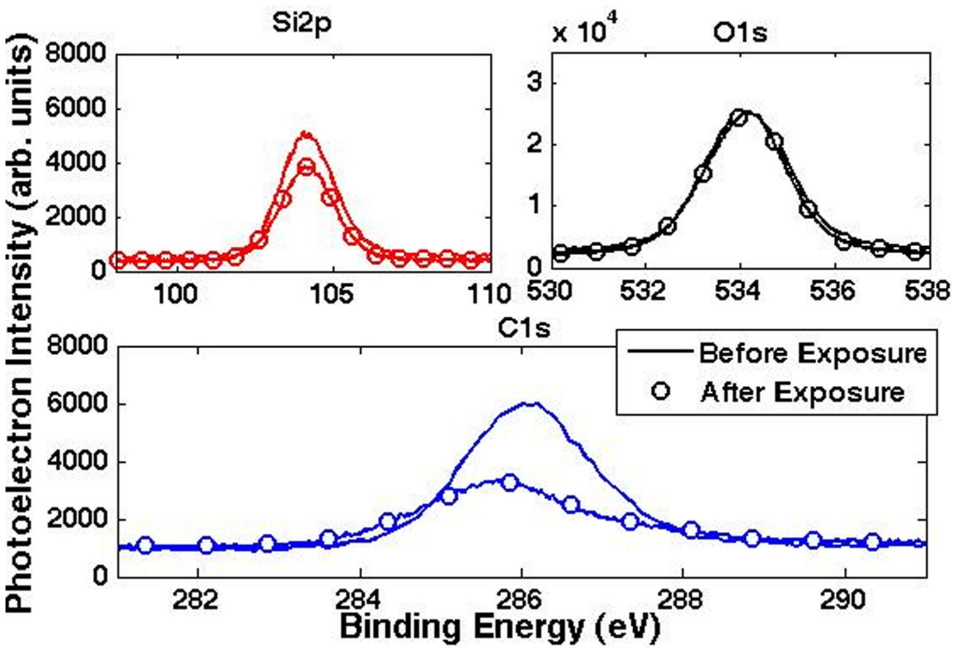

FIG. 6. XPS results showing chemical shift of C 1s peak after plasma exposure

stress-induced currents, resulting in an increase in leakage currents under high electric-field stress. Additionally, this oxide layer formation may be attributed to surface-layer densification that can lead to increased dielectric permittivity.[20]

In the case of VUV irradiation on as-deposited samples, the opposite behavior was observed. The XPS spectra measured before and after exposure to 10 eV photons are shown in Fig. 7. Both the O 1s and Si 2p peaks remain unchanged before and after exposure, indicating that VUV radiation has little if any effect on their atomic concentrations. However, after VUV exposure, the relative concentration of carbon *increases* significantly!

The *opposite* observed effects of exposing UV-cured PPLK to plasma and as-deposited PPLK to VUV radiation can be explained as follows. PPLK materials are made from silsesquioxane (SSQ) copolymers which contain methyl, p-hydroxyl-α-benzyl, and hydroxyl functional chemical groups.[21] The decrease in carbon concentration in the plasma exposed sample can be attributed to the demethylation of the UV-cured sample as in other SSQ based low-k materials.

Curing of PPLK using ultraviolet light at 400 °C under vacuum causes the decomposition and removal of the photoactive compound as well as the condensation of the hydroxyl groups of the silanol groups and/or the phenol group.[21] It is hypothesized that this same effect can be caused by VUV radiation: VUV photons are absorbed by as deposited PPLK and, as with UV radiation, the energetic photons leads to a similar decomposition and removal of the photoactive compound as well as the condensation of the hydroxyl groups. Hence, the concentration of carbon at the surface should thus increase after VUV exposure.

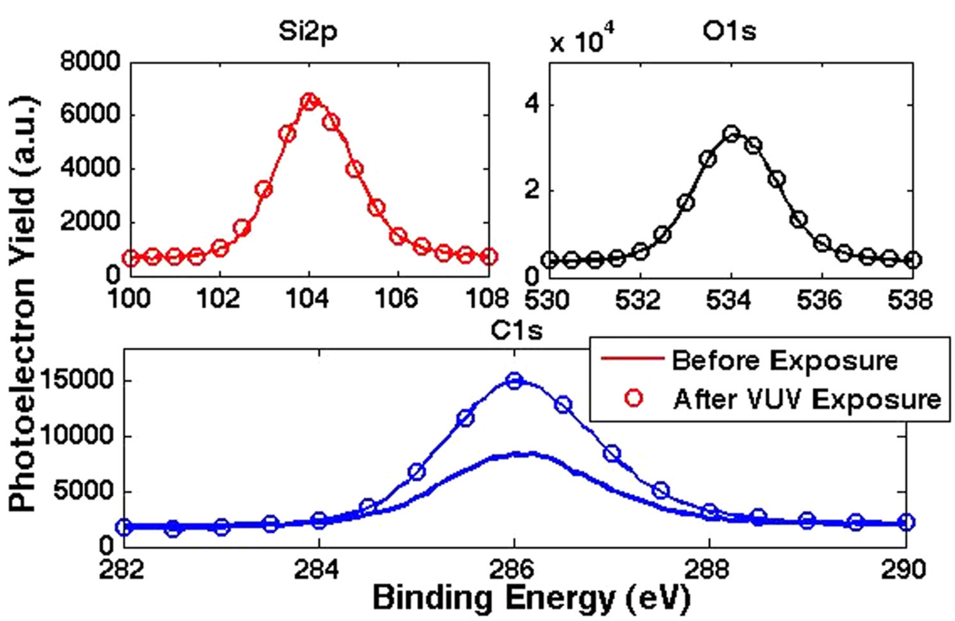

FIG. 7. XPS results indicating increase in carbon concentration near the sample surface after 10 eV VUV exposure.

V. CONCLUSIONS

For photopatternable low-k materials, Schottky emission was found to be the only identifiable leakage-current mechanism and was observed for electric field strengths between 4 and 9 MV/cm. At electric fields between 0 and 4 MV/cm and from 9 MV/cm until breakdown, the conduction is likely due to the combined effects of a number of different mechanisms. Plasma exposure was shown to result in (1) leakage-current degradation at moderate to high electric fields and (2) decreased breakdown strength. Additionally, VUV exposure was found to *decrease* leakage currents in a manner similar to UV-curing for as-deposited samples. These effects were confirmed using XPS, which also showed carbon loss on the surface due to plasma exposure in UV-cured samples. For as-deposited samples, XPS measurements showed *increased* concentration of carbon at the surface after VUV exposure, which can be explained by photon-induced decomposition and removal of the photoactive compound as well as the condensation of the hydroxyl groups in as-deposited PPLK.

ACKNOWLEDGMENTS

This work has been supported by the Semiconductor Research Corporation under Contract No. 2012-KJ-2359 and by the National Science Foundation under Grant No. CBET-1066231

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