Defects in low-*k* organosilicate glass and their response to processing as measured with electron-spin resonance

H. Ren,[1] M. T. Nichols,[1] G. Jiang,[2] G. A. Antonelli,[3] Y. Nishi,[4] and J. L. Shohet[1,a)]
[1]*Department of Electrical and Computer Engineering, Plasma Processing and Technology Laboratory, University of Wisconsin-Madison, Madison, Wisconsin 53706, USA*
[2]*Novellus Systems, Tualatin, Oregon 97062, USA*
[3]*Novellus Systems, Albany, New York 12203, USA*
[4]*Stanford University, Stanford, California 94305, USA*

(Received 27 December 2010; accepted 15 February 2011; published online 8 March 2011)

Defect concentrations in low-*k* organosilicate glass films deposited on high-resistivity silicon were measured with electron-spin resonance. Bulk dangling bonds were detected. Both plasma exposure and ultraviolet exposure were used. During argon electron cyclotron resonance plasma exposure, ion and photon bombardment increased the measured defect concentrations. Ultraviolet lamp exposure was also shown to increase the defect concentrations. Dielectric samples with various dielectric constants were examined showing that as the value of the dielectric constant was lowered, the defect concentrations were shown to increase significantly. © *2011 American Institute of Physics*.
[doi:10.1063/1.3562307]

By providing lower interconnect capacitance, low-*k* dielectrics are being utilized to increase the speed of integrated circuits.[1] They are considered as good candidates for interconnect applications.[2] However, in order to achieve a lower value of dielectric constant, either carbon-doping, higher porosity, or a combination of both are introduced,[3] which tends to result in a variety of defects. Understanding the nature and concentrations of the electrically active defects are important in determining the reliability of integrated circuits and pursuing potential applications of these materials.[4,5]

Electron-spin resonance (ESR) spectroscopy is a very effective tool for detecting defects in dielectrics.[6] It has been applied to various high-*k* dielectrics.[7–9] However, ESR measurements have been rarely done on low-*k* dielectrics because ESR measurements usually require high-resistivity substrates that maintain the high Q value of the ESR cavity.[10] However, a source of high-resistivity 300-mm-diameter substrates is difficult to find since the float-zone method is not used to fabricate these wafers. In order to use low-resistivity wafers, long-term averaging of the ESR signals is required.[11] The difficulty with this method, however, is that the low signal-to-noise ratio may result in ambiguity in interpreting the defects.

In order to carry out more sensitive ESR measurements of low-*k* organosilicate glass (SiCOH), this material was deposited on three-inch diameter high-resistivity (8000 Ω cm) wafers using plasma-enhanced chemical vapor deposition (PECVD). Two dielectric film samples with different dielectric constants (k=2.65 and 2.75) were fabricated using different recipes. In addition, some of the samples were ultraviolet (UV)-cured. After the UV-curing, the dielectric constant was reduced from 2.75 to 2.55. The dielectric properties are summarized in Table I. The dissipation factor was estimated to be 2000, resulting in clear ESR signals.

First, defects in pristine k=2.75 SiCOH and their response to plasma and UV exposure were investigated. For plasma exposure, electron-cyclotron resonance (ECR) argon plasma was used. In order to separate charged-particle and photon bombardment, the dielectric samples were partially covered with a capillary-array window.[12] UV exposure was made with a HgAr pen lamp (4.9 eV).

The ESR signals are shown in Fig. 1. The defects in pristine SiCOH (k=2.75) are shown in curve (a). After plasma exposure, the defects in dielectric samples after photon bombardment are shown in curve (b). The defects in the samples exposed to the entire plasma are shown in curve (c). The fingerprint of the defects, known as the g-factor, was calculated as g=2.0033. After examining the high concentration of the defects, we believe this defect signal links to the bulk dangling bonds.[11]

The ESR signals can be fitted, using least-squares, into Lorentzian derivatives which have the form of

$$f'_{\mathrm{Lorentz}}(B) = -\frac{\dfrac{2A(B-B_0)}{\sigma}}{\left[1+\left(\dfrac{B-B_0}{\sigma}\right)^2\right]^2}, \quad (1)$$

where A represents the amplitude of the signal, B_0 can be used to determine the g-factor of the defects, and σ is defined as the width of the signal. The fitting parameters including A, B_0, and σ as in Eq. (1) for all ESR signals and corresponding concentrations were summarized in Table II. From Table II, we see that both charged-particle and photon bombardment increase the defect concentrations. However, photon bombardment increases the defect concentrations more significantly. The defect concentrations for SiCOH are at the level

TABLE I. PECVD SiCOH dielectric samples on high-resistivity wafers.

Sample No.	Dielectric constant	UV cured or not	Dielectric thickness (nm)
1	2.75	Pristine	50
2	2.65	Pristine	50
3	2.55	UV-cured	60

a)Electronic mail: shohet@engr.wisc.edu.

 © 2011 American Institute of Physics

Downloaded 08 Mar 2011 to 128.104.181.42. Redistribution subject to AIP license or copyright; see http://apl.aip.org/about/rights_and_permissions

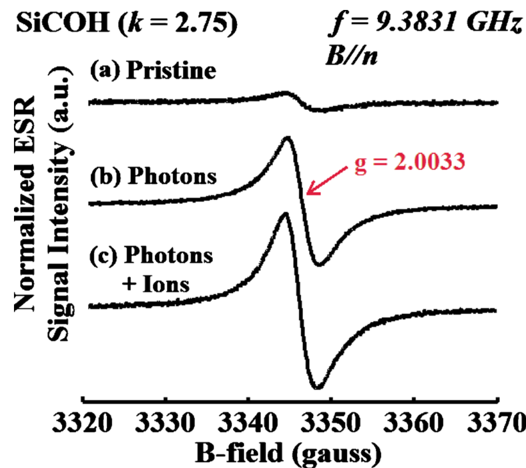

FIG. 1. (Color online) ESR signals for (a) pristine SiCOH (k=2.75) without any treatments, (b) after photon bombardment of plasma exposure, and (c) after full plasma exposure.

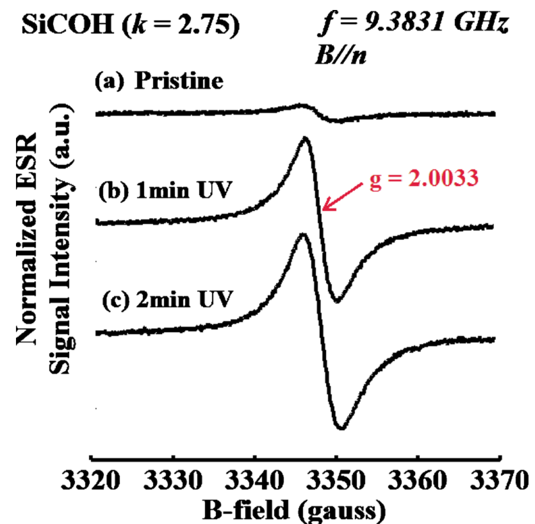

FIG. 2. (Color online) ESR signals for (a) pristine SiCOH (k=2.75) without any treatments, (b) 1 min UV lamp exposure, and (c) 2 min UV lamp exposure.

of 10^{13} to 10^{14} cm^{-2}, which are an order of magnitude larger than these for interfacial defects in high-k dielectrics.[7] It is likely that the photons introduce defects in SiCOH by chemical condensation.[13]

Then, in order to determine the effects of UV photon bombardment on the dielectrics, exposures with the UV lamp were made on the dielectric samples[11] with several photon fluences. The ESR signals are shown in Fig. 2. As the UV photon fluence increases, the defect concentrations increase significantly.

To understand whether UV lamp exposure can be made equivalent to UV curing, the UV-cured SiCOH were examined with ESR, along with pristine samples with a lower dielectric constant. The ESR signals are shown in Fig. 3. By comparison between signals (a) and (b) in Fig. 3, it is shown that the defect-state concentration increases as more carbon doping and porosity were using in fabricating the dielectric. Carbon doping is believed to introduce more dangling electrons by breaking silicon bonds.[14] Increasing the porosity may also contribute to the increase in dangling electrons since it is known that defect-bonding structures gather around the porogen residues.[15]

By comparison between signals (a) and (c) in Fig. 3, it is further shown that UV curing can also introduce defects in the bulk dielectric. Although the dielectric constant was lowered, the defect concentration increases. However, the magnitude of the increase in the defect concentration as a result of UV curing is much smaller than that for UV lamp exposure. This mitigation is likely to be due to the thermal effects during UV curing at a temperature of 400 °C, which is absent for UV lamp exposure.[16] The increase in the defect concentrations does not depend on the path to a lower dielectric constant, i.e., either using a different recipe or by UV curing.

In order to verify that the dangling bonds are silicon dangling bonds rather than carbon dangling bonds, Fourier transform infrared spectroscopy measurements were made on the three samples, as shown in Table III. Concentrations of the carbon-related bonds including $Si-CH_3$ and CH_x bonds were measured. It is seen that for the pristine sample with k=2.65, the concentrations of both bonds are much higher than those of the other two samples. However, as mentioned above, and shown in Fig. 3, no obvious changes in defect concentration were observed. Hence, it is unlikely that the defects are carbon-dangling bonds and thus they must come from breaking the silicon bonds.

In conclusion, the defects in low-k SiCOH films deposited on high-resistivity substrates were identified and shown to be changed by either or both plasma exposure and UV lamp exposure. When a different deposition recipe and/or UV curing were used to lower the dielectric constant, it was

TABLE II. Fitting parameters and defect concentrations of the different SiCOH dielectrics.

Dielectric films and treatments		$[B_0, A, \sigma]$ (G, 1, G)	Concentrations (cm^{-2})
Pristine SiCOH (k=2.75)	As-is	3346.32, 0.043, 4.02	1.17×10^{13}
	Plasma photons	3346.17, 0.321, 3.93	8.54×10^{13}
	Photons+ions	3346.16, 0.413, 3.93	1.10×10^{14}
	UV exposure 1 min	3346.10, 0.438, 3.93	1.16×10^{14}
	UV exposure 2 min	3346.13, 0.940, 4.12	2.62×10^{14}
Pristine SiCOH (k=2.65)		3346.42, 0.091, 3.88	2.40×10^{13}
UV-cured SiCOH (k=2.55)		3346.59, 0.093, 4.03	2.54×10^{13}

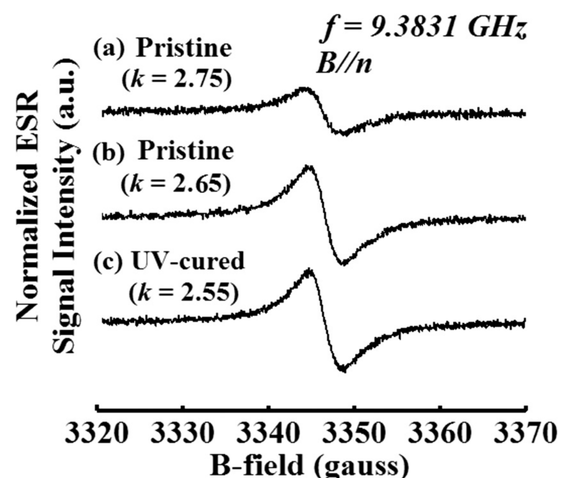

FIG. 3. ESR signals for (a) pristine SiCOH (k=2.75), (b) pristine SiCOH (k=2.65), and (c) UV-cured SiCOH (k=2.55).

Downloaded 08 Mar 2011 to 128.104.181.42. Redistribution subject to AIP license or copyright; see http://apl.aip.org/about/rights_and_permissions

TABLE III. Carbon-related bond concentrations in SiCOH samples.

Ratio of bond concentrations	Pristine (k=2.75) (%)	Pristine (k=2.65) (%)	UV-cured (k=2.55) (%)
$Si-CH_3/Si-O$	3.3	6.6	3.5
$CH_x/Si-O$	3.5	8.9	3.2

also shown that the defect concentrations increased. Compared with UV exposure, UV curing has a smaller effect on the increase the defect concentrations. Thus, a tradeoff was observed between dielectric constant and defect concentrations for SiCOH.

We thank M. Ivancic for helping set up the ESR experiments. This work is supported by the Semiconductor Research Corporation under Contract No. 2008-KJ-1781.

[1]D. Shamiryan, T. Abell, F. Lacopi, and K. Maex, Mater. Today **7**, 34 (2004).
[2]L. L. Mercado, C. Goldbery, S.-M. Kuo, T.-Y. Lee, and S. K. Pozder, IEEE Trans. Device Mater. Reliab. **3**, 111 (2003).
[3]K. Maex, M. R. Baklanov, D. Shamiryan, F. Lacopi, S. H. Brongersma, and Z. S. Yanovitskaya, J. Appl. Phys. **93**, 8793 (2003).
[4]A. Grill, J. Appl. Phys. **93**, 1785 (2003).
[5]A. A. Volinsky, J. B. Vella, and W. W. Gerberich, Thin Solid Films **429**, 201 (2003).
[6]C. P. Poole and H. A. Farach, *ASM Handbook* (ASM International, Materials Park, Ohio, 1986), Vol. 10, pp. 253–266.
[7]H. Ren, S. L. Cheng, Y. Nishi, and J. L. Shohet, Appl. Phys. Lett. **96**, 192904 (2010).
[8]G. J. Park, T. Hayakawa, and M. Nogami, J. Phys.: Condens. Matter **15**, 1259 (2003).
[9]A. Stesmans and V. V. Afanas'ev, Appl. Phys. Lett. **85**, 3792 (2004).
[10]M. Tabib-Azar, D. Akinwande, G. E. Ponchak, and S. R. LeClair, Rev. Sci. Instrum. **70**, 3083 (1999).
[11]B. C. Bittel, P. M. Lenahan, and S. W. King, Appl. Phys. Lett. **97**, 063506 (2010).
[12]H. Ren, G. A. Antonelli, Y. Nishi, and J. L. Shohet, J. Appl. Phys. **108**, 094110 (2010).
[13]J. Y. Zhang and I. W. Boyd, Mater. Sci. Semicond. Process. **3**, 345 (2000).
[14]C. Ye, Z. Ning, T. Wang, X. Yu, Y. Wei, and X. Qian, J. Electrochem. Soc. **154**, G63 (2007).
[15]A. M. Urbanowicz, K. Vanstreels, D. Shamiryan, S. De Gendt, and M. R. Baklanov, Electrochem. Solid-State Lett. **12**, H292 (2009).
[16]D. M. Gage, J. F. Stebbins, L. Peng, Z. Cui, A. Al-Bayati, K. P. MacWilliams, H. M'Saad, and R. H. Dauskardt, J. Appl. Phys. **104**, 043513 (2008).

Downloaded 08 Mar 2011 to 128.104.181.42. Redistribution subject to AIP license or copyright; see http://apl.aip.org/about/rights_and_permissions