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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:

$$H = \mu_B B \cdot g \cdot S + I \cdot A \cdot S \quad (1)$$

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]:

$$g_{eff}\mu_B H_{res} = h\nu \quad (2)$$

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 2.5×20 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.

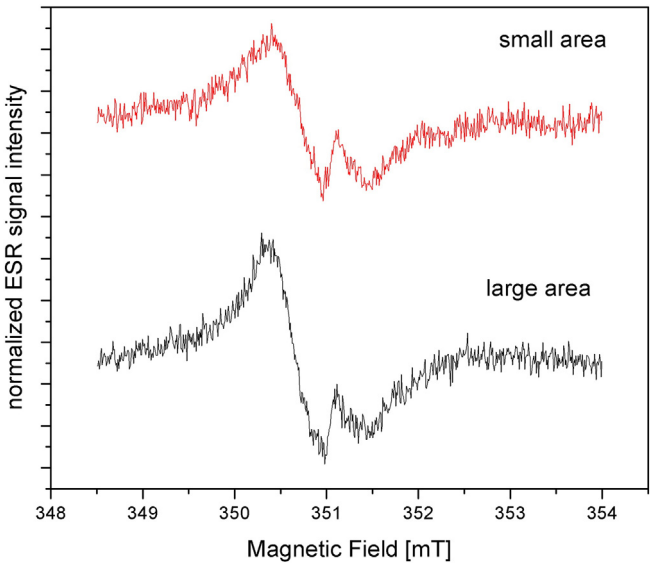

Fig. 1. ESR spectra for pristine samples with same edge area but different SiCOH area. The defect concentration of the large-area sample is 1.24 times larger than that of the small-area sample.

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

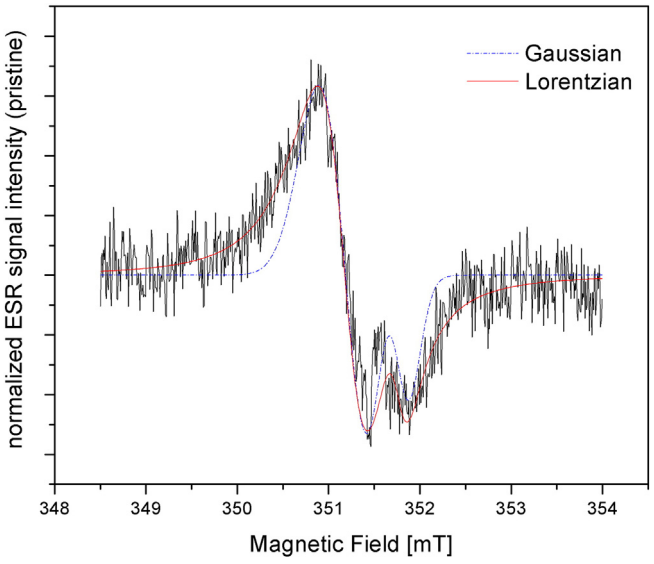

Fig. 2. Comparison of the observed ESR line shape with Lorentzian and Gaussian line shapes.