Damage by radicals and photons during plasma cleaning of porous low-*k* SiOCH. II. Water uptake and change in dielectric constant

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Porous dielectric materials provide lower capacitances that reduce RC time delays in integrated circuits. Typical low-*k* materials include porous SiOCH—silicon dioxide with carbon groups, principally CH_3, lining the pores. With a high porosity, internally connected pores provide pathways for reactive species to enter into the material. Fluorocarbon plasmas are often used to etch SiOCH, a process that leaves a fluorocarbon polymer on the surface that must later be removed. During cleaning using Ar/O_2 or He/H_2 plasmas, reactions of radicals that diffuse into the SiOCH and photons that penetrate into the SiOCH can remove $–CH_3$ groups. Due to its higher reactivity, cleaning with Ar/O_2 plasmas removes more $–CH_3$ groups than He/H_2 plasmas, and so produce more free radical sites, such as $–SiO_2•$ (a $–SiO_2–CH_3$ site with the $–CH_3$ group removed). Upon exposure to humid air, these free radical sites can chemisorb H_2O to form hydrophilic Si–OH which can further physisorb H_2O through hydrogen bonding to form Si–OH(H_2O). With the high dielectric constant of water, even a small percentage of water uptake can significantly increase the effective dielectric constant of SiOCH. In this paper, we report on results from a computational investigation of the cleaning of SiOCH using Ar/O_2 or He/H_2 plasmas and subsequent exposure to humid air. The authors found that plasma cleaning with He/H_2 mixtures produce less demethylation than cleaning with Ar/O_2 plasmas, as so results in less water uptake, and a smaller increase in dielectric constant. The water that produces the increase in dielectric constant is roughly half chemisorbed and half physisorbed, the latter of which can be removed with mild heating. Sealing the pores with NH_3 plasma treatment reduces water uptake and helps prevent the increase in dielectric constant. © *2012 American Vacuum Society*.
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I. INTRODUCTION

Low dielectric constant (low-*k*) materials are now used for the inter-layer dielectric in the fabrication of microelectronics devices to lower the RC time constant for signal propagation.[1] One such low-*k* material is porous SiO_2 with hydrophobic methyl groups ($–CH_3$) lining the pores –SiOCH. Pristine SiOCH is essentially hydrophobic because of the presence of $–CH_3$ groups on the pore walls which prevent SiO_2 from adsorbing significant amounts of water from humid air. The water is adsorbed following diffusion into the SiOCH through interconnected pores. As a result SiOCH usually does not contain more than a few percent of physisorbed water in its volume even when the humidity is high.[2] This physisorbed water can be driven out with mild heating (200–300 °C) without harming the integrity of the SiOCH.[1]

The CF_x polymers which are deposited during the etching of SiOCH in fluorocarbon plasmas must be removed as these compounds may cause compatibility issues in subsequent processing steps.[3] These polymers can also introduce some hydrophilic properties to SiOCH as they are not as hydrophobic as $–CH_x$groups.[2] The removal of the CF_x layer is ideally performed using an oxygen containing plasma due to the efficiency of oxidation of the polymer by oxygen radicals.[4–6] However, O_2 plasma cleaning can also remove the hydrophobic $–CH_3$ groups from SiOCH creating free radical sites such as $–SiO_2•$ (a $–SiO_2–CH_3$ site with the $–CH_3$ group removed). Exposure of plasma cleaned SiOCH to humid air results in water uptake due to reaction of H_2O with these free radical sites. The end result is formation of hydrophilic $–SiO_2$–OH. That is, hydrophobic $–CH_3$ groups from $–SiO_2–CH_3$ are replaced by hydrophilic –OH groups. $–SiO_2$–OH enables further water uptake by creating $–SiO_2$–OH(H_2O) through hydrogen bonding.[7–9] Given the high dielectric constant of water (≈80), loss of hydrophobic $–CH_3$ groups after O_2 plasma cleaning of SiOCH and incorporation of water from humid air can cause a significant increase in the dielectric constant. For example, in one study after exposure to an O_2 plasma, the dielectric constant of SiOCH increased from 2.5 to 20 within 9 min of exposure to humid air.[1] Comparison of O_2 plasma ashing of photoresist (PR) with wet cleaning showed an increase in dielectric constant from 2.6 to 3.2 for the plasma ashing, and an increase to 2.9 with wet cleaning. These trends were attributed to the greater propensity for water uptake following the O_2 plasma cleaning.[10]

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SiOCH is relatively stable when H_2 plasmas are used for cleaning as there is minimal removal of $–CH_3$ groups.[11] When correlating SiOCH etch rates with damage produced by plasma cleaning, He/H_2 mixtures resulted in one third the damage produced by Ar/O_2 mixtures under similar conditions.[12] Given that He/H_2 plasma cleaning is relatively benign to the underlying SiOCH, these systems are being investigated for PR mask removal.[13]

An unavoidable outcome of plasma cleaning of SiOCH is illumination with UV and vacuum ultraviolet (VUV) photons. For example, plasmas containing O_2 produce photon fluxes in the 130–145 nm range which have penetration distances >100 nm. In He/H_2 plasmas, the resonance radiation from He at 58.4 nm penetrates only $\approx$20 nm.[14] These UV/VUV photons can produce Si–C bond scission in $–SiO_2–CH_3$ which can accelerate the $–CH_3$ removal process.[15–17] Since $–CH_3$ removal by O atoms is exothermic, demethylation can be enhanced by VUV fluxes but is not a prerequisite for demethylation. However, the deeper penetration depth into SiOCH of photons from Ar/O_2 plasmas magnifies the influence they have. On the other hand, demethylation by the intrinsically less reactive He/H_2 plasmas is greatly enhanced by the Si–C bond scission produced by VUV photons. However, the shorter penetration depth of VUV fluxes produced in He/H_2 plasmas limits the range of this enhancement. These processes can be synergistic. For example, Uchida *et al.*[17] investigated scission of $–SiO_2–CH_3$ in SiOCH exposed to capacitively coupled plasmas sustained in N_2/H_2 mixtures in which the fluxes of UV, VUV, and radicals to the SiOCH were separately controlled. In the absence of energetic ion bombardment (as would likely be the case during plasma cleaning), the rate of scission of $–SiO_2–CH_3$ and increase in dielectric constant were largest when exposed simultaneously to radicals and UV/VUV fluxes.

One of the strategies to reduce or eliminate the increase in dielectric constant resulting from water intake is to seal the pores and so reduce the rate of diffusion of H_2O into the porous network. A number of different techniques have been developed for pore sealing, including densification of the surface by plasma treatment or formation of a sealing layer of Si–N and C–N compounds with a NH_3 plasma. Pretreatment with He plasmas is thought to create active surface sites which localize and accelerate the chemical reactions responsible for pore sealing by NH_3 containing plasmas.[18–20] The sealing processes are uncertain but at least two mechanisms have been discussed. The first proposes that NH_3 plasma treatment catalyzes pore collapse and so produces a dense nonporous layer at the surface.[21] The second proposes that chemisorption of NH_x radicals result in Si–N and C–N bonding which leads to bridging of the opening of the pores.[18–20]

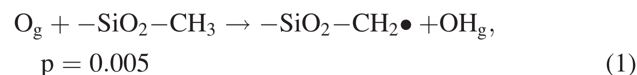
In this paper, we discuss reaction mechanisms and computationally investigate the change in dielectric constant due to water uptake from humid air after cleaning CF_x polymer from SiOCH with Ar/O_2 and He/H_2 plasmas. This study is a follow-up to a more general investigation of damage mechanisms of SiOCH by plasma cleaning (including VUV photons) discussed in Part I.[22] The change in the dielectric constant of the SiOCH was assessed based on the amount of water adsorbed during exposure to the humid air.

The reaction mechanism for damage of SiOCH in Ar/O_2 and He/H_2 is discussed in Part I,[22] and so will be only briefly reviewed in Sec. II along with the mechanism for water uptake and increase in dielectric constant. A comparison of low-*k* degradation (that is, increase in dielectric constant of SiOCH) after Ar/O_2 and He/H_2 plasma cleaning is discussed in Sec. III and preservation of low-*k* properties by pore sealing is discussed in Sec. IV. Comparison of our results with experiments is in Sec. V and our concluding remarks are in Sec. VI.

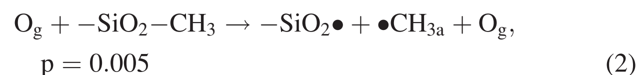
II. SURFACE REACTION MECHANISMS

Reaction mechanisms were developed for plasmas sustained in He/H_2 and Ar/O_2 mixtures and their interactions with porous SiOCH, and are discussed in detail in Part I.[22] In this work, reactions were included with H_2O molecules diffusing into the SiOCH from humid air and assessments were made of the change in dielectric constant of the SiOCH based on the amount of water in the pores. As in Part I, the Hybrid Plasma Equipment Model was employed to obtain the energy and angular distributions of fluxes of charged and neutral species, and of photon fluxes, incident onto the surface.[23] These fluxes and the reaction mechanisms were implemented in the Monte Carlo Feature Profile Model (MCFPM) with which the evolution of the SiOCH properties are predicted.[24] The MCFPM resolves the porous material with approximately atomic resolution. The cell size in this work is square with $0.4\ nm \times 0.4\ nm$ dimensions, which is an effective radius of 0.2 nm. The creation of pores in the MCFPM mesh is discussed in Ref. 25. The internal surfaces of the pores in SiO_2 were lined with a single layer of $–CH_3$ to approximate the structure of SiOCH as discussed in Ref. 26.

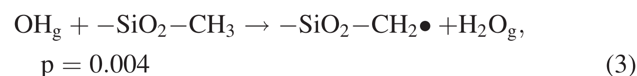
When SiOCH is processed in an O_2 containing plasma, the carbon in $–CH_3$ groups is etched as CO/CO_2 from sites below the surface which O atoms reach by diffusion through the interconnected porous network.[12,27,28] Photons produced by the plasma having wavelengths of <145 nm and penetrating into the SiOCH can break the Si–C bond and initiate a series of reactions starting with production of an adsorbed or trapped $\bullet CH_{3a}$ radical which is removed by further reaction with O and O_2.[15,16] The dominant reactions for methyl group removal or demethylation in O_2 plasmas are discussed in Part I and are summarized as[12,15,22,27–29]



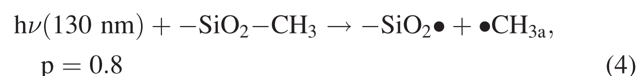
$$O_g + -SiO_2-CH_3 \rightarrow -SiO_2-CH_2\bullet + OH_g, \quad p = 0.005 \tag{1}$$



$$O_g + -SiO_2-CH_3 \rightarrow -SiO_2\bullet + \bullet CH_{3a} + O_g, \quad p = 0.005 \tag{2}$$



$$OH_g + -SiO_2-CH_3 \rightarrow -SiO_2-CH_2\bullet + H_2O_g, \quad p = 0.004 \tag{3}$$



$$h\nu(130\ nm) + -SiO_2-CH_3 \rightarrow -SiO_2\bullet + \bullet CH_{3a}, \quad p = 0.8 \tag{4}$$

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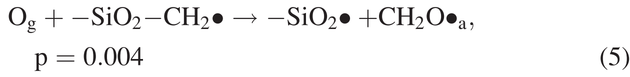
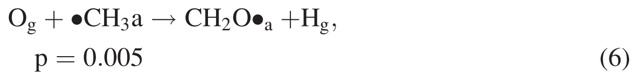

$$O_g + -SiO_2-CH_2\bullet \rightarrow -SiO_2\bullet + CH_2O\bullet_a, \quad p = 0.004 \tag{5}$$

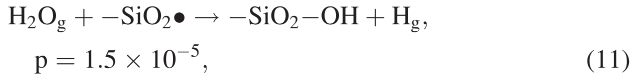

$$O_g + \bullet CH_3a \rightarrow CH_2O\bullet_a + H_g, \quad p = 0.005 \tag{6}$$

$$O_g + CH_2O\bullet_a \rightarrow CO_g + H_2O_g, \quad p = 0.004 \tag{7}$$

$$O_{2g} + CH_2O\bullet_a \rightarrow CO_{2g} + H_2O_g, \quad p = 0.004 \tag{8}$$

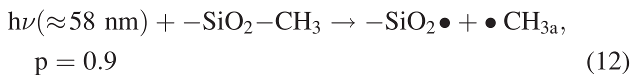
$$O_{2g} + \bullet CH_{3a} \rightarrow CH_2O\bullet_a + OH_g, \quad p = 0.004 \tag{9}$$

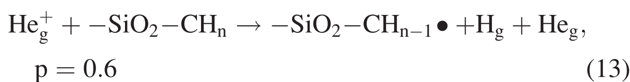
$$O_{2g} + CH_2O\bullet_a \rightarrow CO_{2g} + H_2O_g, \quad p = 0.004 \tag{10}$$

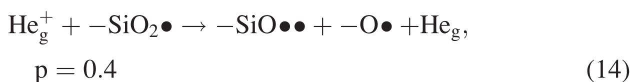

$$H_2O_g + -SiO_2\bullet \rightarrow -SiO_2-OH + H_g, \quad p = 1.5 \times 10^{-5}, \tag{11}$$

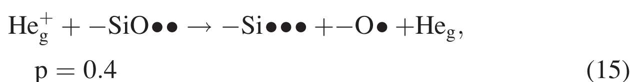
where the probability of reaction is p. Subscript "g" denotes a gas phase species, subscript "a" denotes an adsorbed or trapped species, the symbol "•" represents a dangling bond or free radical site, and a preceding "–"represents bonding to the solid. The number of "•" symbols denotes the number of dangling bonds. Note that there is a chain reaction possibility where H abstraction by O or OH from $–SiO_2–CH_3$ produces OH or H_2O which can further react in the demethylation process.

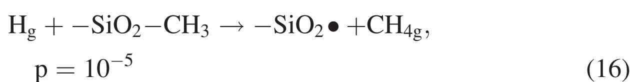
He/H_2 plasmas remove $–CH_3$ groups from SiOCH at a slower rate primarily because the reactions for $–CH_3$ removal are either endothermic or have lower probabilities than in Ar/O_2 plasmas, and the reaction products are themselves less reactive. As a result, photons from He/H_2 plasmas which produce Si–C bond cleavage to separate $–CH_3$ from Si can greatly accelerate the demethylation by enabling the $\bullet CH_{3a}$ to be removed by H atoms as CH_4.[18,19,29] After $–CH_3$ removal from $–SiO_2–CH_3$, H atoms can passivate the free radical site $–SiO_2\bullet$ forming $–SiO_2–H$ where the H is bonded to Si. However, He^+ or photons can break the Si–O bond in $–SiO_2\bullet$ and generate another free radical site –SiO••, and a successive strike can produce –Si•••. H can passivate –Si••• as $–Si–H_n$ (n=1,2,3). $Si–H_n$ bonding is hydrophobic in nature and can block water uptake.[30] The analogous process in Ar/O_2 plasmas produce hydrophilic $–SiO_2–OH$ sites. The interaction between He/H_2 plasmas and SiCOH is discussed in Part I[22] and is summarized as[12,15,18,19,30]

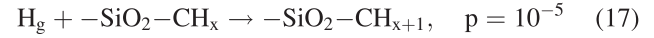

$$h\nu(\approx 58\text{ nm}) + -SiO_2-CH_3 \rightarrow -SiO_2\bullet + \bullet CH_{3a}, \quad p = 0.9 \tag{12}$$

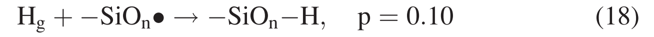

$$He^+_g + -SiO_2-CH_n \rightarrow -SiO_2-CH_{n-1}\bullet + H_g + He_g, \quad p = 0.6 \tag{13}$$


$$He^+_g + -SiO_2\bullet \rightarrow -SiO\bullet\bullet + -O\bullet + He_g, \quad p = 0.4 \tag{14}$$

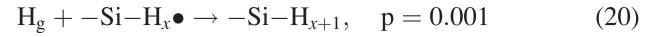

$$He^+_g + -SiO\bullet\bullet \rightarrow -Si\bullet\bullet\bullet + -O\bullet + He_g, \quad p = 0.4 \tag{15}$$

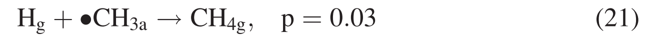

$$H_g + -SiO_2-CH_3 \rightarrow -SiO_2\bullet + CH_{4g}, \quad p = 10^{-5} \tag{16}$$

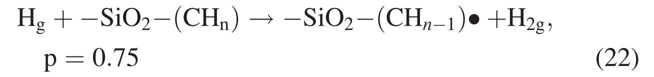

$$H_g + -SiO_2-CH_x \rightarrow -SiO_2-CH_{x+1}, \quad p = 10^{-5} \tag{17}$$


$$H_g + -SiO_n\bullet \rightarrow -SiO_n-H, \quad p = 0.10 \tag{18}$$

$$H_g + -Si\bullet\bullet\bullet \rightarrow -Si-H\bullet\bullet, \quad p = 0.01 \tag{19}$$


$$H_g + -Si-H_x\bullet \rightarrow -Si-H_{x+1}, \quad p = 0.001 \tag{20}$$

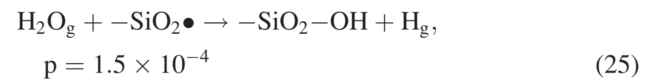

$$H_g + \bullet CH_{3a} \rightarrow CH_{4g}, \quad p = 0.03 \tag{21}$$

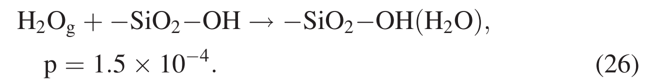

$$H_g + -SiO_2-(CH_n) \rightarrow -SiO_2-(CH_{n-1})\bullet + H_{2g}, \quad p = 0.75 \tag{22}$$

$$H_g + -O\bullet \rightarrow -OH, \quad p = 0.01. \tag{23}$$

After Ar/O_2 or He/H_2 plasma cleaning and upon exposure to humid air, free radical ($–SiO_2\bullet$) or passivated ($–SiO_2–OH$) sites formed after $–CH_3$ removal can react with water. Any remaining $\bullet CH_{3a}$ generated by photon produced Si–C bond scission in $–SiO_2–CH_3$ can also be etched by H_2O. The general sequence of events is that $–SiO_2\bullet$ on the pore-walls react with H_2O to form hydrophilic $–SiO_2–OH$. Additional water uptake can occur by reaction of $–SiO_2–OH$ with H_2O to form hydrogen bonded $–SiO_2–OH(H_2O)$. The volume averaged uptake of H_2O with its dielectric constant of 80 results in an increase of the dielectric constant of the SiOCH and a degradation of the low-k properties. These reactions are summarized as[7–9,15]

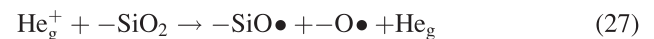
$$H_2O_g + \bullet CH_{3a} \rightarrow CH_{4g} + OH_g, \quad p = 1.2 \times 10^{-4} \tag{24}$$


$$H_2O_g + -SiO_2\bullet \rightarrow -SiO_2-OH + H_g, \quad p = 1.5 \times 10^{-4} \tag{25}$$

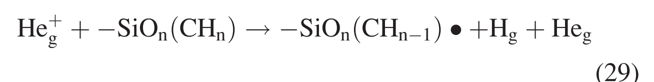

$$H_2O_g + -SiO_2-OH \rightarrow -SiO_2-OH(H_2O), \quad p = 1.5 \times 10^{-4}. \tag{26}$$

The OH_g produced during water exposure can then initiate reactions as discussed above for Ar/O_2 plasma cleaning. Computationally, water exposure was addressed in the following manner. Fluxes of H_2O and O_2 commensurate with humid atmospheric pressure air were directed toward the surface of the SiOCH with trajectories randomly chosen isotropically in angle and from a Maxwellian velocity distribution for room temperature. Gas phase collisions were included but are unimportant for the size of porosity we are addressing. The method of computation was otherwise identical to that for low pressure processing.

During the He/H_2 plasma cleaning step, active sites are produced that assist in pore sealing during a subsequent Ar/NH_3 plasma treatment.[18–20] He^+ and VUV photons break Si–O bonds and remove H from $–CH_3$ groups lining the pores to create the active sites. The bond breaking and site activation reactions are summarized as[18–20,26]


$$He^+_g + -SiO_2 \rightarrow -SiO\bullet + -O\bullet + He_g \tag{27}$$

$$h\nu + -SiO_2 \rightarrow -SiO\bullet + -O\bullet \tag{28}$$


$$He^+_g + -SiO_n(CH_n) \rightarrow -SiO_n(CH_{n-1})\bullet + H_g + He_g \tag{29}$$

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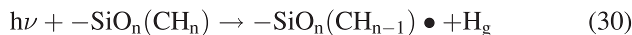
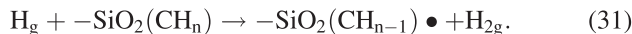
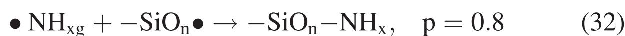


$$h\nu + -\mathrm{SiO_n(CH_n)} \rightarrow -\mathrm{SiO_n(CH_{n-1})} \bullet + \mathrm{H_g} \tag{30}$$

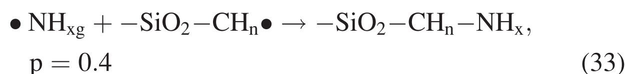


$$\mathrm{H_g} + -\mathrm{SiO_2(CH_n)} \rightarrow -\mathrm{SiO_2(CH_{n-1})} \bullet + \mathrm{H_{2g}}. \tag{31}$$

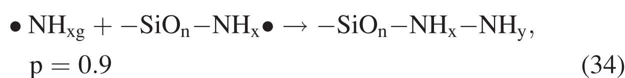
Following He/H_2 plasma treatment, NH_n ($n = 1{,}2$) species created in Ar/NH_3 plasmas are chemisorbed at activated sites on SiOCH forming Si–N and C–N bonds.[18–20,26] Chemical reactions between NH_x radicals and activated Si sites produce compounds such as –Si–NH_n ($n = 1{,}2$), –Si–NH–Si– and $SiNH_x$–NH_y. In SiOCH, C–N bonding is also possible forming –CH_x–NH_y compounds which are important in bridging and sealing the pore openings. The model treats these chemisorbed species as precursors to further adsorption of NH_x which form N–N bonds linking C or Si atoms from opposite pore walls. This N–N bonding results in, for example, –Si(HN)–(NH)(CH_n)Si– bridging compounds across pores. Our reaction mechanism for sealing SiOCH is discussed in detail in Ref. 26, and is summarized as[18]



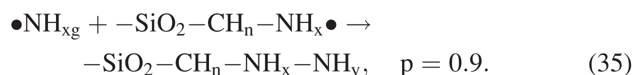
$$\bullet\mathrm{NH_{xg}} + -\mathrm{SiO_n}\bullet \rightarrow -\mathrm{SiO_n}-\mathrm{NH_x}, \quad p = 0.8 \tag{32}$$



$$\bullet\mathrm{NH_{xg}} + -\mathrm{SiO_2}-\mathrm{CH_n}\bullet \rightarrow -\mathrm{SiO_2}-\mathrm{CH_n}-\mathrm{NH_x}, \quad p = 0.4 \tag{33}$$



$$\bullet\mathrm{NH_{xg}} + -\mathrm{SiO_n}-\mathrm{NH_x}\bullet \rightarrow -\mathrm{SiO_n}-\mathrm{NH_x}-\mathrm{NH_y}, \quad p = 0.9 \tag{34}$$



$$\bullet\mathrm{NH_{xg}} + -\mathrm{SiO_2}-\mathrm{CH_n}-\mathrm{NH_x}\bullet \rightarrow -\mathrm{SiO_2}-\mathrm{CH_n}-\mathrm{NH_x}-\mathrm{NH_y}, \quad p = 0.9. \tag{35}$$

Such a sealing layer can prevent H_2O molecules from entering the porous network and so reduce the degree of low-k degradation. Experimentally, it has been observed that after such sealing, humid air exposure does not significantly increase the fractional water volume compared to pristine SiOCH.[19] This result also indicates that H_2O from humid air does not react with –NH_x compounds to remove the sealing layer.

Prior to plasma exposure, pristine SiOCH typically contains $<2\%$ of physisorbed H_2O which can be removed by moderate heating ($\approx 200\,^\circ C$) without otherwise detrimentally affecting the material.[1,2,19] As a result, in our model, there is no adsorbed water nor hydrophilic groups present in the porous volume before plasma treatment. The consequences of water uptake are measured by the effective dielectric constant of SiOCH, k', which accounts for the volume fraction of the water and the porosity after humid air exposure[31]

$$k_P = k_W \frac{2k_A + \dfrac{V_W}{V_P}(k_W - k_A)}{2k_W - \dfrac{V_W}{V_P}(k_W - k_A)}. \tag{36}$$

$$k' = k_S \frac{k_S + k_P + V_P(k_P - k_S)}{k_S + k_P - V_P(k_P - k_S)}. \tag{37}$$

where dielectric constants are k_W for water (80), k_A for air (1.0), k_P for a pore, and k_S for nonporous SiOCH (≈ 3.2). V_P is the volume fraction of pores and V_W is the volume fraction of water. k' as a function of water volume V_W is shown in Fig. 1 for a porosity $V_P = 30\%$. An increase in V_W of even a few percent for a given porosity increases k' by significant amounts, in this case to a dielectric constant of 5 for $V_W = 6\%$.

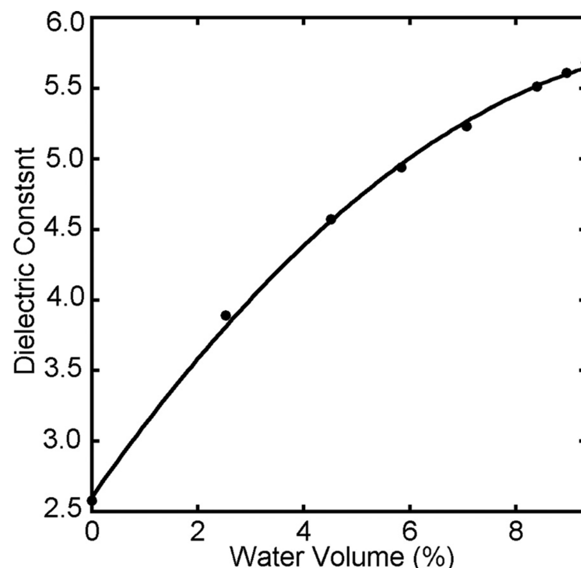


FIG. 1. Typical dependence of dielectric constant of SiOCH as a function of adsorbed water volume.

The plasma conditions are the same as in Part I.[22] The inductively coupled plasmas (ICPs) treated a wafer 15 cm in diameter. The reactor was 26 cm in diameter with a wafer-to-coil height of 10 cm. The gas mixtures were $Ar/O_2 = 5/95$ and $He/H_2 = 75/25$ at a pressure of 10 mTorr, flow rate of 100 sccm, and ICP power of 300 W applied at 10 MHz. An rf bias at 10 MHz with amplitude of 20 V was used. The base case properties of the SiOCH are a porosity of 30%, pore radius of 0.8 nm with standard deviation of 10%, and interconnectivity of 100%. This results in a dielectric constant of $k = 2.55$.

The probabilities for surface site modification, –CH_3 etching reactions and sealing have been determined by extensive parameterization of the models to be qualitatively consistent with experimental results available in the literature. The mechanism for demethylation is described in Part I[22] and for sealing in Ref. 26. Bounds of reaction probabilities are set based on thermodynamic properties and change in enthalpy of reactions, and within those bounds parameterization and comparison to experiments refine the mechanism. Although the majority of these reactions have a dependence on substrate temperature, our mechanism assumes a fixed substrate temperature of 300 K while including energy dependencies for gas phase radicals. Some examples of works that guided the development of the reaction mechanisms and validation are discussed in Sec. VI.

III. LOW-k DEGRADATION: Ar/O_2 AND He/H_2 CLEANING

We treated the pristine porous SiOCH of Fig. 2(a) separately with 800 s exposure to Ar/O_2 and He/H_2 plasmas. The Ar/O_2 plasma etched the –CH_3 groups to ≈ 30 nm depth

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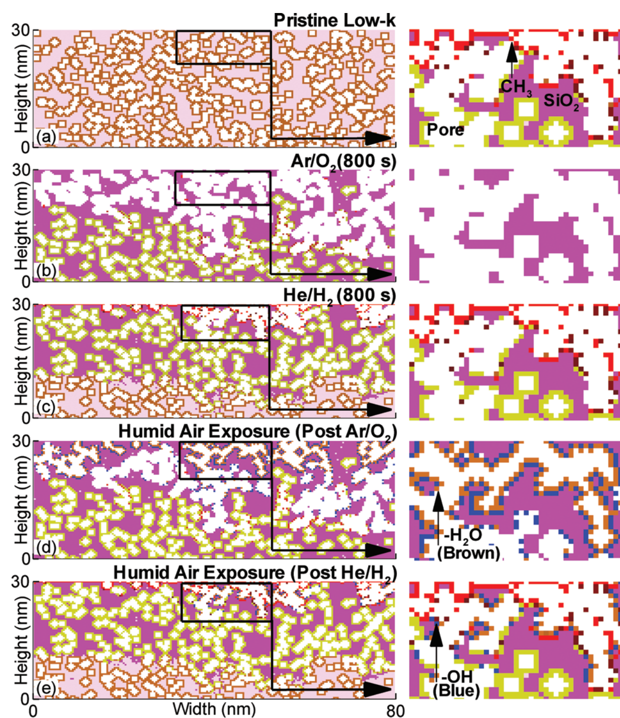
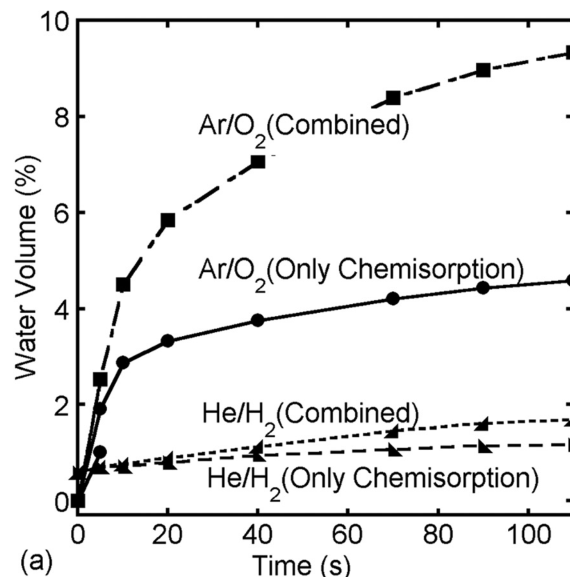


FIG. 2. (Color) Demethylation of SiOCH during Ar/O_2 and He/H_2 plasma treatment and water uptake following treatment. (a) Pristine SiOCH, (b) after 800 s of treatment by Ar/O_2 plasma, (c) after 800 s of He/H_2 plasma treatment, (d) Ar/O_2 plasma treated profile after 120 s exposure to 2% humid air, and (e) He/H_2 treated profile after 120 s exposure to 2% humid air. Sites having lost $–CH_3$ adsorb water when exposed to humid air and form $–SiO_2–OH(H_2O)$. [Color coding: light pink, SiO_2; brown, $–CH_3$; bright pink, cleaved SiO_2*; olive, $\bullet CH_{3a}$ sites after Si–C scission; blue, –OH; brown, hydrogen bonded H_2O (to OH).]

while the maximum etching depth for He/H_2 plasmas was ≈10 nm. After plasma exposure, the SiOCH was exposed to air having 2% humidity for 120 s. The profiles of the pristine SiOCH after plasma exposure and humid air exposure are shown in Fig. 2. Water uptake and dielectric constant as a function of air exposure time are shown in Fig. 3. After this exposure to humid air, the total $V_W = 9\%$ after Ar/O_2 plasma treatment, and after He/H_2 plasma treatment $V_W = 2\%$.

The V_W is composed to two components: chemisorbed $–SiO_2–OH$ and hydrogen bonded $–SiO_2–OH(H_2O)$. In $–SiO_2–OH$, the –OH is chemically bonded to $–SiO_2$ (bond strength 8.3 eV) and so is not removable by heating without damaging the SiOCH.[1] On the other hand, physisorbed hydrogen bonded H_2O can be driven out from the SiOCH with heating to 200–300 °C without damaging the substrate.[1] The water uptake after Ar/O_2 plasma exposure is roughly half chemisorbed and half physisorbed. After He/H_2 plasma exposure, the majority of water is chemisorbed. The higher water volume after Ar/O_2 plasma treatment is due to the higher rate of demethylation, leaving more Si• free radical sites which chemically bond OH. Since $–CH_3$ removal from $–SiO_2–CH_3$ is the precondition for chemisorbed water uptake or $–SiO_2–OH$ formation, water adsorption is proportional to the fraction of $–CH_3$ groups removed. Since Ar/O_2 plasmas produce more free radical sites through $–CH_3$ removal than He/H_2 plasmas, SiOCH cleaned by Ar/O_2 plasmas adsorbed more water. After a critical amount of water adsorption, the increase in V_W as a function of time slows. This is in part due to the blocking of pore openings by $–SiO_2–OH–(H_2O)$.



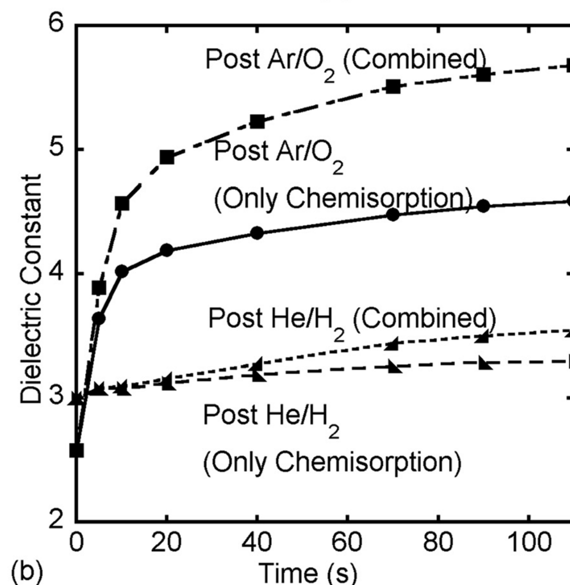


FIG. 3. SiOCH properties after plasma cleaning and exposure to humid air. (a) Adsorbed water volume after cleaning as a function of time. (b) Increase in dielectric constant k as a function of time due to water uptake. Chemisorbed water is $SiO_2–OH$ while the total includes the contribution of chemisorption and hydrogen bonded water $SiO_2–OH(H_2O)$. The increase in water volume and k slows with time as $–SiO_2–OH(H_2O)$ compounds block the pore openings.

With the increase in V_W, there is an accompanying increase in dielectric constant—from 2.55 to 5.5 for Ar/O_2 plasma cleaning, and from 2.55 to 3.5 for He/H_2 plasma cleaning. The proportions of these increases that are attributable to chemisorbed $–SiO_2–OH$ and hydrogen bonded $–SiO_2–OH(H_2O)$ are shown in Fig. 3(b). About 60% of the increase in the dielectric constant (to 4.5) following Ar/O_2 plasma exposure is attributable to chemisorption with the

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remaining increase due to hydrogen bonded H_2O, the latter of which is in principle reversible by heating. Of the increase in k to 3.5 for He/H_2 plasma cleans, the increase attributable to $–SiO_2–OH$ is 3.25. As such, the irreversible increase in k is only 0.25.

We deposited an ≈10 nm thick CF_x polymer layer on the top surface of SiOCH using a capacitively coupled plasma sustained in an $Ar/C_4F_8/O_2 = 80/2015/5$ mixture at 40 mTorr, as shown in Fig. 4(a). The conditions are the same as in Part I[22] except operating at a lower bias to prevent etching. The polymer layer was then removed with a short 20 s exposure to either the Ar/O_2 or He/H_2 plasmas. The short exposure was long enough to remove the polymer layer but not long enough to produce deep damage into the SiOCH by diffusion of radicals. The concurrent flux of 10^{16} cm^{-2} s^{-1} of photons from the plasmas produces Si–C bond scission deeper into the SiOCH than the plasma damage produced by O or H radicals. During subsequent humid air exposure, H_2O molecules etch adsorbed $\bullet CH_{3a}$ and passivate the $–SiO_2\bullet$ free radical sites to form $–SiO_2–OH$ and $–SiO_2–OH(H_2O)$, as shown in Fig. 4, which increases the dielectric constant k. This is an example of where photon penetration into the SiOCH, even in the absence of further reactions with radicals from the plasma, can lead to low-k degradation by humid air exposure.

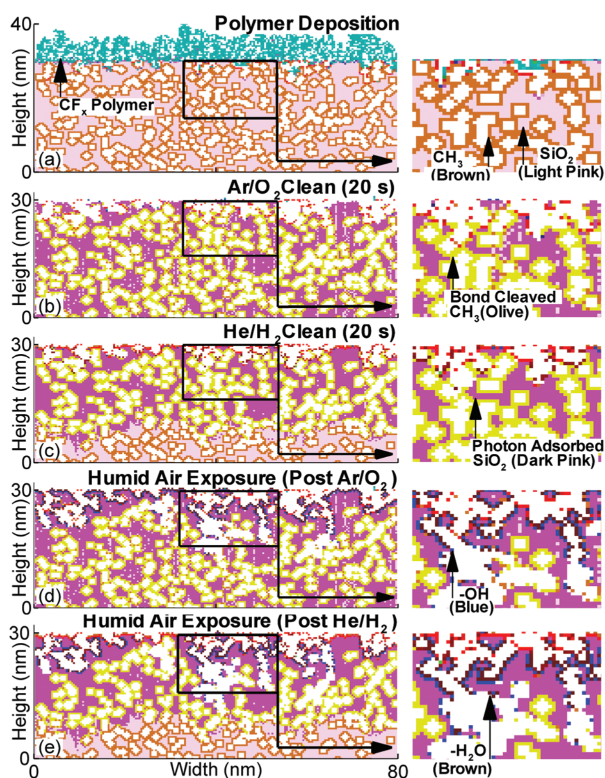

FIG. 4. (Color) CF_x polymer cleaning from flat SiOCH. (a) Initial material with deposited CF_x polymer. CF_x polymer removal with 20 s (b) Ar/O_2 and (c) He/H_2 plasma cleaning. Post cleaning profiles following 120 s of 2% humid air for (d) Ar/O_2 and (e) He/H_2 plasma cleaning. [Color coding: light pink, SiO_2; brown, $–CH_3$; bright pink, cleaved SiO_2*; olive, $\bullet CH_{3a}$ sites after Si–C scission; blue, –OH; brown, hydrogen bonded H_2O (to OH); cyan, CF_x polymer.]

IV. MAINTAINING LOW-*k* INTEGRITY BY PORE SEALING

We investigated the consequences on water uptake of pore sealing using Ar/NH_3 plasmas as a means of preserving low-k integrity.[18–20,26] The procedure and processes for pore sealing using Ar/NH_3 plasmas are discussed in Sec. II and Ref. 26. After an Ar/O_2 plasma clean, we treated the SiOCH with a He plasma for ≈30 s to activate surface sites [Reactions (27)–(30)] and then to an Ar/NH_3 plasma for 30 s to seal the pores [Reactions (31)–(35)]. Ar/O_2 treated SiOCH profiles after surface activation and sealing are shown in Fig. 5(a). Surface pore blocking sites [olive-green in Fig. 5(a)] are Si–N and C–N compounds which are formed during NH_3 plasma exposure. Approximately 70% of the surface pores are sealed.

For He/H_2 plasma cleaning, the photon and ion fluxes are able to activate the surface in the absence of an additional He plasma activation step. Moreover, He/H_2 plasmas produce hot H atoms that are capable of abstracting H from $–SiO_2(CH_n)$ producing $–SiO_2(CH_{n-1})\bullet$, a precursor to sealing. As a result, the Ar/NH_3 plasma sealing step was performed directly after the He/H_2 plasma cleaning step. The Ar/NH_3 plasma sealed profile after He/H_2 plasma cleaning is shown in Fig. 5(b). Approximately 90% of the surface pores were sealed.

After pore sealing by the Ar/NH_3 plasma, Si–N and C–N compounds which bridge the pore openings block the pathways through which water molecules diffuse to enter the

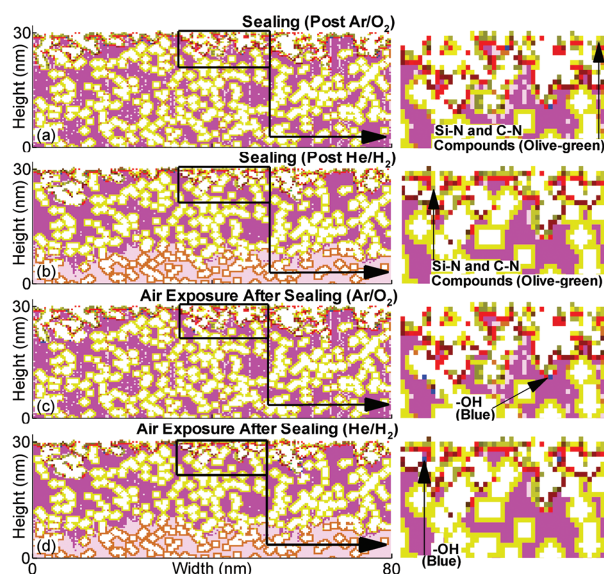

FIG. 5. (Color) Consequences of pore sealing with an Ar/NH_3 plasma. (a) NH_3 plasma sealed and Ar/O_2 plasma cleaned profile where a 30 s He plasma pretreatment was used for surface activation before the sealing step. (b) NH_3 plasma sealed and He/H_2 plasma cleaned profile. (c) Ar/O_2 plasma cleaned and sealed profile, and (d) He/H_2 plasma cleaned and sealed profile following 120 s of 2% humid air exposure. After sealing, most of the pore openings in the surface are blocked by Si–N or C–N compounds and no significant water uptake was observed (blue sites indicate –OH) during humid air exposure. [Color coding: light pink, SiO_2; brown, $–CH_3$; bright pink, cleaved SiO_2*; olive, $\bullet CH_{3a}$ sites after Si–C scission; blue, –OH; brown, hydrogen bonded H_2O (to OH); cyan, CF_x polymer; olive-green (near porous surface), Si–N and C–N compounds responsible for pore sealing.]

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SiOCH. The only significant water adsorption is on the top surface, as shown in Figs. 5(c) and 5(d). The volume of adsorbed water and dielectric constant when using both cleaning methods with and without sealing are shown in Fig. 6. Low-*k* degradation after pore sealing was not significant for either of the cleaning methods. The increase in dielectric constant was from 2.55 to no more than 2.7. The small increase in the dielectric constant resulted from incomplete sealing as the C–N and Si–N compounds are unable to bridge all of the pore openings. Although the average pore size is 0.8 nm which is in principle sealable by this method, the statistical variation in pore size produces some pores having sizes that exceed the sealable limit (about 1.1 nm). Also, during cleaning of the polymer, the plasmas remove $–CH_3$ groups from surface pores which enlarge the pore opening. As a result, there are a few pores (in this case, about 30% for the Ar/O_2 plasma clean and 10% for the He/H_2 plasma clean) which remain unsealed and which provide a pathway for H_2O molecules to diffuse into the SiOCH.[26] This effect will become more severe as the pore sizes increase and the fraction of pores that are sealed decreases.

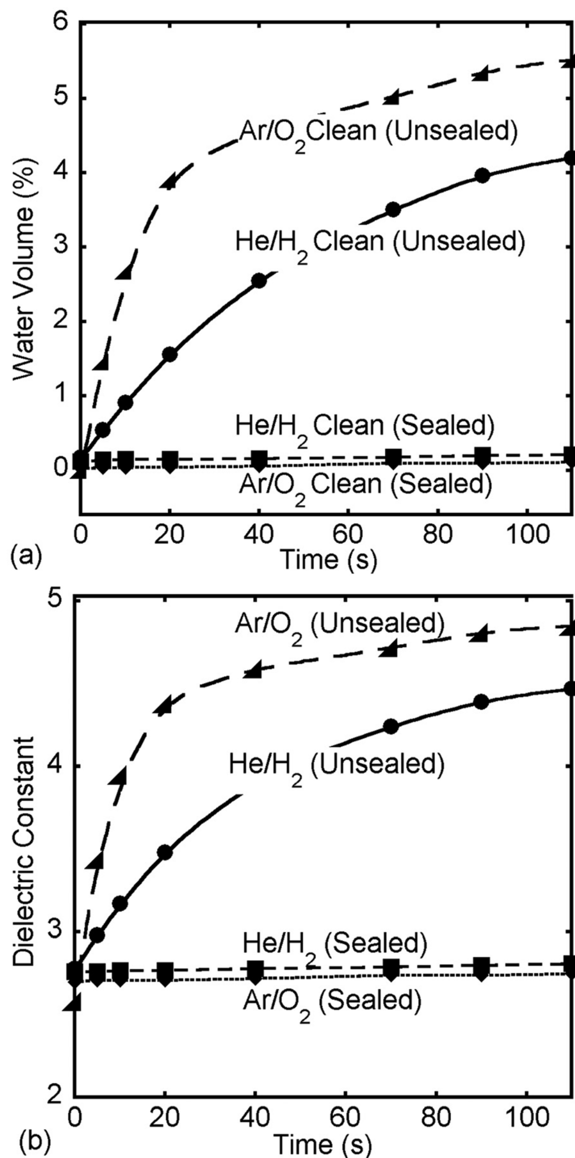

FIG. 6. Water uptake and *k* degradation by humid air in post-plasma cleaned SiOCH when sealed and unsealed for the conditions of Fig. 5: (a) adsorbed water volume and (b) dielectric constant. NH_3 plasma sealing was able to block the pathways through which H_2O molecules enter into the lattice.

V. COMPARISON WITH EXPERIMENTAL TRENDS

The details of water uptake and increase in dielectric constant following humid air exposure of plasma damaged SiOCH depend on the precise processing steps and properties of the SiOCH (e.g., structure, porosity, interconnectivity). As a result, direct comparisons with experiments are difficult. However, trends from the experiments are useful for qualitative validation of the model. The general trends observed in experiments are that oxygen containing plasma exposure of SiOCH followed by exposure to air can produce significant increases in the *k*-value of the SiOCH. For example, Maex *et al.*[1] exposed SiOCH to an O_2 plasma (300 mTorr, rf power 300 W, 300 °C) for 9 min, and upon exposure to air (humidity not specified), the *k*-value increased from 2 to 20.[1] This is a larger increase that we predict, perhaps attributable to the elevated substrate temperature during plasma exposure, 300 °C, which may accelerate S–C bond scission by O atoms. Our computed trends of more water uptake following Ar/O_2 plasma exposure compared to He/H_2 plasmas correlate with experimental observations of damage in these systems. C depletion in Ar/O_2 plasmas, which is the precursor to water adsorption, is 3–5 times more severe compared to He/H_2 plasmas.[12] Urbanowicz *et al.* found that He plasma pretreatment followed by a NH_3 plasma was able to seal SiOCH pores to sufficient degree to block water uptake from humid air—no low-*k* degradation was observed.[19] We also found that after plasma sealing for both of the cleaning methods, the uptake of water was insignificant.

It has been reported that for a porosity of ≈30%, the fractional volume of adsorbed water at first increases with an increase in humidity for a humidity range of 0–15%. The rate of increase slows when the water volume is >10%.[31] Fractional water volume and dielectric constant following 800 s of Ar/O_2 plasma treatment and humid air exposure are shown in Fig. 7 for a humidity of 0–7.5%. The water volume and dielectric constant at first rapidly increase and then saturate at $V_W = 8.3\%$ and $k = 5.6$. These trends are essentially the same as those observed by Kikkawa *et al.* where for a range of humidity of 0–10%, the dielectric constant increased to more than 4.[31] These trends are in part attributable to saturation of the available free radical sites produced by the plasma damage, and blocking of surface pores by $–SiO_2–OH(H_2O)$ that limit the amount of water uptake and *k* degradation.

Possemme *et al.*[32] investigated the carbon depletion and increase in *k*-value of SiOCH having a low 8% porosity (lp-SiOCH) and a high 45% porosity (hp-SiOCH) following plasma ashing in various gas mixtures. They found that increases in *k*-value were greatest with hp-SiOCH and O_2 containing plasmas, with the increases being correlated

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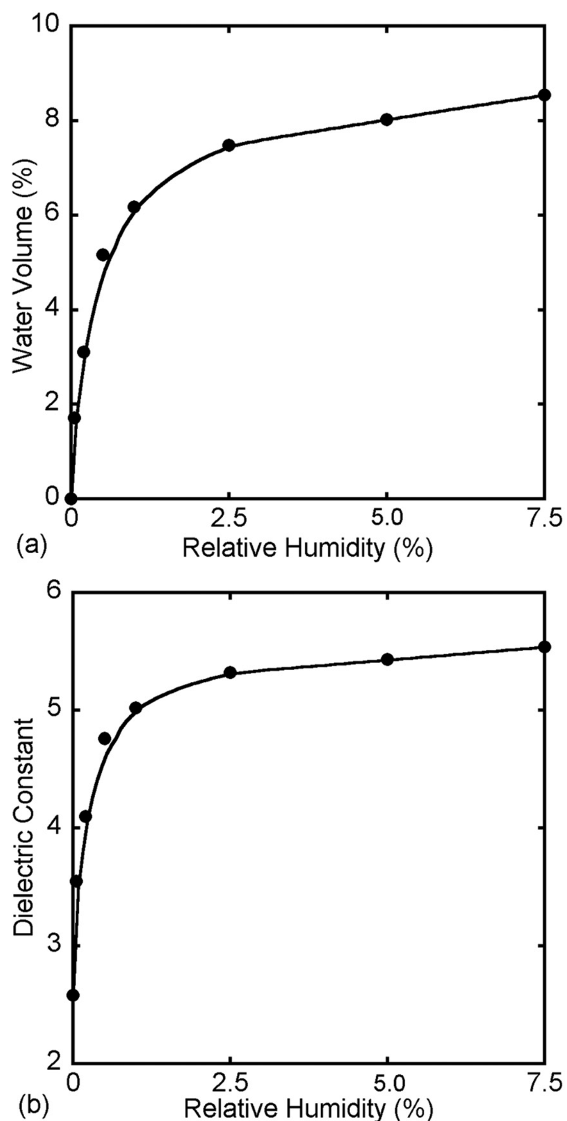

Fig. 7. Low-k degradation as a function of humidity when 800 s Ar/O_2 plasmas SiOCH was exposed to air: (a) adsorbed water volume and (b) dielectric as a function of humidity. Both water volume and k initially linearly increase with humidity initially and then saturate due, in part, to the blocking of pore openings by $–SiO_2–OH(H_2O)$ compounds.

dominantly with the water uptake by the hp-SiOCH and less correlated with carbon-depletion.

VI. CONCLUDING REMARKS

We computationally investigated low-k degradation by humid air after Ar/O_2 and He/H_2 plasma cleaning of porous SiOCH. Both of these cleaning methods remove hydrophobic $–CH_3$ groups from $–SiO_2–CH_3$ compounds creating free radical sites $–SiO_2$•. When these sites are exposed to H_2O from humid air, formation of $–SiO_2–OH$ and $–SiO_2–OH(H_2O)$ increases the dielectric constant. While hydrogen bonded H_2O can be removed by applying a moderate temperature (200–300 °C), the rise of k due to $–SiO_2–OH$ formation cannot be so easily reversed. Plasma cleaning using He/H_2 mixtures which less aggressively etch $–CH_3$ groups compared to Ar/O_2 plasmas will result in SiOCH adsorbing less water and will produce a smaller increase in dielectric constant. Even with short plasma exposure (short enough that plasma produced radicals do not diffuse deeply into the SiOCH), VUV photon fluxes are able to penetrate deeply below the surface, producing Si–C bond scission and free radical sites. These free radical sites will adsorb water upon exposure to air. Pore sealing using, for example, Ar/NH_3 plasmas which block water uptake, may be quite effective in maintaining the low-k integrity of the film.

ACKNOWLEDGMENT

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