Integration Challenges of Nanoporous Low Dielectric Constant Materials

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(Invited Paper)

***Abstract*—The reliable integration of nanoporous low dielectric constant (k) materials is challenging due to their vulnerability to delamination, cohesive cracking, and diffusion. We review selected reliability issues for the integration of nanoporous low-k dielectrics regarding UV curing, diffusion, and damage evolution. Depth-dependent UV curing by the UV standing wave effect is presented. It is demonstrated that significant enhancement in fracture energies at both interfaces of low-k films can be obtained by tailoring UV curing depth profiles and employing the underlying barrier as an optical spacer. The effects of nonionic surfactants on diffusion and damage evolution in nanoporous low-k films are discussed.**

***Index Terms*—Dielectric films, environmental testing, failure, reliability testing, ultraviolet radiation effects.**

I. Introduction

THE ADVANCES of ultralarge scale integrated circuits are being limited by the challenges in the development and reliable integration of new insulating materials with reduced dielectric constant k for Cu interconnects [1]. The reduction in the k value, which is critically required to mitigate the RC delay, has been achieved by decreasing density (increasing nanoporosity) [2], [3]. However, decreasing density significantly sacrificed the mechanical reliability of the nanoporous low-k materials: Adhesive and cohesive fracture resistance diminished (Fig. 1) and environment-assisted crack growth accelerated (Fig. 2) as density decreased [4]. Nanoporous low-k dielectrics with the compromised mechanical properties suffered delamination and cohesive cracking during harsh processes such as chemical mechanical planarization (CMP), wafer dicing, and packaging [4]–[10].

Another challenge that the introduction of porosity to the brittle low-k dielectrics incurred is molecular diffusion. The pores in nanoporous materials containing more than $\sim$20 vol.% porosity are nearly always interconnected and the films are frequently exposed to molecular species in process or service environments allowing permeation of the molecules [11], [12].

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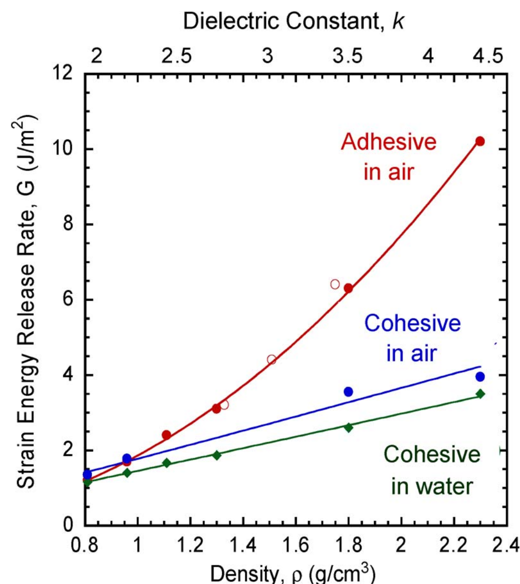

Fig. 1. Fracture resistance as a function of the density of organosilicate thin-film glasses. The dielectric constant corresponding to the density is also shown. Adhesive and cohesive fracture energies were measured using four-point bend and double cantilever beam specimens, respectively. Cohesive fracture energies in air and water were measured at a crack growth rate of 10^{-5} m/s (from [4]).

Organic molecules from CMP slurries were shown to diffuse readily in hydrophobic nanoporous low-k films, however nonclassically and very differently depending on their molecular weight and structure when confined in the interconnected nanopores [12]. Diffusion of reactive molecules such as water, hydroxide ion, and hydrogen peroxide is of great concern because they not only increase the k value [13] but also accelerate environment-assisted cracking [4]–[6].

Significant efforts have been directed to improving the mechanical properties of low-k films by postdeposition treatments such as thermal [14], plasma [15], e-beam [14], [16], and UV curing [14], [17]–[19]. UV curing has been demonstrated to significantly increase the elastic modulus, hardness, and fracture energy while inducing relatively minor increase in dielectric properties [14], [17]–[26]. However, the adhesive fracture energy at the bottom interface (with a Si substrate or a SiCN underlying layer on a Si substrate) and the cohesion in the middle of the low-k film are remarkably insensitive to UV curing compared to adhesion at the top interface irradiated by UV light [17], [19], [23]. We demonstrated the insensitivity

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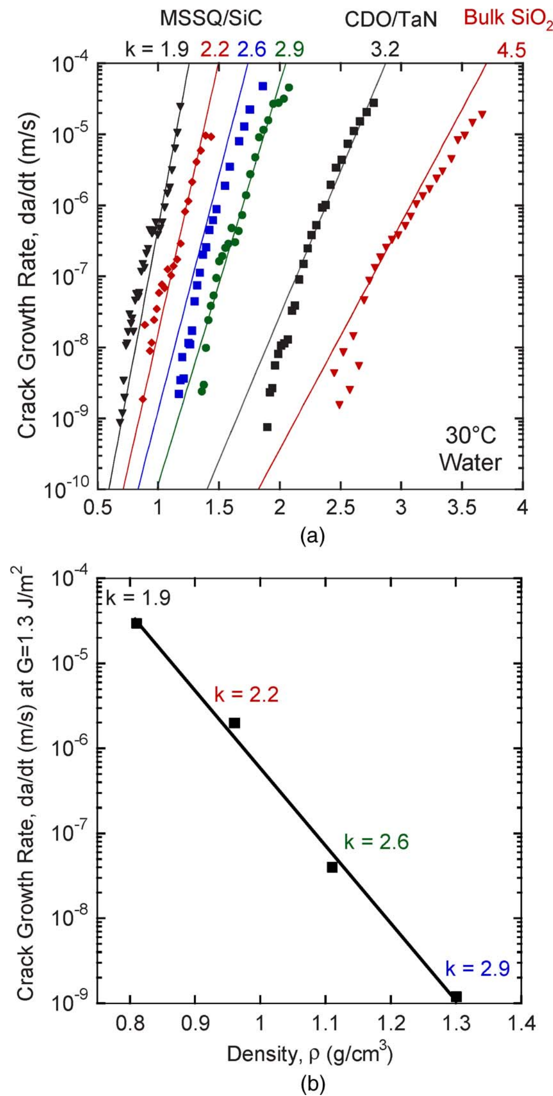

Fig. 2. Environment-assisted crack growth behavior for organosilicate films of varying density measured in water showing (a) the crack growth rate as a function of applied strain energy release rate G and (b) the crack growth rate at $G = 1.3$ J/m^2 as a function of density. Crack growth data for bulk silica were included for comparison. A 0.5 g/cm^3 decrease in film density resulted in over five orders of magnitude increase in crack growth rate (from [4]).

of the fracture energy at the bottom to UV curing is related to depth-dependent UV curing through the low-k film thickness by the UV standing wave effect [17], [19]. It was shown that UV light intensity at the bottom interface of the low-k film on a highly reflecting underlying layer has a minimum value due to destructive light interference, which leads to the relatively small increase in the fracture energy at the bottom by the UV curing.

Despite extensive efforts to improve mechanical properties of nanoporous low-k dielectrics, they are prone to easily fail in the form of cracking and delamination during CMP [4]–[10]. Damage evolution during CMP involves the synergistic effects of both process stress and chemistry, although damage has mostly been attributed to the effects of CMP stress [8], [27], [28]. Stresses arise not only from the abrasive contact with the rotating CMP pad but also from the inherent film stresses that arise from thermal expansion mismatch and film growth processes. While the effects of stress on fracture processes are

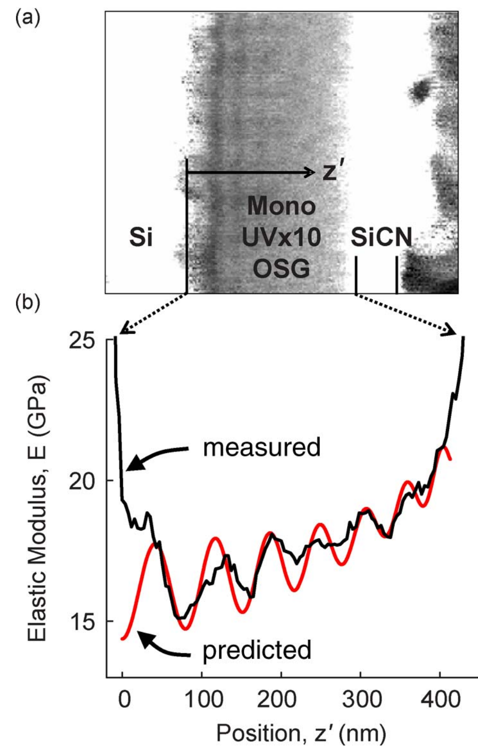

Fig. 3. (a) FM signal image of a cross section of a specimen containing a monochromatic UVx10 organosilicate film. White and black colors indicate high and low stiffness, respectively. (b) Elastic modulus depth profile of the monochromatic UVx10 film measured by FM-AFM is compared with predicted one by the standing wave simulation (from [19]).

well understood, it is not always appreciated that the chemistry of the process or service environments can greatly affect crack growth in thin-film structures. Even small changes in CMP slurry or post-CMP cleaning solution chemistry are known to have dramatic effects on resulting damage [4]–[6], [29], [30].

In this paper, we review selected reliability issues for the integration of nanoporous low-k dielectrics regarding UV curing, diffusion, and damage evolution. The depth-dependent UV curing by the UV standing wave effect is presented. It is demonstrated that significant enhancement in fracture energies at both interfaces of low-k films can be obtained by tailoring the UV curing depth profiles and employing the underlying barrier as an optical spacer. The effects of surfactants on diffusion and damage evolution in nanoporous low-k films are discussed.

II. UV Curing

Postdeposition UV curing of organosilicate glass (OSG) thin films has demonstrated the ability to significantly influence glass structure and improve mechanical properties such as elastic modulus, hardness, and fracture energy [14], [17]–[26]. The most significant changes in the glass structure are reduction in Si–CH_3 terminal groups and subsequent formation of Si–O network bonds characterized by Fourier transform infrared and nuclear magnetic resonance spectroscopies [23], [25], [26]. However, the adhesive fracture energy at the bottom interface and the cohesion in the middle of the OSG film are remarkably insensitive to UV curing compared to adhesion at the top interface [17], [19], [23].

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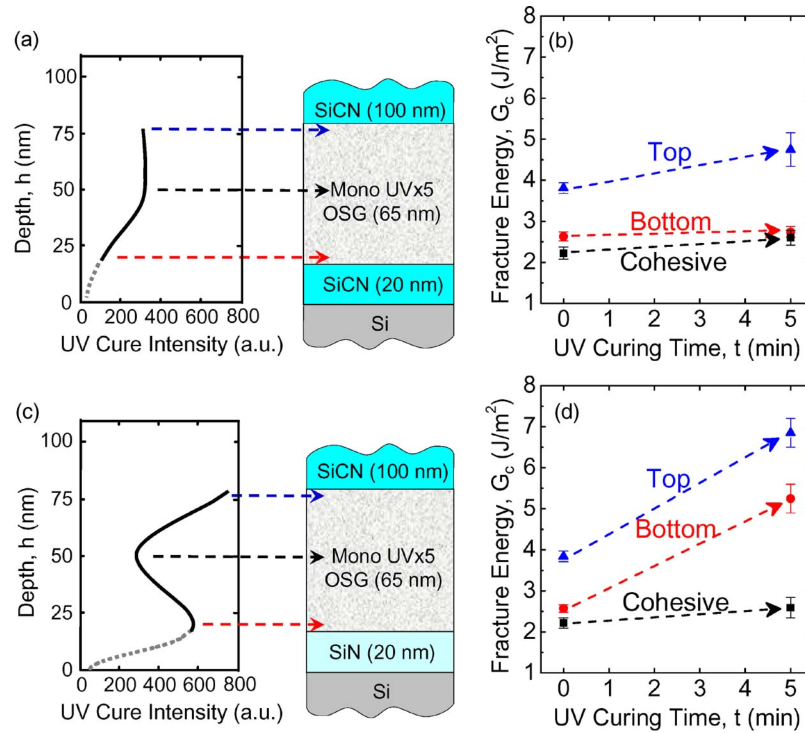

Fig. 4. Simulated UV cure intensity depth profiles in 65-nm-thick OSG deposited on (a) SiCN and (c) SiN, and measured fracture energies for the OSG on (b) SiCN and (d) SiN, respectively. Monochromatic UV light with a wavelength of 172 nm was used for the curing (from [31]).

It was demonstrated that the insensitivity of the fracture energy at the bottom to UV curing is related to depth-dependent UV curing through the OSG film thickness by the UV standing wave effect [17], [19]. UV light intensity at the bottom interface of the OSG on a highly reflecting underlying layer had a minimum value due to destructive light interference, which led to the relatively small increase in the fracture energy at the bottom by the UV curing. It was shown that the UV cure intensity at the bottom is a minimum regardless of whether the UV light is monochromatic or broadband, because the superposition of the standing waves of each wavelength which the UV spectrum consists of always results in the minimum intensity at the bottom by destructive light interference [19].

The nonuniform curing that resulted through the film thickness was apparent by observing a corresponding change in the elastic stiffness of the film [17], [19]. Force modulation atomic force microscopy (FM-AFM) technique was used to measure the oscillation of the elastic modulus through the film thickness of the monochromatic UV-cured OSG film [17], [19]. Fig. 3(a) shows the FM signal and the oscillation was so obvious that the modulus variations appeared visually as ripples parallel to the film plane. In Fig. 3(b), the measured elastic modulus was compared with the elastic modulus simulated by the standing wave model [19]. The model prediction matched the observed variations with surprising accuracy, which certainly implied that the depth-dependent UV curing was caused by the UV standing wave effect [19].

It was recently demonstrated how to maximize the UV light intensity and therefore the fracture energy at both top and bottom interfaces of the OSG film by exploiting the UV standing wave effect and an underlying barrier layer as an optical spacer [31]. A UV transparent SiN layer was used for the underlying optical spacer layer and compared to a UV-absorbing SiCN layer. Fig. 4 shows the simulated UV cure intensity depth profiles in a 65-nm-thick OSG film deposited on SiCN and SiN, respectively, and their measured fracture energies. As shown in the simulated UV cure intensity depth profile for the OSG on SiCN [Fig. 4(a)], UV cure intensity at the bottom is very small because of strong UV light absorption by the SiCN underlying layer. Consequently, fracture energy at the bottom was not improved by the UV curing, although fracture energy at the top increased noticeably [Fig. 4(b)]. On the contrary, the UV transparent SiN underlying layer had totally different results. The simulated UV cure intensity depth profile showed maximum UV cure intensities both at the top and bottom [Fig. 4(c)]. The measured fracture energy was dramatically increased not only at the top but also at the bottom [Fig. 4(d)]. A promising application of this paper is the possibility of fabricating films with graded mechanical and physical properties with a single postdeposition UV curing process.

III. Diffusion

The lateral solvent diffusion technique [32]–[37] was recently adopted to characterize the diffusion of CMP slurries and post-CMP cleaning solutions into nanoporous low-k thin films [11], [12], [36]. This technique was originally developed to study pore size and connectivity by observing the diffusion of solvent into porous films. The top surface of the film is first hermetically sealed with an optically transparent SiN or SiCN capping layer. The silicon substrates containing the films are cleaved to expose a fresh through-thickness surface of the film

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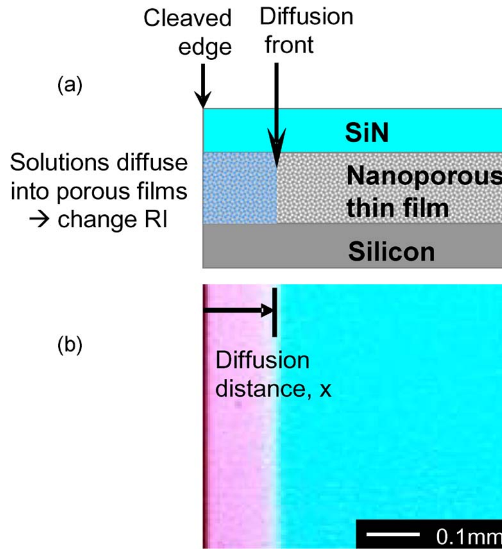

Fig. 5. Lateral solvent diffusion technique adopted to measure diffusion through a hydrophobic nanoporous thin film. (a) Schematic diagram of the cross-sectional view of a test specimen. (b) Optical image showing the change in color due to the diffusion of solutions into the films as a result of the change in refractive index (top down view) (from [12]).

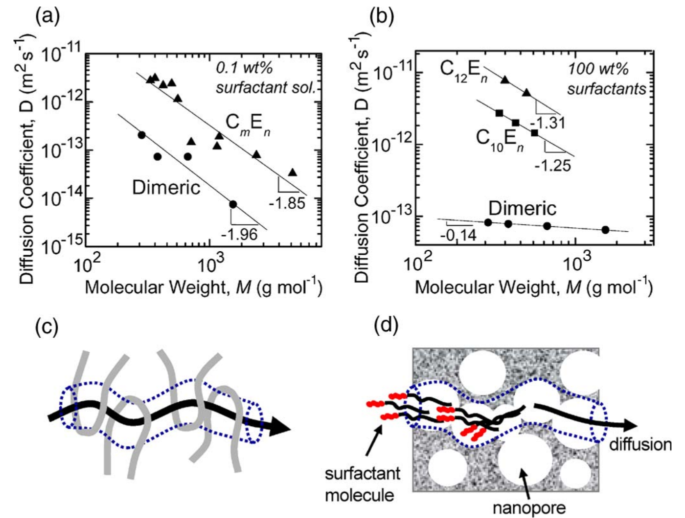

Fig. 6. Diffusion coefficients in terms of M in log-log scale for (a) 0.1 wt.% surfactant aqueous solutions and (b) 100 wt.% surfactants. Slopes were calculated from the linear fits. Schematic diagrams of diffusion by reptation: (c) the classical reptation model regards a polymer chain (a black solid line) in an entangled melt or concentrated solution as being within a virtual tube (dotted lines) defined by the locus of its intersections with other melt molecules (gray solid lines) and (d) short-chain surfactants diffuse through an real tube formed by interconnected nanopores in nanoporous glass (from [12]).

and immersed in the solution of interest [Fig. 5(a)]. Diffusion of the solution into the plane of the film from the freshly exposed film surface results in a change in the refractive index (RI) and color of the film that can be easily monitored by optical observation through the top surface of the films using an optical microscope [Fig. 5(b)]. Diffusion distance x is measured as a function of square root of diffusion time $t^{0.5}$. Generally, a linear relationship is observed, which is characteristic of 1-D Fickian diffusion with diffusion distance given by $x = (Dt)^{0.5}$, where D is the diffusion coefficient that can be calculated from the x versus $t^{0.5}$ plot [11], [12].

The lateral diffusion technique was used to measure diffusion coefficients of nonionic surfactants ubiquitously employed in a wide range of technologies [12]. For example, they are essential components of CMP slurries for emerging classes of nanoporous glass films where they are vital for the control of wetting, removal rate, slurry stability, and selectivity. In the case of nanoporous low-k films, molecular-assisted diffusion of such CMP slurries into the films can have dramatic effects on the resulting dielectric constant [11], [13], [36], [38], [39]. The behavior of surfactant molecules in these films was not well understood and the lack of the knowledge has generated the misconception that surfactants do not penetrate the films but adsorb on the film surface and simply assist water diffusion into the pores [13], [38], [39].

Surfactants were demonstrated to diffuse readily into nanoporous OSG films with pore sizes ≤ 2.1 nm [12]. Polyoxyethylene alkyl ethers (C_mE_n) with various hydrophobic alkyl tail lengths m and hydrophilic ethylene oxide head lengths n were selected as monomeric (linear) surfactants to systematically study the roles of the hydrophobic and hydrophilic group lengths in the diffusion. Dimeric (branched) surfactants were also tested to reveal the effect of the molecular structure of surfactants on the diffusion. The measured diffusion coefficients of the surfactants were found to be sensitive to molecular weight M, the chain lengths of hydrophilic and hydrophobic groups, and molecular structure of surfactants [Fig. 6(a) and (b)]. Moreover, the diffusion coefficients of the surfactant aqueous solutions in the nanoporous OSG films were nearly proportional to M^{-2}, as shown in Fig. 6(a). This coincided with the scaling-law predicted for molecular reptation where $D \sim M^{-2}$ which was proposed by de Gennes [40] to explain the motion of a polymer molecule in a concentrated (or molten) polymer network. According to the reptation model, the motion of polymer molecules above a critical entanglement length are confined within virtual tubes that are defined by the locus of intersections (or points of entanglement) with adjacent molecules [Fig. 6(c)] [41]. The motion of the surfactants that are well below the entanglement molecular weight do not exhibit reptation mobility as they are not long enough to provide entanglement confinement. However, instead of the fictitious tube anticipated in the reptation model [Fig. 6(c)], the short-chain surfactant molecules in the nanoporous glass films are physically confined in real tubes formed by interconnected nanometer-sized pores, exhibiting the reptation mobility [Fig. 6(d)].

IV. Damage Evolution

Damage in the form of cracking and delamination of low-k materials remains a significant challenge for the CMP processing of Cu interconnects in microelectronic devices [1]. The evolution of cracks in interconnect structures during CMP is a kinetic process involving the synergistic effects of process stress and chemistry, namely, environment-assisted crack growth [6], [29], [42], although damage has mostly been attributed to the effects of stress. However, chemical composition of the CMP slurry may have more significant effects on the growth of cracks and associated damage compared to

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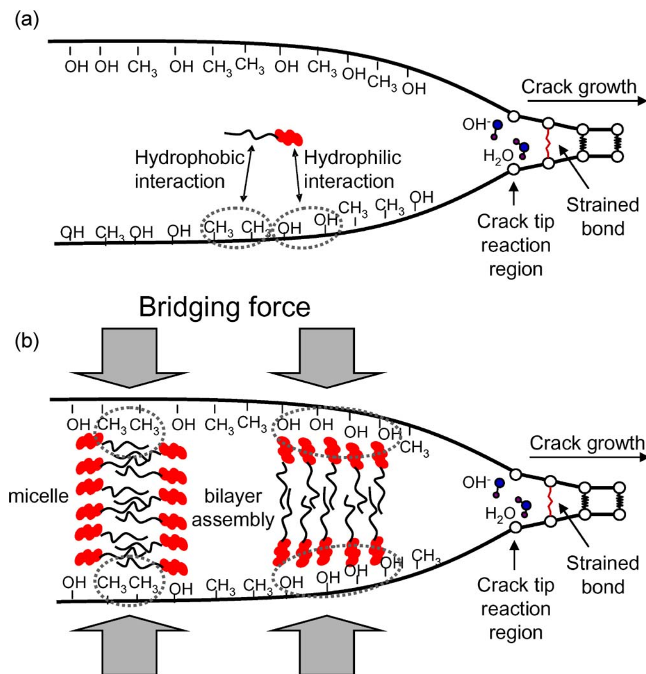

Fig. 7. Schematic illustration of (a) the interaction of a nonionic surfactant molecule with the OSG crack surfaces and (b) two possible surfactant micelle–bilayer bridging assemblies between the crack surfaces (from [7]).

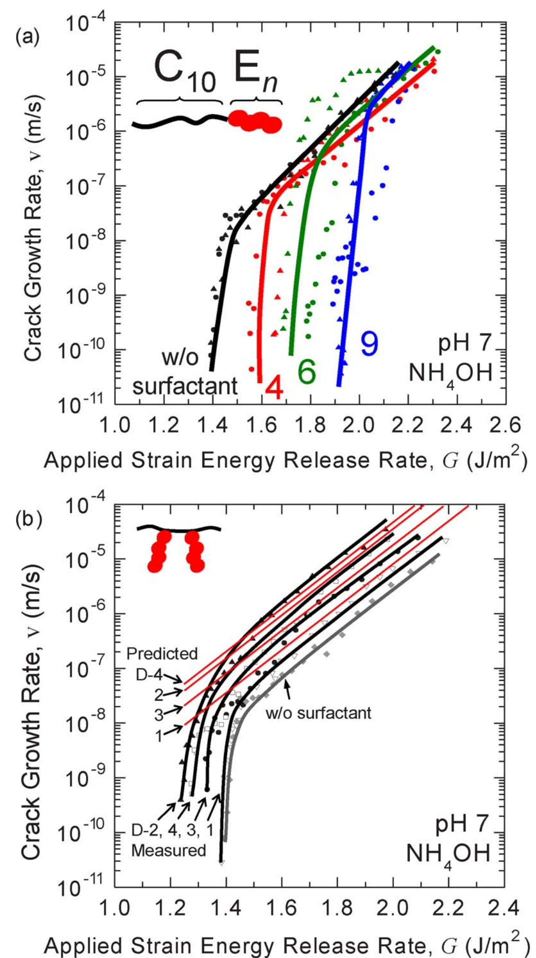

Fig. 8. Crack growth rates of a nanoporous OSG film as a function of G observed for pH 7 NH_4OH aqueous solutions with 0.1 wt.% of (a) $C_{10}E_n$ and (b) dimeric surfactants. Straight red lines in (b) show the predicted crack growth rates using the chemical reaction model (from [7]).

mechanical loads. Even small changes in CMP slurry or post-CMP cleaning solution chemistry are known to have dramatic effects on resulting damage [4]–[6], [29], [30]. Environment-assisted crack growth in OSG films is a time-dependent mode of fracture that involves a stress-enhanced chemical reaction between strained Si–O network bonds at the crack tip and reactive environmental species such as water and hydroxide ion [5], [43]–[48]. Increasing humidity or aqueous solution pH accelerates crack growth rates in OSG films [4]–[6], [47], [48]. Hydrogen peroxide also significantly accelerates the crack growth due to its strong affinity for electrons that weakens the Si–O crack tip bonds by reducing the electron density in the bonding orbitals [6]. On the contrary, alkali metal ions suppress the crack growth rate by blunting the crack tip [7].

Surfactants in aqueous CMP solutions were recently demonstrated to significantly affect the crack growth rate in nanoporous OSG thin films [7]. This involves the transport of surfactant molecules from the test environment into the nanoscale confined crack and their subsequent interaction with the crack surfaces. These molecular interactions include hydrophilic interactions between the hydrophilic groups on the surfactant molecule and hydroxide terminal groups on the crack surfaces, and hydrophobic interactions between the hydrocarbon chain of the surfactant and methyl groups on the crack surfaces, as schematically shown in Fig. 7(a). Even small changes in the lengths of either the hydrophobic or hydrophilic groups, together with the molecular structure of the surfactants, had dramatic effects on the growth rate of cracks. The linear C_mE_n surfactants significantly suppressed the crack growth [Fig. 8(a)] while the branched dimeric surfactants accelerated the crack growth [Fig. 8(b)].

The suppression of crack growth rates was described in terms of bridging of the crack surfaces by surfactant molecules [Fig. 7(b)] or the formation of nanobubbles in the surfactant-containing solution. The bridging contribution was measured with the *in situ* AFM characterizations of the surfactant self-assemblies and their bridging force in the aqueous solutions [7]. As shown in the AFM topography image of interface between a nanoporous film surface and NH_4OH pH 10 water without surfactant [inset, Fig. 9(a)], the interface was featureless flat. However, in the presence of 0.1 wt.% $C_{18}E_{20}$ surfactant in the solution, the surfactant aggregates self-assembled on the nanoporous film surface appeared [Fig. 9(a)]. By pushing and pulling the surfactant aggregates with an AFM tip, significant bridging force was detected, as shown in the force–displacement plot [Fig. 9(b)]. Alternatively, the acceleration of crack growth rates observed for dimeric surfactants was explained in terms of their effect on decreasing the surface energy of the fracture surfaces. This paper suggested the potential role of tailoring surfactant additions as crack inhibiting agents for optimized CMP slurries.

V. CONCLUSION

Selected reliability issues for the integration of nanoporous low-k dielectrics regarding UV curing, diffusion, and damage

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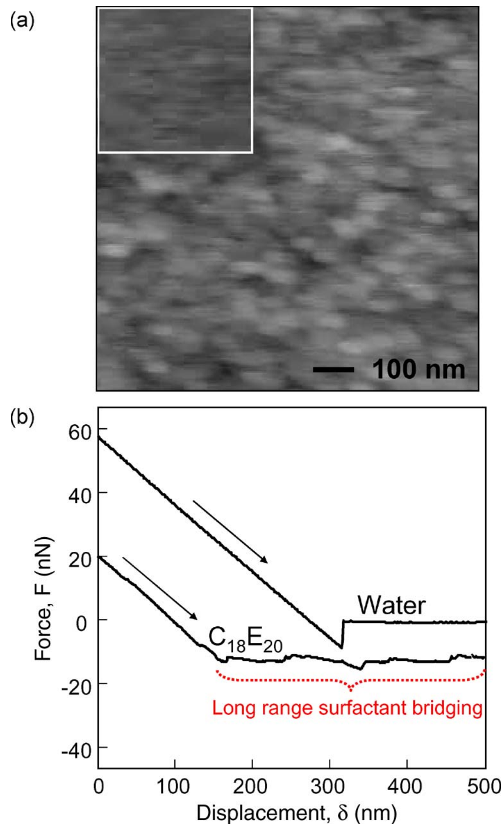

Fig. 9. *In situ* AFM characterizations of the surfactant self-assemblies and their bridging force measured in the aqueous solutions. (a) AFM image of $C_{18}E_{20}$ aggregates adsorbed to the interface between a nanoporous film surface and NH_4OH pH 10 water containing 0.1 wt.% $C_{18}E_{20}$ surfactant. An inset shows an AFM image of interface between a nanoporous film surface and NH_4OH pH 10 water without surfactant. (b) AFM force–displacement curves measured between a nanoporous film surface and NH_4OH pH 10 water with and without 0.1 wt.% $C_{18}E_{20}$ surfactant, respectively. Arrows indicate the direction of AFM probe retraction. Significant long range surfactant bridging was observed for the $C_{18}E_{20}$ solution (from [7]).

evolution were reviewed. The insensitivity of the fracture energy at the bottom interface of the OSG film to UV curing was shown related to the depth-dependent UV curing by the UV standing wave effect. It was demonstrated that the interfacial fracture energy can be maximized with UV standing waves together with an optical spacer underlying layer. A UV transparent SiN optical spacer layer can be selected to maximize curing at both sides of the OSG film with marked increases in interfacial fracture energy. On the contrary, a UV-absorbing SiCN underlying layer resulted in significantly reduced UV intensities and small improvements of the interfacial fracture energies. The lateral diffusion technique was used to measure diffusion coefficients of the nonionic surfactants in nanoporous low-k thin films. The surfactants were demonstrated to diffuse readily into the films, and the measured diffusion coefficients were found sensitive to molecular weight, the chain lengths of hydrophilic and hydrophobic groups, and molecular structure of surfactants. The reptation mobility was observed for the surfactant molecules confined in the interconnected nanopores. Finally, the crack growth rates in the nanoporous low-k film were found to be sensitive to nonionic surfactant additions where molecular structure and weight were demonstrated to be important variables. Crack growth rates were suppressed with the monomeric surfactants and accelerated with the dimeric surfactants, which were explained in terms of the bridging model and the reaction kinetic model, respectively.

REFERENCES

[1] Semicond. Ind. Assoc., International Technology Roadmap for Semiconductors, 2007 Edition, Interconnect, San Jose, CA, 2007.
[2] D. Shamiryan, T. Abell, F. Iacopi, and K. Maex, "Low-k dielectric materials," *Mater. Today*, vol. 7, no. 1, pp. 34–39, Jan. 2004.
[3] A. Grill, "Porous pSICOH ultralow-k dielectric for chip interconnects prepared by PECVD," *Annu. Rev. Mater. Res.*, vol. 39, pp. 49–69, 2009.
[4] E. P. Guyer, M. Patz, and R. H. Dauskardt, "Fracture of nanoporous methyl silsesquioxane thin-film glasses," *J. Mater. Res.*, vol. 21, no. 4, pp. 882–894, 2006.
[5] E. P. Guyer and R. H. Dauskardt, "Effect of solution pH on the accelerated cracking of nanoporous thin-film glasses," *J. Mater. Res.*, vol. 20, no. 3, pp. 680–687, 2005.
[6] E. P. Guyer and R. H. Dauskardt, "Fracture of nanoporous thin-film glasses," *Nat. Mater.*, vol. 3, no. 1, pp. 53–57, Jan. 2004.
[7] T. Kim, T. Konno, and R. H. Dauskardt, "Surfactant-controlled damage evolution during chemical mechanical planarization of nanoporous films," *Acta Mater.*, vol. 57, no. 16, pp. 4687–4696, Sep. 2009.
[8] C. Yuan, W. D. van Driel, R. van Silfhout, O. van der Sluis, R. A. B. Engelen, L. J. Ernst, F. van Keulen, and G. Q. Zhang, "Delamination analysis of Cu/low-k technology subjected to chemical-mechanical polishing process conditions," *Microelectron. Reliab.*, vol. 46, no. 9–11, pp. 1679–1684, Sep.–Nov. 2006.
[9] K. Mosig, T. Jacobs, K. Brennan, M. Rasco, J. Wolf, and R. Augur, "Integration challenges of porous ultra low-k spin-on dielectrics," *Microelectron. Eng.*, vol. 64, no. 1–4, pp. 11–24, Oct. 2002.
[10] W. D. van Driel, "Facing the challenge of designing for Cu/low-k reliability," *Microelectron. Reliab.*, vol. 47, no. 12, pp. 1969–1974, Dec. 2007.
[11] E. P. Guyer, J. Gantz, and R. H. Dauskardt, "Aqueous solution diffusion in hydrophobic nanoporous thin-film glasses," *J. Mater. Res.*, vol. 22, no. 3, pp. 710–718, 2007.
[12] T. Kim, K. Mackie, Q. Zhong, M. Peterson, T. Konno, and R. H. Dauskardt, "Surfactant mobility in nanoporous glass films," *Nano Lett.*, vol. 9, no. 6, pp. 2427–2432, 2009.
[13] S. Kondo, K. Fukaya, K. Yamada, T. Miyazaki, M. Fujita, D. Abe, S. Kunisaki, T. Enomoto, and S. Tominaga, "Damageless Cu chemical mechanical polishing for porous SiOC/Cu interconnects," *Microelectron. Eng.*, vol. 84, no. 11, pp. 2615–2619, Nov. 2007.
[14] D. M. Gage, K. S. Yim, A. Al-Bayati, A. Demos, H. M'Saad, and R. H. Dauskardt, "UV, E-beam, and thermal curing of low-k organosilicates: Effects on glass structure and mechanical properties," in *Proc. Adv. Metallization Conf.*, 2007, pp. 433–438.
[15] H. Namatsu and K. Minegishi, "The effect of plasma cure temperature on spin-on glass," *J. Electrochem. Soc.*, vol. 140, no. 4, pp. 1121–1125, Apr. 1993.
[16] G. Kloster, T. Scherban, G. Xu, J. Blaine, B. Sun, and Y. Zhou, "Porosity effects on low-k dielectric film strength and interfacial adhesion," in *Proc. IEEE Int. Interconnect Technol. Conf.*, 2002, pp. 242–244.
[17] T. Kim, N. Tsuji, N. Kemeling, K. Matsushita, D. Chumakov, H. Geisler, E. Zschech, and R. H. Dauskardt, "Depth dependence of UV curing of organosilicate low-k thin films," *J. Appl. Phys.*, vol. 103, p. 064 108, 2008.
[18] J. J. Y. Ma, S. F. C. Tseng, K. W. T. Chien, and V. W. W. Ruan, "Stress migration related reliability concerns," in *Proc. 43rd Annu. IEEE Int. Reliab. Phys. Symp.*, 2005, pp. 690–691.
[19] T. Kim, N. Tsuji, K. Matsushita, N. Kobayashi, D. Chumakov, H. Geisler, E. Zschech, and R. H. Dauskardt, "Tuning depth profiles of organosilicate films with ultraviolet curing," *J. Appl. Phys.*, vol. 104, no. 7, p. 074 113, Oct. 2008.
[20] K. Yoneda, M. Kato, S. Kondo, N. Kobayashi, N. Matsuki, K. Matsushita, N. Ohara, A. Fukazawa, and T. Kimura, "Impacts of UV cure for reliable porous PECVD SiOC integration," in *Proc. IEEE Int. Interconnect Technol. Conf.*, 2005, pp. 220–222.
[21] T. Kim, N. Tsuji, N. Kemeling, K. Matsushita, and R. H. Dauskardt, "Non-uniform UV curing effects on mechanical and fracture properties of organosilicate low-k thin films," in *Proc. Adv. Metallization Conf.*, 2006, pp. 389–394.
[22] T. Kim, N. Tsuji, N. Kemeling, K. Matsushita, N. Kobayashi, D. Chumakov, E. Zschech, and R. H. Dauskardt, "Depth dependence of UV curing of organosilicate low-k thin films," in *Proc. Adv. Metallization Conf.*, 2007, pp. 455–458.

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[23] D. M. Gage, J. F. Stebbins, L. Peng, Z. Cui, A. Al-Bayati, K. P. MacWilliams, H. M'Saad, and R. H. Dauskardt, "Effects of UV cure on glass structure and fracture properties of nanoporous carbon-doped oxide thin films," *J. Appl. Phys.*, vol. 104, no. 4, p. 043 513, Aug. 2008.

[24] Y. Lin, Y. Xiang, T. Y. Tsui, and J. J. Vlassak, "PECVD low-permittivity organosilicate glass coatings: Adhesion, fracture and mechanical properties," *Acta Mater.*, vol. 56, no. 17, pp. 4932–4943, Oct. 2008.

[25] F. Iacopi, Y. Travaly, B. Eyckens, C. Waldfried, T. Abell, E. P. Guyer, D. M. Gage, R. H. Dauskardt, T. Sajavaara, K. Houthoofd, P. Grobet, P. Jacobs, and K. Maex, "Short-ranged structural rearrangement and enhancement of mechanical properties of organosilicate glasses induced by ultraviolet radiation," *J. Appl. Phys.*, vol. 99, no. 5, pp. 053 511-1–053 511-7, Mar. 2006.

[26] F. Iacopi, G. Beyer, Y. Travaly, C. Waldfried, D. M. Gage, R. H. Dauskardt, K. Houthoofd, P. Jacobs, P. Adriaensens, K. Schulze, S. E. Schulz, S. List, and G. Carlotti, "Thermomechanical properties of thin organosilicate glass films treated with ultraviolet-assisted cure," *Acta Mater.*, vol. 55, no. 4, pp. 1407–1414, Feb. 2007.

[27] J.-M. Paik, H. Park, Y.-C. Joo, and K.-C. Park, "Effect of dielectric materials on stress-induced damage modes in damascene Cu lines," *J. Appl. Phys.*, vol. 97, no. 10, p. 104 513, May 2005.

[28] T. A. Ring, P. Feeney, D. Boldridge, J. Kasthurirangan, S. Li, and J. A. Dirksen, "Brittle and ductile fracture mechanics analysis of surface damage caused during CMP," *J. Electrochem. Soc.*, vol. 154, no. 3, pp. H239–H248, 2007.

[29] E. P. Guyer and R. H. Dauskardt, "Effect of CMP slurry environments on subcritical crack growth in ultra low-k dielectric materials," in *Proc. IEEE Int. Interconnect Technol. Conf.*, 2003, pp. 89–91.

[30] E. P. Guyer and R. H. Dauskardt, "Accelerated crack growth of nanoporous low-k glasses in CMP slurry environments," in *Proc. IEEE Int. Interconnect Technol. Conf.*, 2004, pp. 236–238.

[31] T. Kim, D. Chumakov, E. Zschech, and R. H. Dauskardt, "Tailoring UV cure depth profiles for optimal mechanical properties of organosilicate thin films," *Appl. Phys. Lett.*, vol. 95, no. 7, p. 071 902, Aug. 2009.

[32] D. Shamiryan and K. Maex, "Solvent diffusion in porous low-k dielectric films," in *Proc. Mater. Res. Soc. Symp.*, 2003, vol. 766, pp. 229–234.

[33] T. Abell, D. Shamiryan, M. Patz, and K. Maex, "Correlation between diffusion, porosity and pore sealing for low k dielectrics," in *Proc. Adv. Metallization Conf.*, 2003, pp. 549–553.

[34] T. Abell, J. Schuhmacher, Z. Tokei, Y. Travaly, and K. Maex, "Lateral solvent diffusion characterization of low k dielectric plasma damage and ALD barrier film closure," *Microelectron. Eng.*, vol. 82, no. 3/4, pp. 411–415, Dec. 2005.

[35] M. A. Worsley, M. Roberts, S. Bent, S. M. Gates, T. Shaw, W. Volksen, and R. D. Miller, "Detection of open or closed porosity in low-k dielectrics by solvent diffusion," *Microelectron. Eng.*, vol. 82, no. 2, pp. 113–118, Oct. 2005.

[36] C. Couturier, P. Leduc, T. Farjot, and G. Passemard, "Diffusion of aqueous solutions in nanoporous ultra low-k films," in *Proc. Adv. Metallization Conf.*, 2006, pp. 395–399.

[37] D. Shamiryan, M. R. Baklanov, P. Lyons, S. Beckx, W. Boullart, and K. Maex, "Diffusion of solvents in thin porous films," *Colloids Surf., A Physicochem. Eng. Asp.*, vol. 300, no. 1/2, pp. 111–116, Jun. 2007.

[38] S. Kondo, K. Fukaya, N. Ohashi, T. Miyazaki, H. Nagano, Y. Wada, T. Ishibashi, M. Kato, K. Yoneda, E. Soda, S. Nakao, K. Ishigami, and N. Kobayashi, "Direct CMP on porous low-k film for damage-less Cu integration," in *Proc. IEEE Int. Interconnect Technol. Conf.*, 2006, pp. 164–166.

[39] S. Kondo, M. Shiohara, K. Maruyama, K. Fukaya, K. Yamada, S. Ogawa, and S. Saito, "Effect of the hydrophilic-lipophilic balance (HLB) of surfactants included in the post-CMP cleaning chemicals on porous SiOC direct CMP," in *Proc. IEEE Int. Interconnect Technol. Conf.*, 2007, pp. 172–174.

[40] P. G. de Gennes, "Reptation of a polymer chain in the presence of fixed obstacles," *J. Chem. Phys.*, vol. 55, no. 2, pp. 572–579, Jul. 1971.

[41] J. Klein, "Evidence for reptation in an entangled polymer melt," *Nature*, vol. 271, no. 5641, pp. 143–145, Jan. 1978.

[42] T. Kim, Q. Zhong, M. Peterson, H. Tam, T. Konno, and R.H. Dauskardt, "Stress and slurry chemistry effects on CMP damage of ultra-low-k dielectrics," in *Proc. IEEE Int. Interconnect Technol. Conf.*, 2007, pp. 129–131.

[43] S. M. Wiederhorn, "Influence of water vapor on crack propagation in soda-lime glass," *J. Am. Ceram. Soc.*, vol. 50, no. 8, pp. 407–414, Aug. 1967.

[44] B. R. Lawn, "Diffusion-controlled subcritical crack growth in the presence of a dilute gas environment," *Mater. Sci. Eng.*, vol. 13, pp. 277–283, 1973.

[45] T. A. Michalske and S. W. Freiman, "A molecular interpretation of stress corrosion in silica," *Nature*, vol. 295, no. 5849, pp. 511–512, Feb. 1982.

[46] T. A. Michalske and B. C. Bunker, "Slow fracture model based on strained silicate structures," *J. Appl. Phys.*, vol. 56, no. 10, pp. 2686–2693, Nov. 1984.

[47] R. F. Cook and E. G. Liniger, "Stress-corrosion cracking of low-dielectric-constant spin-on-glass thin films," *J. Electrochem. Soc.*, vol. 146, no. 12, pp. 4439–4448, Dec. 1999.

[48] J. J. Vlassak, Y. Lin, and T. Y. Tsui, "Fracture of organosilicate glass thin films: Environmental effects," *Mater. Sci. Eng.*, vol. 391, no. 1/2, pp. 159–174, Jan. 2005.

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