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The effects of vacuum-ultraviolet radiation on defects in low-k organosilicate glass (SiCOH) as measured with electron-spin resonance

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ABSTRACT

Defect concentrations in SiCOH low-k dielectrics deposited on high-resistivity silicon substrates were measured with Electron Spin Resonance (ESR). CP4 and HF treatments were used in order to eliminate dangling bonds from the backside of the silicon substrate as well as the sample edges. Two kinds of defects with characteristic $g = 2.0054–2.0050$ and $g = 2.0018–2.0020$ were detected in pristine samples and quantified using Lorentzian fitting. The defect with the g factor of 2.0054–2.0050 is likely to be from the silicon-dangling bonds. The defect with the g factor of 2.0018–2.0020 is most likely from carbon-related centers. Upon exposure to VUV synchrotron radiation ($h\nu = 12$ eV), the concentration of the silicon-dangling bonds is found to increase significantly.

1. Introduction

Silicon-based low-k dielectric materials have been widely used in microelectronic integrated circuits as interlayer dielectrics because they can increase the speed by providing low capacitance to reduce interconnect delay (resistance-capacitance delay). However, in order to achieve a lower dielectric constant value, both carbon-doping and higher porosity are introduced, which often result in a variety of defects [1,2]. Therefore, it is important to measure and identify the defects as well as determine their concentrations.

Electron-spin resonance spectroscopy is a very effective tool to detect many defects in dielectrics and it has been applied to various high-k dielectrics, such as HfO_2 [3]. However, ESR measurements have seldom been made on low-k organosilicate glass (SiCOH). One of the reasons is that ESR measurements usually require a high-resistivity substrate to maintain the high value of quality factor (Q factor) in the ESR cavity [4] or measurements in the liquid-He temperature range (~4.3 K) to freeze out dopants in silicon [5,6]. In this work, in order to obtain a clear spectroscopic signal, SiCOH was deposited on 250 μm high-resistivity (3000 Ω-cm) wafers. After this step, the ESR measurements were made with an X-band Bruker Elexsys 500E EPR spectrometer.

2. Theory

When a dielectric sample with certain defect states (unpaired electrons) is immersed in a radiofrequency modulated magnetic field, the defect states absorb energy through their magnetic susceptibility. The susceptibility of different defects is related to different relaxation mechanisms as a function of frequency. An electron-spin resonance experiment generally consists of measuring the absorption of microwave power at a fixed frequency as a function of an applied laboratory magnetic field B. The physical factors which determine the ESR spectrum are most succinctly presented in terms of the so called spin Hamiltonian "H". It is possible to write a spin Hamiltonian containing two terms:

$$\mathrm{H} = \mu_B B \cdot g \cdot S + I \cdot A \cdot S \tag{1}$$

where the first term is the electronic Zeeman interaction, and the second represents the hyperfine interaction between the electron of spin S and a single nucleus of spin I. In Eq. (1), μ_B is the Bohr magnetron $\frac{eh}{4\pi m_e}$ and A is the hyperfine tensor. The *g*-factor, which was measured in the experiments, has three principal-axis components. Relating the experimental spectra to Eq. (1) requires that the spin Hamiltonian be diagonalized to the so called "resonance condition"H_{res}.

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For single-crystal samples, the ESR spectrum is usually obtained for rotations about one or more sample axes. These angular dependences are then fit to a resonance condition of the appropriate form, resulting in the values of the principal-axis components of *g*. However, in powdered or amorphous samples, all angular orientations are represented with equal probability. Averaging of the resonance condition over all angles results in a mathematically well-defined absorption envelope called the "powder pattern" [7].

When dealing with amorphous samples, it is useful to define an effective *g* value corresponding to a particular value of H_{res} and the microwave frequency according to the relation [8]:

$$g_{eff}\mu_B H_{res} = h\nu \tag{2}$$

where *h* is Planck's constant.

3. Experimental details

In this work, the thickness of the SiCOH films was 60 nm with a dielectric constant (k) of 2.4. The sample was cut with a dicing saw into $2.5 \times 20\ \text{mm}^2$ slices. SiCOH was deposited on 250 μm high-resistivity (3000 Ω-cm) wafers. In order to eliminate dangling bonds from the silicon substrate as well as edge defects, CP4 (HF:Nitric:Acetic) [9] and hydrofluoric acid (HF) treatments were used. The CP4 etch solution (50% HF:70% Nitric:100% Acetic) was primarily used to etch silicon and is commonly used to prepare electron spin resonance samples to remove surface and edge damage. The nitric acid oxidizes the silicon surface and the HF then removes the oxide. Acetic acid is used as a diluent, which improves the polishing effect of the etchant by preventing dissociation of HNO_3. A chemically stable wax (Crystalbond 590) was used to protect the SiCOH layer during CP4 etching, allowing the edges of the sample and the backside surface of the substrate to be placed into the CP4 solution without damaging the SiCOH.

To determine whether the defects measured by ESR are from SiCOH, the samples were treated in two ways before ESR measurement. The first method used HF before CP4 etching to etch the samples. The SiCOH was etched off by using a 5% (by volume) HF solution for 10 min. A reflectometer and a Fourier transform infrared spectrometer (FTIR) were used to determine when the SiCOH was fully removed. CP4 was then used to remove the defects from both the surfaces of the sample and the diced edges. The second method used CP4 alone. The chemically stable wax was used to glue two SiCOH layers face to face. The waxed assembly was then inserted into the etchant for 1 min. The presence of the wax allowed etching only of the back surface of the substrate and the edges, thus leaving the SiCOH on the sample. A comparison can then be made between the samples prepared in these two ways to elucidate the defects in SiCOH.

4. Results

ESR measurements showed that the samples with the SiCOH layer have a higher defect concentration than bare Si samples. In addition, samples with the same edge area but different surface areas could be made by adjusting the area of SiCOH that was covered by the wax. These partly covered samples have a smaller area of SiCOH but the same edge length. Following this, ESR measurements were made with the B field parallel to the sample normal. The results showed that the samples had lower defect concentrations compared with those samples that had larger SiCOH areas. The ESR spectra are shown in Fig. 1. It can be easily seen that the amplitude of the "small area" signal is smaller than the "large area" signal. Since the edge lengths and substrate areas of these samples are the same, it is plausible that the defects measured by ESR are actually from SiCOH and/or its interface with the Si substrate, but not from the substrate backside or the edges.

The line shape of ESR spectra was found to be very nearly Lorentzian. Fig. 2 shows a comparison of the observed line shape with Lorentzian and Gaussian fittings. The g value remained unchanged for both the Lorentzian and Gaussian fittings.

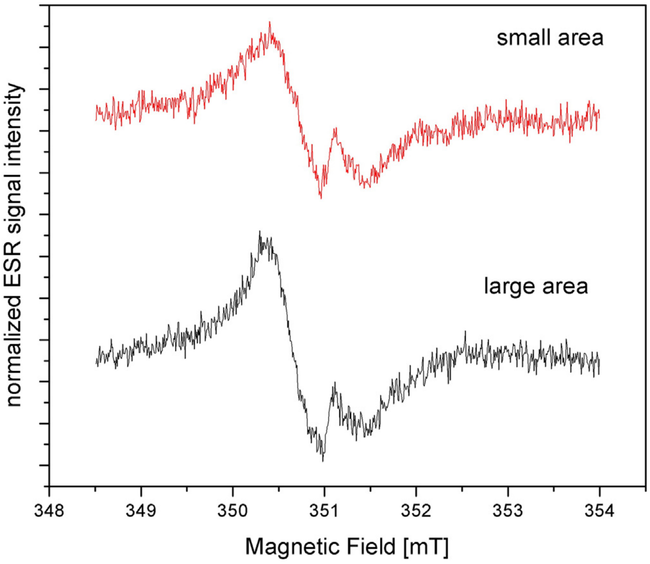

Fig. 1. ESR spectra for pristine samples with same edge area but different SiCOH area. The defect concentration of the large-area sample is 1.24 times larger than that of the small-area sample.

Experimentally, the first derivative of the absorption spectrum signal is written as a Lorentzian derivative. The integral of the Lorentzian distribution is used to determine the concentration of the defects. A 0.0003% KCl weak-pitch (10^{13}spins/cm) and DPPH (2,2-diphenyl-1-picrylhydrazyl) samples was used to calibrate the system.

To identify the defect states, the ESR signal was fitted with two defect states (Fig. 3). The g-factors for these defect states were found to be 2.0054 and 2.0020respectively. The defect with $g = 2.0050–2.0054$ is likely to be either the silicon-dangling bonds in the bulk of the SiCOH [10–13]or the Pb-type defects at the Si substrate/oxide interface under the SiOCH layer [6]. The g-value of the second defect ($g = 2.0018–2.0020$) could be associated with the presence of either oxygen vacancies in the bulk of SiCOH [14] or carbon-related centers [15,16]. The defect concentration of the silicon dangling bonds was found to

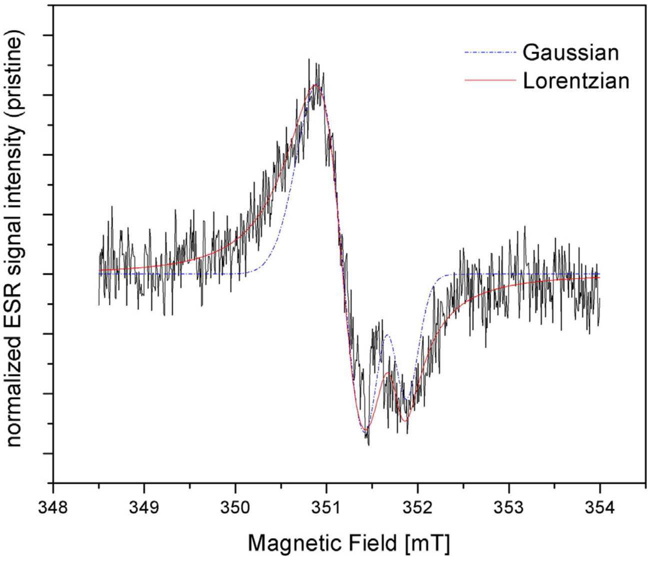

Fig. 2. Comparison of the observed ESR line shape with Lorentzian and Gaussian line shapes.

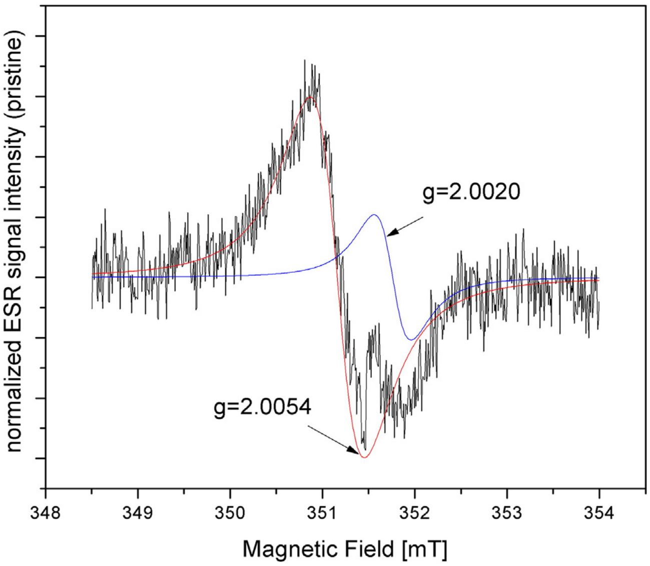

Fig. 3. Measured ESR signals with defect-state fitting.

be about 4.3×10^{12} spins/cm^{2}and the concentration of the carbon-related defects was 1×10^{12} spins/cm^2.

In order to investigate the influence of vacuum ultraviolet (VUV) radiation on the defect concentration, samples were exposed to synchrotron radiation at the Taiwan National Radiation Research Center. The samples were exposed for either 10 or 40 min and the photon beam energy was 12 eV. The fluence was in the order of 10^{15} photons/cm^2. Following VUV exposure, ESR measurements were made. The ESR spectra (Fig. 4) show that there were more silicon dangling bonds in the VUV-exposed samples than in the pristine samples. However, it is hard to identify the VUV influence on the carbon-related centers. This is because the defect concentrations of these centers are small compared with those of the silicon dangling bonds. Moreover, the ESR signal increased significantly with longer VUV exposure times. This observation importantly indicates that exposure of the low-k insulators to VUV radiation during lithographic patterning or plasma processing may impair their electrical properties by introducing additional defects.

The concentration of the silicon dangling bonds for 10 and 40 min exposure samples was 3.5 and 7.2 times higher compared with the concentrations in the pristine samples as shown in Table 1.

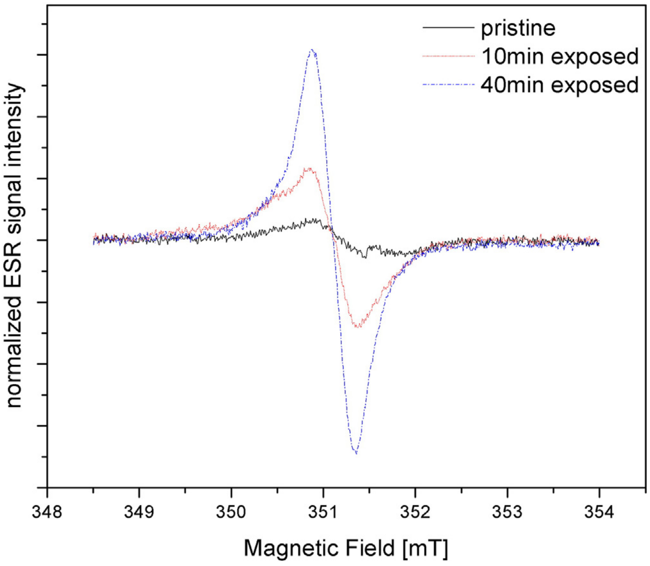

Fig. 4. ESR spectra for pristine and VUV-exposed samples.

Table 1
absolute values of the defect concentrations Unrealistic accuracy, round up to max 2 digits(unrealistic accuracy for the noise level shown, round up to max 2 digits)(unrealistic accuracy for the noise level shown, round up to max 2 digits).

	Defect state	Concentration(cm^{-2})
Pristine	Silicon dangling bond	4.3×10^{12}
12 eV 10 min exposed	Silicon dangling bond	1.5×10^{13}
12 eV 40 min exposed	Silicon dangling bond	3.1×10^{13}

5. Discussion and conclusions

In summary, the defect concentrations in low-k SiCOH films deposited on high resistivity substrates could be detected by using electron spin resonance. Two types of defect states were detected by Lorentzian fitting: (1) silicon dangling bonds at $g = 2.005$ and (2) defect centers at $g = 2.002$ tentatively ascribed to carbon-related centers. In addition, VUV radiation increased the concentration of silicon dangling bonds in SiCOH. The defect concentration also increased with longer exposure time. This is likely caused by electron depletion by photoemission from defects during VUV irradiation [17,18]. That is, before VUV irradiation, the silicon dangling bonds are filled with electrons. The electrons are then depleted by photoemission during irradiation. Since the band gap for SiCOH is approximately 8 eV [19], the 12 eV photons are able to generate electron photoemission. This VUV induced radiation damage was also observed in SiO$_2$/Si system: A VUV photon with energy larger than the band gap energy of SiO$_2$ (8.9 eV [20]) generates an electron-hole pair in the SiO2 film leading to positive oxide charging [21,22]. In addition, dangling bonds may be generated by photolysis of hydrogen from the defect. This is consistent with the fact that the energy threshold for Si–H bond photolysis at the surface of H-passivated Si is ~7.9 eV [23]. Moreover, VUV exposure can cause a loss of methylated species [24,25]. For example, 12 eV VUV photons were able to cause Si-CH$_3$ depletion. It is possible that the loss of the –CH$_3$ group results in additional Si dangling bonds near the surface of the SiCOH films. Furthermore, VUV photons will produce holes in the SiOCH valence band which, upon trapping by defects, may generate ESR-active centers as it known to occur in SiO$_2$ layers thermally grown on silicon [26].

Contrary to the expectations, the revealed spectroscopic features of paramagnetic defects in the porous SiOCH-based low-k insulators differ from the defects routinely encountered in bulk amorphous SiO$_2$ [7,8,27] or in the SiO$_2$ layers thermally grown on Si [12,24] predominantly exhibiting E'-type signals with characteristic powder pattern and zero-crossing at $g \approx 2.0005$ in the adsorption-derivative ESR spectra. This observation points towards different kind of precursor activated during VUV exposure. If in bulk silica Si–Si bridges in the oxide are hypothesized to be the most probable E′-center precursors [28] alternative bonding configurations involving Si and C atoms may be more relevant to the porous SiOCH layers. Upon VUV irradiation, the precursor activation may occur by dissociating the passivating hydrogen atom by hole trapping as it is found in the SiO$_2$ layers thermally grown on silicon [26].

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References

[1] D. Shamiryan, T. Abell, F. Iacopi, K. Maex, Low-k dielectric materials, Mater. Today 7 (2004) 34.
[2] K. Maex, M.R. Baklanov, D. Shamiryan, F. Lacopi, S.H. Brongersma, Z.S. Yanovitskaya, Low dielectric constant materials for microelectronics, J. Appl. Phys. 93 (2003) 8793.

[3] H. Ren, S.L. Cheng, Y. Nishi, J.L. Shohet, Effects of vacuum ultraviolet and ultraviolet irradiation on ultrathin hafnium-oxide dielectric layers on (100) Si as measured with electron-spin resonance, Appl. Phys. Lett. 96 (2010) 192904.

[4] M. Tabib-Azar, D. Akinwande, G.E. Ponchak, S.R. LeClair, Evanescent microwave probes on high-resistivity silicon and its application in characterization of semiconductors, Rev. Scientific Instrum. 70 (1999) 3083.

[5] S. Shamuilia, V.V. Afanas'ev, P. Somers, A. Stesmans, Y.-L. Li, Z.S. Tokei, G. Groeseneken, K. Maex, Internal photoemission of electrons at interfaces of metals with low-κ insulators, Appl. Phys. Lett. 89 (2006) 2909.

[6] V.V. Afanas'ev, A. Nguyen, M. Houssa, A. Stesmans, Z.S. Tokei, M.R. Baklanov, High-resolution electron spin resonance analysis of ion bombardment induced defects in advanced low-κ insulators ($k = 2.0–2.5$), Appl. Phys. Lett. 102 (2013) 172908.

[7] D.L. Griscom, Defects in amorphous insulators, J. Non-Cryst. Solids 31 (1978) 241.

[8] D.L. Griscom, Electron spin resonance in glasses, J. Non-Cryst. Solids 40 (1980) 211.

[9] ANU Centre for Sustainable Energy Systems (CSES), HNA (HF:Nitric:Acetic) Etch Full Procedure (Also Known As 'CP4 Etch'), 2009.

[10] S.C. Agarwal, Nature of localized states in amorphous semiconductors-a study by electron spin resonance, Phys. Rev. B 7 (1973) 685.

[11] D.L. Griscom, E.J. Friebele, Fundamental radiation-induced defect centers in synthetic fused silicas: atomic chlorine, delocalized E' centers, and a triplet state, Phys. Rev. B 34 (1986) 7524.

[12] J.F. Conley, P.M. Lenahan, H.L. Evans, R.K. Lowry, T.J. Morthorst, Observation and electronic characterization of "new" E' center defects in technologically relevant thermal SiO2 on Si: An additional complexity in oxide charge trapping, J. Appl. Phys. 76 (1994) 2872.

[13] M.J. Mutch, P.M. Lenahan, S.W. King, Defect chemistry and electronic transport in low-κ dielectrics studied with electrically detected magnetic resonance, J. Appl. Phys. 119 (2016) 094102.

[14] P.J. Caplan, E.H. Poindexter, B.E. Deal, R.R. Razouk, ESR centers, interface states, and oxide fixed charge in thermally oxidized silicon wafers, J. Appl. Phys. 50 (1979) 5847.

[15] V.V. Afanas'ev, A. Stesmans, M.O. Andersson, Electron states and microstructure of thin a-C: H layers, Phys. Rev. B 54 (1996) 10820.

[16] T.A. Pomorski, B.C. Bittel, P.M. Lenahan, E. Mays, C. Ege, J. Bielefeld, D. Michalak, S.W. King, Defect structure and electronic properties of SiOC: H films used for back end of line dielectrics, J. Appl. Phys. 115 (2014) 234508.

[17] J.L. Lauer, H. Sinha, M.T. Nichols, G.A. Antonelli, Y. Nishi, J.L. Shohet, "Charge trapping within UV and vacuum UV irradiated low-k porous organosilicate dielectrics", J. Electrochem. Soc. 157 (2010) G177.

[18] H. Sinha, J.L. Lauer, M.T. Nichols, G.A. Antonelli, Y. Nishi, J.L. Shohet, Effect of vacuum ultraviolet and ultraviolet irradiation on capacitance-voltage characteristics of low-k-porous organosilicate dielectrics, Appl. Phys. Lett. 96 (2010) 052901.

[19] H. Zheng, S.W. King, V. Ryan, Y. Nishi, J.L. Shohet, Bandgap measurements of low-k porous organosilicate dielectrics using vacuum ultraviolet irradiation, Appl. Phys. Lett. 104 (2014) 062904.

[20] T.H. DiStefano, D.E. Eastman, The band edge of amorphous SiO2 by photoinjection and photoconductivity measurements, Solid State Commun. 9 (1971) 2259–2261.

[21] R.J. Powell, G.F. Derbenwick, Vacuum ultraviolet radiation effects in SiO2, IEEE Trans. Nucl. Sci. 18 (6) (1971) 99–105.

[22] T. Yunogami, T. Mizutani, K. Suzuki, S. Nishimatsu, Radiation damage in SiO2/Si induced by VUV photons, J. Appl. Phys. 28 (1989) 2172.

[23] A. Pusel, U. Wetterauer, P. Hess, Photochemical hydrogen desorption from H-terminated silicon (111) by VUV photons, Phys. Rev. Lett. 81 (1998) 645.

[24] T.V. Rakhimova, A.T. Rakhimov, Y.A. Mankelevich, D.V. Lopaev, A.S. Kovalev, A.N. Vasil'eva, S.M. Zyryanov, Low k films modification under EUV and VUV radiation, J. Phys. D: Appl. Phys. 47 (2014) 025102.

[25] J. Lee, D.B. Graves, The effect of VUV radiation from Ar/O2 plasmas on low-k SiCOH films, J. Phys. D. Appl. Phys. 44 (2011) 325203.

[26] V.V. Afanas'ev, J.M.M. de Nijs, P. Balk, A. Stesmans, Degradation of the thermal oxide of the Si/SiO2/Al system due to vacuum ultraviolet irradiation, J. Appl. Phys. 78 (1995) 6481.

[27] M. Kumeda, H. Nagano, T. Shimizu, ESR study on silica exposed to glow-discharge plasma and UV light, Jpn. J. Appl. Phys. 29 (1990) 356.

[28] R. Tohmon, H. Mizuno, Y. Ohki, K. Sasagane, K. Nagasawa, Y. Hama, Correlation of the 5.0-and 7.6-eV absorption bands in SiO 2 with oxygen vacancy, Phys. Rev. B 39 (1989) 1337.