The nature of the defects generated from plasma exposure in pristine and ultraviolet-cured low-*k* organosilicate glass

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Defects in low-*k* organosilicate glass produced during air and nitrogen plasma exposure were investigated. The defects, through the measurements of electron-spin resonance and Fourier-transform infrared spectroscopy, were found to be silicon-dangling bonds. Air-plasma exposure increases the defect concentrations by breaking silicon–hydrogen bonds. Nitrogen-plasma exposure as well as free-radical exposure has only a small influence on the bond breaking. It was also shown that ultraviolet curing improves the chemical-damage resistance of the dielectric. © *2011 American Institute of Physics*. [doi:10.1063/1.3601922]

Low-*k* porous organosilicate glass (SiCOH) is a good candidate for interconnect applications in the manufacturing of microelectronic devices.[1,2] However, because of porosity and carbon-doping, these low-*k* dielectric materials have large leakage currents, resulting in undesirably short lifetimes.[3] It has been shown that the defect bonding structures in the dielectric layers, as well as potential copper contamination due to the structure of the interconnects, are responsible for these large leakage currents.[4–7] It was found that defects in the dielectric layers lead to intrinsic leakage currents without the presence of metal layers.[5] Hence, an investigation of the nature of the defects in SiCOH along with methods to reduce them is critical for industrial application of these materials.[8]

For high-*k* dielectrics, specific processing steps were undertaken to exclusively modify each bonding structure of concern so that the resulting changes in defect concentration, as measured by electron spin resonance (ESR), can be directly linked to changes to specific chemical bonds.[9] However, the corresponding bonding structures of the defects in SiCOH have not yet been determined.[5] Now, the ability to deposit SiCOH on high-resistivity[10] substrates makes it possible to quantify the defect concentrations in a similar way.[6]

In this letter, we extend this work to explore the nature of the defects in low-*k* dielectrics, such as SiCOH and search for potential methods to reduce the defect concentrations. By using air and nitrogen plasma exposure, we show that the defects can be linked to particular bonding structures. In addition, we identify the source of the defects. Finally, the effects of ultraviolet (UV) curing, which is widely used to improve the mechanical properties of SiCOH,[11] were investigated to determine the effects of UV curing on changes to defect concentrations during plasma exposure.

SiCOH was deposited on 3 in. diameter high-resistivity (8000 Ω cm) wafers using plasma-enhanced chemical vapor deposition. Two sets of samples were selected: pristine SiCOH with dielectric constant $k=2.65$ and UV-cured SiCOH with dielectric constant $k=2.55$. The noncured SiCOH film was 50 nm thick and the UV-cured SiCOH was 60 nm thick. This increase in thickness is due to the UV-curing process. The UV cure was made at a temperature of 400 °C with ambient nitrogen. The UV photon energy was between 3 and 6 eV with a total fluence of approximately 1×10^{16} photons/cm^2.

The samples were exposed to an electron-cyclotron resonance air plasma. The power and pressure were set to 200 W and 10 mtorr, respectively. Air plasma has been used in the past to modify the chemical structure of SiCOH films during processing.[12] Pure oxygen plasma was not used in this work because of the difficulty in controlling damage to the dielectric.[13]

To separate the effects of ion and photon bombardment, a capillary-array window was used as an ion filter.[11] In addition, to further separate the effects of free radicals from the ion and photon bombardment, a gas-gap filter (shown in Fig. 1) was also employed. The filter consisted of an aluminum plate placed 3 mm above the sample. For all exposures, a negative dc bias was applied to the sample material. Since the ion trajectories are anisotropic (essentially normal to the gas-gap filter), few ions will penetrate to the covered area. On the other hand, free radicals will be created in the plasma with isotropic trajectories and can travel around the filter, where that they can interact with the sample. Hence, the gas-radical effect can be separated from the ion and photon bombardment effects.

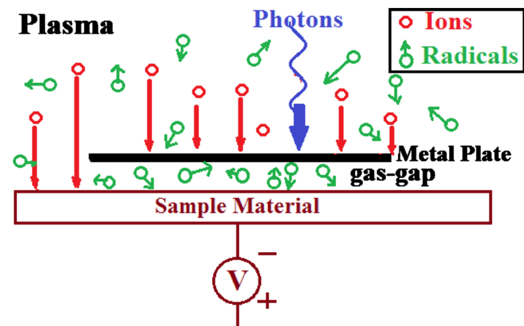

FIG. 1. (Color online) Design of the gas-gap filter to investigate the radical effects on SiCOH films.

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TABLE I. Modifications of defect concentrations in noncured and UV-cured SiCOH samples due to plasma exposure.

Plasma exposure		Noncured SiCOH (2.4×10^{13} spins/cm^2)	UV-cured SiCOH (2.54×10^{13} spins/cm^2)
Air plasma (10 mTorr)	Ion effect	↑47.1%	↑33.9%
	Photon effect	↗8.6%	↗7.5%
	Radicals	↗3.1%	↗2.2%
Nitrogen plasma (7 mTorr)	Ion effect	↗11.2%	↗13.3%
	Photon effect	↗4.2%	↗2.6%
	Radicals	→±0.3%	→±0.1%
Oxygen plasma (the difference between air and nitrogen plasma) (3 mTorr)	Ion effect	↑35.9%	↗20.6%
	Photon effect	↗4.4%	↗4.9%
	Radicals	→2.7	↗2.1%

Both pristine and UV-cured SiCOH films were exposed to a number of plasma exposures as shown in Table I. The modification of the defect concentrations, measured by ESR spectroscopy, was shown in Fig. 2. The defects were identified with by identifying the ESR "fingerprint"[14] called the g factor, which was g=2.0033. The ESR signals can be fitted into a Lorentzian derivative form using a least-squares criterion as described in previous letter.[6] The defect concentrations were calculated and summarized in Table I. To further separate the effects of the two major gas components, i.e., oxygen and nitrogen, a sample was also exposed to a pure nitrogen plasma with similar power and pressure settings. The effects from oxygen-plasma exposure were considered to be the difference between air and nitrogen plasma exposure.

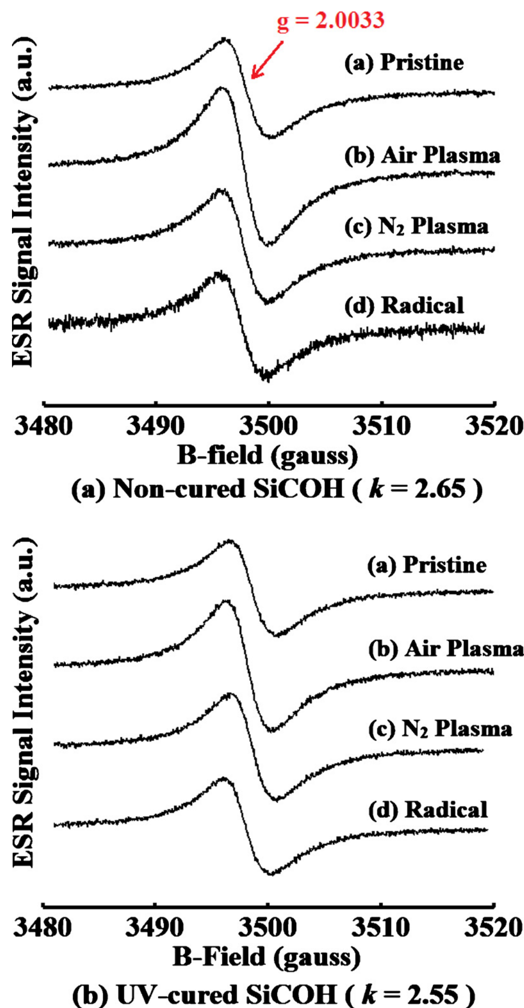

FIG. 2. (Color online) ESR signals for (a) noncured SiCOH (k=2.65) and (b) UV-cured SiCOH (k=2.55) with various treatments.

From Table I, it can be seen that for all different types of plasma exposure, ion bombardment has the most significant effect on increasing the defect concentrations while radicals have only a small effect on the concentration. Oxygen plasma, due to its reactive property, has a stronger effect on increasing the defects than does nitrogen plasma. Because plasma exposure was made simultaneously to both pristine and UV-cured samples, a comparison can be made between them to determine the effects of UV curing. It is seen that for the SiCOH films that were UV cured, they become more damage-resistant to oxygen-plasma exposure, i.e., the increase in defect concentration was mitigated.

The defects were linked to bonding structures with Fourier transform infrared (FTIR) spectroscopy measurements. The FTIR response of the chemical bonds of SiCOH films to plasma exposure is shown in Fig. 3. Multiple chemical bonds were identified: Si–$(CH_3)_m$ at 700–900 cm^{-1}, Si–O stretch at 970–1250 cm^{-1}, C=O at 1710 cm^{-1}, Si–H at 2000 cm^{-1}, and CH_x at 2970 cm^{-1}.[4,15]

From Fig. 3, it is seen that air-plasma exposure reduces Si–H bonds significantly while the carbon-related bonds, such as CH_x and Si–$(CH_3)_m$ maintain their concentrations at the same level. With long exposure time, more Si–H bonds were broken because the number of defect states kept increasing as shown in Fig. 2. Hence, these consistent results verify that the observed defects with a g-factor of 2.0033 are directly related to the breaking of the Si–H bonds. That is, the defects were from unpaired electrons in broken silicon bonds, i.e., silicon dangling bonds.

Furthermore, nitrogen-plasma exposure does not modify the Si–H bond concentration significantly. It is also unlikely that a synergistic effect can take place between the oxygen and nitrogen plasmas.[16] Instead, in Ref. 16, the effects of oxygen and nitrogen plasma were shown to add linearly. This further confirms that oxygen-ion bombardment is the main damage source during air-plasma exposure. In addition, free radicals only weakly modify the chemical bonds, which is consistent with our ESR measurements of defect concentration.

During air-plasma exposure, less damage from breaking Si–H bonds was observed in UV-cured SiCOH films, as shown in Fig. 3, resulting in less increase in defect concentration than is shown in Fig. 2. Thus, we can also conclude

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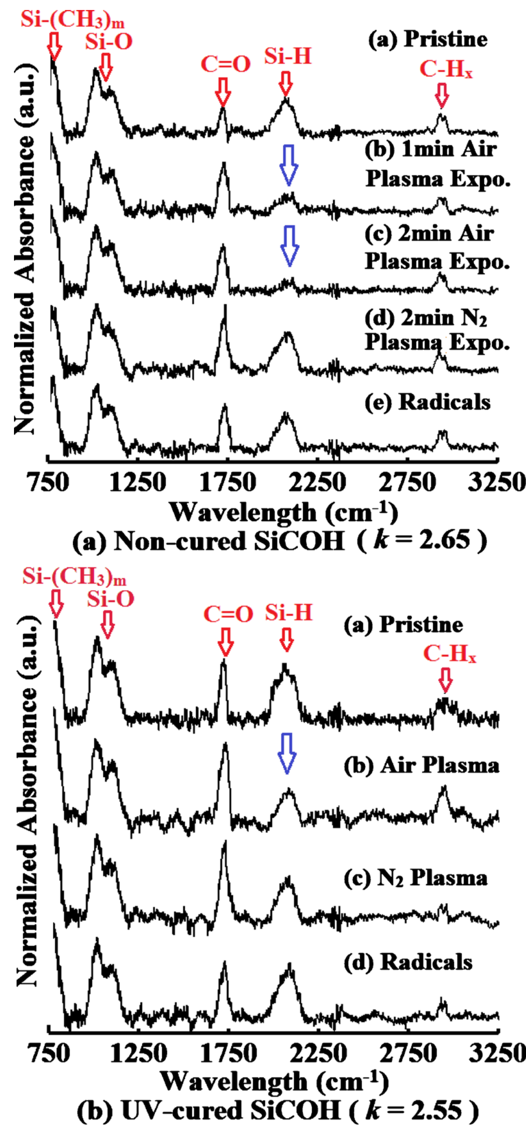

FIG. 3. (Color online) FTIR results for (a) noncured SiCOH (k=2.65) and (b) UV-cured SiCOH (k=2.55) with various treatments.

that UV-cured SiCOH films are more chemically stable with respect to Si–H bonds than noncured SiCOH.

In addition, the leakage currents for pristine SiCOH, as a function of voltage stress, were measured using a mercury probe. It was seen that after air plasma exposure, the leakage currents increased significantly while just photon bombardment only contributed a small amount to the increase. As seen in Table I, the ion bombardment increases the defect concentration more than does photon bombardment. Thus, it is verified that the defects, mainly modified by ion bombardment, are sources of the leakage currents in SiCOH.

In conclusion, defects with g=2.0033 were linked to the breaking of Si–H bonds. The effects from different damage sources during plasma exposure were separated. It was found that during air-plasma exposure, oxygen-ion bombardment is more damaging compared with nitrogen-ion bombardment, photon bombardment, and radical flux. UV curing makes SiCOH films more chemically damage-resistant.

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