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Effect of vacuum-ultraviolet irradiation on the dielectric constant of low-k organosilicate dielectrics

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Vacuum ultraviolet (VUV) irradiation is generated during plasma processing in semiconductor fabrications, while the effect of VUV irradiation on the dielectric constant (k value) of low-k materials is still an open question. To clarify this problem, VUV photons with a range of energies were exposed on low-k organosilicate dielectrics (SiCOH) samples at room temperature. Photon energies equal to or larger than 6.0 eV were found to decrease the k value of SiCOH films. VUV photons with lower energies do not have this effect. This shows the need for thermal heating in traditional ultraviolet (UV) curing since UV light sources do not have sufficient energy to change the dielectric constant of SiCOH and additional energy is required from thermal heating. In addition, 6.2 eV photon irradiation was found to be the most effective in decreasing the dielectric constant of low-k organosilicate films. Fourier Transform Infra-red Spectroscopy shows that these 6.2 eV VUV exposures removed organic porogens. This contributes to the decrease of the dielectric constant. This information provides the range of VUV photon energies that could decrease the dielectric constant of low-k materials most effectively. © *2014 AIP Publishing LLC*.
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The next-generation of microelectronic interconnects requires the utilization of dielectric layers with lower and lower dielectric constants (k value) to overcome signal propagation delays.[1,2] Today, low-k organosilicate dielectrics are used mainly as insulators.[3] Ultraviolet-assisted curing is used to decrease the permittivity of these low-k materials as well as to strengthen their mechanical properties. However, the effect of vacuum ultraviolet (VUV) irradiation on the dielectric constant of low-k films as a function of energy is still unknown. This work shows that the effect of VUV irradiation on the dielectric constant of low-k samples is energy sensitive: photons with energies higher than 6.0 eV decrease the dielectric constant and irradiation with lower energies (4.5–5.9 eV) does not decrease the permittivity. Fourier transform infra-red spectroscopy (FTIR) measurements show that the higher energy VUV photons remove organic porogens, which leads to the permittivity decrease.

Previous investigations of VUV-induced changes to SiCOH samples utilized either an Xe excimer lamp[4] with a single wavelength or a H_2/N_2 plasma[5] filtered by MgF_2/quartz windows to expose the test samples. These methods did draw some initial conclusions about the effects of VUV irradiation on low-k thin films, but were not sufficient, because VUV irradiation generated during plasma processing has a limited energy range since it is primary line radiation. Thus, exposure with one wavelength or even with a mixture of several wavelengths cannot determine the optimal effects of VUV irradiation on the insulator. Therefore, to expand this work, low-k dielectric test samples were irradiated with monochromatic VUV synchrotron radiation at the University of Wisconsin-Synchrotron Radiation Center (SRC). The advantage of a synchrotron is that it generates radiation with no charged particles and can be varied over a continuum of photon energies.

The VUV photon beam was oriented to be normally incident on the surface of 150-nm thick porous SiCOH samples (k = 3.1) at a pressure of 10^{-8} Torr. The samples were deposited in a plasma-enhanced chemical-vapor-deposited (PECVD) reactor in the presence of several inert and reactive gases with an organosilane precursor. The VUV beam on the surface of the wafer had a cross-sectional area of $2.5 \times 0.1\ \text{cm}^2$ and the exit slit width of the synchrotron beam monochromator was set to 500 μm to maximize the photon flux. The accumulated photon fluence for each exposure was chosen to be 1.3×10^{14} photons/cm^2, which is comparable to the VUV photon fluence emitted during a typical plasma process.[6,7] Test samples were separately exposed to photon energies between 4.5 and 8.9 eV with the same photon dose at room temperature. It must be mentioned that since the bandgap of the test sample is around 7.9 eV,[8] VUV exposure with photon energies much higher than the band-gap of the dielectric samples was not used since charge accumulation would take place during exposure due to photoemission.[9,10] The goal here is to identify the ranges of photon energies that could decrease the permittivity of SiCOH, but not induce significant charge accumulation.

To investigate the change of dielectric constant of a SiCOH sample caused by VUV irradiation, the following procedure was followed. First, the thickness of the dielectric layer was measured with a Filmetrics F-20 Optimal reflectometer at the Wisconsin Center for Applied Microelectronics (WCAM). Next, a probe station was used to measure the capacitance-voltage (C-V) characteristics of the SiCOH samples. The probe station consists of three

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movable micro positioners with 5-μm diameter tungsten probe tips and the sample under test is positioned on an electrically floating stainless-steel wafer platen that can be moved in the *x-y* directions using micrometers.[11] Then, before the measurement, a titanium-metal layer was deposited on the surface of the dielectric to form a Metal-Oxide-Semiconductor (MOS) structure. The MOS structure was connected with shielded cables to an HP 4285A precision inductance-capacitance-resistance (LCR) meter.[12] Measurements of the MOS C-V characteristics were made in the high-frequency regime (2 MHz).[13] The CV characteristics were examined to determine the effect of VUV irradiation on the dielectric constant of the low-k samples as a function of photon energy.

Figure 1 shows a comparison of dielectric constants after VUV exposure for a range of photon energies. The as-deposited sample with no photon irradiation is shown as a control. Comparing the k value of the VUV exposed samples with the as-deposited sample without VUV exposure, it is seen in Figure 1 that after VUV exposure with photon energies between 4.5 and 5.9 eV, the dielectric constant did not decrease during exposure. However, under photon irradiation with energies higher than 6.0 eV, the k values are lower than those of the as-deposited sample. The dielectric constant reaches its lowest value ($k = 2.84$) with 6.2 eV exposure. Since all test samples are exposed to the same photon fluence, it can be concluded that the optimal photon energy that can decrease the dielectric constant of the test SiCOH sample is approximately 6.2 eV.

To investigate the reason for the change of dielectric constant, the procedures of SiCOH deposition and curing should first be explained. To create porosity in low-k dielectrics, organic porogens are utilized during film deposition, but they must be removed after the deposition process.[1] Porogen removal is also believed to be one of the most important reasons that the curing procedure could lower the permittivity of low-k dielectrics.[1,14] To investigate the relationship between porogen removal and VUV exposure on tested SiCOH samples, FTIR was used to detect the changes induced by VUV irradiation to chemical bonds within the dielectric layers. Figure 2 shows the FTIR spectra of the SiCOH before and after 6.2 eV VUV exposure with a photon fluence of 1.3×10^{14} photons/cm^2. The spectra show the characteristic absorption for SiCOH.[1,14] They are: (1) C-H$_x$ stretching from organic porogens (3050–2850 cm^{-1}), (2) C-H$_3$ symmetric bending from Si-(CH$_3$)$_x$ ($\sim$1275 cm^{-1}), (3) Si-C stretching from Si-(CH$_3$)$_x$ (750–850 cm^{-1}), and (4) Si-O-Si antisymmetric stretching (1000–1250 cm^{-1}).[15] It was found that the absorbance by the C-H bonds in organic porogens (3050–2850 cm^{-1}) decreases drastically in intensity under 6.2 eV VUV exposure. Since all the experiments were made at room temperature, thermally activated degradation of the porogens[1] could not be the main reason that leads to their removal. Previous investigations of FTIR measurements of both soft bake (150 °C) and full thermally (400 °C) treated SiCOH samples also showed that the heating process does not have much effect in changing the bond densities of C-H$_x$ (3050–2850 cm^{-1}).[16] Instead, we believe that photonic bond breaking dominates the porogen-removal process. Since the dielectric constant of the test samples is lower than their original value when the photon energy reaches 6.0 eV, it can be concluded that VUV irradiation with photon energy at 6.0 eV starts to break the C-H chemical bonds, while photons with lower energies are not sufficient to break the C-H bonds and thus could not decrease the k value of the test sample. To prove this, a comparison between FTIR measurements on as-deposited test samples and 5.9 eV VUV exposed samples are shown in Figure 3. The same photon fluence of 1.3×10^{14} photons/cm^2 was used for both 5.9 eV exposed samples and the previous characteristic absorptions for SiCOH. The FTIR spectra show no difference between the C-H bonds in organic porogens (3050–2850 cm^{-1}) for the as-deposited samples and the exposed samples. Therefore, it can be concluded that photons with energies lower than 6.0 eV cannot break the C-H bonds. Breaking these leads to porogen removal and thus exposing the test samples to these photon energies could not decrease the dielectric constant.

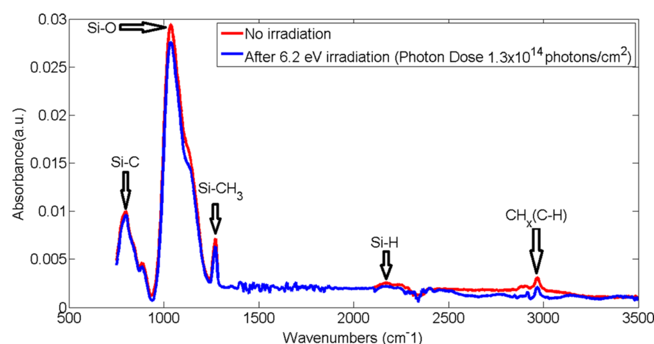

FIG. 2. Comparison of FTIR spectra of SiCOH sample before and after 6.2 eV exposure.

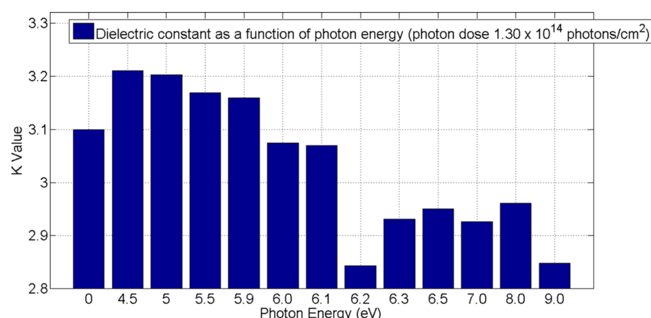

FIG. 1. Effect of VUV irradiation on dielectric constant of SiCOH as a function of photon energy.

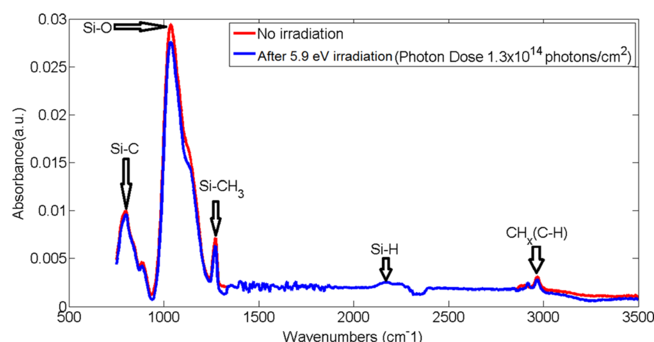

FIG. 3. Comparison of FTIR spectra of SiCOH sample before and after 5.9 eV exposure.

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Moreover, based on the relation between the wavelength of the VUV photons and their penetration depth in low-k dielectrics,[17] photons with energies between 6.0 and 9.0 eV could penetrate entirely through the dielectric layer and thus break the C-H bonds near the surface and in the bulk of the dielectric as well. It must be mentioned that the bond densities for Si-CH_3 (~1275 cm^{-1}) and Si-O-Si stretching (1000–1250 cm^{-1}) in as-deposited SiCOH films also decreased slightly after VUV irradiation. This structural rearrangement and demethylation of the test samples are responsible for the mechanical property changes in SiCOH[18] and does not have much effect on any measured changes of permittivity.

In addition, the k value slightly increases with photon energies from 6.3 to 8.0 eV and then decreases at 9 eV. This is due to the change in the amount of photon absorption as a function of photon energy. The measured absorption ratio can show the amount of absorption when an electromagnetic wave propagates through the material. It also describes how quickly the photon beam loses intensity from absorption as it passes through the material. After the porogen-removal process is activated by 6.0-eV photon irradiation, then photons that are more easily absorbed (higher absorption ratio), remove organic porogen residues in dielectrics more significantly. Prager *et al.*[19] showed that in the low-energy UV range from 2 to 9 eV, the absorption of photons in SiCOH dielectrics reached a maximum value when the photon energy is approximately 6.3 eV and after that the absorption ratio decreased from 6.3 to 7.5 eV and then increased until 9 eV. This trend is inversely correlated to the changes of SiCOH permittivity after VUV irradiation. Sinha *et al.*[20] also showed similar results by measuring the reflectance of SiCOH under vacuum ultraviolet irradiation using a nickel mesh reflectometer. Therefore, if the exposed photon energy is equal to or larger than 6 eV, porogen residues can be removed, and the optimum photon energy that could effectively remove organic porogens (and decrease the k value) in dielectrics lies at the energies that are more easily absorbed. From our investigation, that energy is 6.2 eV.

To prove this, a comparison between the FTIR measurements of pristine, 6.2 eV and 9.0 eV VUV-exposed samples is shown in Figure 4. The figure shows that after 9.0 eV VUV irradiation, the C-H bond concentration of SiCOH did not decrease as much as that which occurred after 6.2 eV exposure. In summary, FTIR results for VUV exposed samples under photon energies equal to or less than 5.9 eV shows no effect on changing the C-H bonds while higher energies could break the C-H bonds. This substantiates the result that the strongest effect occurs under 6.2 eV exposure.

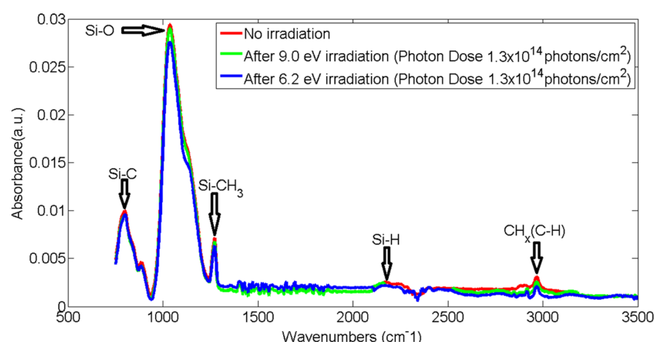

FIG. 4. Comparison of FTIR spectra of pristine SiCOH samples and samples after 6.2 and 9.0 eV VUV exposure.

In conclusion, the effect of vacuum ultraviolet irradiation on the dielectric constant of low-k dielectrics has been investigated. Photon energies higher than 6.0 eV decrease the k values of SiCOH while lower energies do not have this effect. Furthermore, 6.2 eV was found to have the strongest effect on decreasing the permittivity. FTIR spectra showed that 6.2 eV VUV exposure also contributes to the removal of organic porogens that is directly linked to the reduction of the dielectric constant. This holds the potential to be a useful replacement for UV curing in microelectronic processing to improve the properties of low-k dielectrics without external thermal heating procedures. The goal of this work is to optimize the exposing/curing conditions and to improve the electrical, mechanical, and chemical properties of as-deposited SiCOH samples simultaneously and is still under investigation.

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[1] A. Zenasni, V. Jousseaume, and P. Holliger, "The role of ultraviolet radiation during ultralow k films curing: Strengthening mechanisms and sacrificial porogen removal," J. Appl. Phys. **102**, 094107 (2007).
[2] S. Nakao, J. Ushio, T. Ohno, T. Hamada, Y. Kamigaki, M. Kato, K. Yoneda, S. Kondo, and N. Kobayashi, "UV/EB cure mechanism for porous PECVD/SOD low-k SiCOH materials," in *Proceedings of the IEEE 2006 International Interconnect Technology Conference (IITC)* (2006), p. 66.
[3] A. Grill and V. Patel, "Ultralow-k dielectrics prepared by plasma-enhanced chemical vapor deposition," Appl. Phys. Lett. **79**, 803 (2001).
[4] J. Lee and D. B. Graves, "Synergistic damage effects of vacuum ultraviolet photons and O_2 in SiCOH ultra-low-k dielectric films," J. Phys. D: Appl. Phys. **43**, 425201 (2010).
[5] S. Uchida, S. Takashima, M. Hori, M. Fukasawa, K. Ohshima, K. Nagahata, and T. Tatsumi, "Plasma damage mechanisms for low-k porous SiCOH films due to radiation, radicals and ions in the plasma etching process," J. Appl. Phys. **103**, 073303 (2008).
[6] H. Ren, M. T. Nichols, G. Jiang, G. A. Antonelli, Y. Nishi, and J. L. Shohet, "Defects in low-k organosilicate glass and their response to processing as measured with electron-spin resonance," Appl. Phys. Lett. **98**, 102903 (2011).
[7] H. Sinha, H. Ren, A. Sehgal, G. A. Antonelli, Y. Nishi, and J. L. Shohet, "Numerical simulation of vacuum-ultraviolet irradiation of dielectric layers," Appl. Phys. Lett. **96**, 142903 (2010).
[8] H. Zheng, S. W. King, V. Ryan, Y. Nishi, and J. L. Shohet, "Bandgap measurements of low-k porous organosilicate dielectrics using vacuum ultraviolet irradiation," Appl. Phys. Lett. **104**, 062904 (2014).
[9] J. L. Lauer, J. L. Shohet, C. Cismaru, R. W. Hansen, M. Y. Foo, and T. J. Henn, "Photoemission and conduction currents in vacuum ultraviolet irradiation oxide," J. Appl. Phys. **91**, 1242 (2002).
[10] R. J. Powell, "Hole photocurrents and electron tunnel injection induced by trapped holes in SiO_2 films," J. Appl. Phys. **46**, 4557 (1975).
[11] M. T. Nichols, H. Sinha, C. A. Wiltbank, G. A. Antonelli, Y. Nishi, and J. L. Shohet, "Time-dependent dielectric breakdown of plasma-exposed porous organosilicate glass," Appl. Phys. Lett. **100**, 112905 (2012).
[12] M. T. Nichols, K. Mavrakakis, Q. Lin, and J. L. Shohet, "The effects of plasma exposure and vacuum ultraviolet irradiation on photopatternable low-k dielectric materials," J. Appl. Phys. **114**, 104107 (2013).
[13] R. S. Muller and T. I. Kamins, *Device Electronics for Integrated Circuits* (John Wiley and Sons, 2003).

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[14]A. Grill and D. A. Neumayer, "Structure of low dielectric constant to extreme low dielectric constant SiCOH films: Fourier transform infrared spectroscopy characterization," J. Appl. Phys. **94**, 6697 (2003).
[15]S. Eslava, G. Eymery, P. Marsik, F. Iacopi, C. E. A. Kirshhock, K. Maex, J. A. Martens, and M. R. Baklanov, "Optimal property changes in low-k films upon ultraviolet-assisted curing," J. Electrochem. Soc. **155**, G115 (2008).
[16]S. Eslava, F. Iacopi, A. M. Urbanowicz, C. E. A. Kirshhock, K. Maex, J. A. Martens, and M. R. Baklanov, "Ultraviolet-assisted curing of organosilicate glass low-k dielectric by excimer lamps," J. Electrochem. Soc. **155**, G231 (2008).
[17]J. R. Woodworth, M. E. Riley, V. A. Amatucci, T. W. Hamilton, and B. P. Aragon, "Absolute intensities of the vacuum ultraviolet spectra in oxide etch plasma processing discharges," J. Vac. Sci. Technol., A **19**, 45 (2001).
[18]X. Guo, J. E. Jakes, S. Banna, Y. Nishi, and J. L. Shohet, "Effects of plasma and vacuum-ultraviolet irradiation on the mechanical properties of low-k porous organosilicate glass," J. Appl. Phys. **116**, 044103 (2014).
[19]L. Prager, P. Marsik, L. Wennrich, M. R. Baklanov, S. Naumov, L. Pistol, D. Schneider, J. W. Gerlach, P. Verdonck, and M. R. Buchmeiser, "Effect of pressure on efficiency of UV curing of CVD-derived low-k material at different wavelengths," Microelectron. Eng. **85**, 2094 (2008).
[20]H. Sinha, D. B. Straight, J. L. Lauer, N. C. Fuller, S. U. Engelmann, Y. Zhang, G. A. Antonelli, Y. Nishi, and J. L. Shohet, "Reflectance and substrate currents of dielectric layers under vacuum ultraviolet irradiation," J. Vac. Sci. Technol., A **28**, 1316 (2010).

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