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Effect of humidity treatments on porosity and mechanical integrity of mesoporous silica films

Xiaohong Li, Jerome C. Birnbaum,* Rick E. Williford, Glen E. Fryxell, Chris A. Coyle, Glen C. Dunham and Suresh Baskaran

Pacific Northwest National Laboratory, MSIN: K2-44, P.O. Box 999, Richland, WA, USA.
E-mail: jerome.birnbaum@pnl.gov; Fax: 509-375-2186; Tel: 509-372-6017

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The beneficial effects humidity treatments have on molecularly templated mesoporous silica films with respect to elastic modulus, with minimal detrimental effects on porosity and dielectric constant, were identified.

Porous ceramic and hybrid ceramic films are potentially useful as low dielectric constant interlayers in semiconductor interconnects.[1–6] At present, industry is in the process of inserting CVD and spin-coated films in the k = 2.6–3.0 range. Exploratory films with k = 2.2–2.5 are being evaluated within interconnects for the next generation of devices.[7] Silicate/organosilicate dielectric films with $k \geq 2.2$ generally exhibit elastic moduli ≥4.0 GPa. For future technology nodes (< 70 nm) in integrated circuits, that will require extremely low dielectric constants (≤2.0) in high purity films (< 50 ppb metal impurities), one of the key challenges is designing low dielectric constants while maintaining high elastic moduli. The demand for low dielectric constant interlays has led to higher porosity materials. However, higher porosity films lack the structural integrity necessary for the circuitry support. Here we describe the usefulness of humidity treatments in increasing mechanical integrity of porous films with minimal detrimental effect on film porosity or dielectric constant and no change in film quality (*i.e.* surface smoothness and uniformity, and consistent film thickness), illustrated using surfactant-templated mesoporous silicate films as a model example.

The sol used for evaporative-coating to form a thin mesoporous silica film typically contains a silica precursor, *e.g.* TEOS (tetraethyl orthosilicate), surfactant (ionic or non-ionic to generate porosity) and water, dissolved in a polar organic solvent.[2] The sol is aged[8] and the hydrolysis and condensation reactions are catalyzed by the addition of a small amount of acid or base. Evaporative-coating onto a silicon wafer generates a green film composed of templated oligomeric silicic acid units. The film is dried (100–200 °C) to remove the remaining solvent and calcined (250–450 °C) to complete or carry out further cross-linking between oligomeric silica units to form the silica network; this is a dehydroxylation process and water is produced as a side product. Following calcination, the porous ceramic film is chemically treated to dehydroxylate and hydrophobize the film, producing a low dielectric constant film with high mechanical integrity.

Surfactant-templated films were prepared as described above. The deposition solution contained TEOS, water, ethanol, nitric acid, and polyoxyethylene-10-lauryl ether as the surfactant, in a molar ratio of: 1:5:5:0.05:0.17 respectively. The deposition solution was highly pure (< 50 ppb metals).[9] The solution was aged at room temperature for 20–24 h and spin coated at a spin rate of 2000 rpm. Calcination and pore former removal was accomplished employing specific temperatures and environmental conditions reported in Table 1. This was followed by further heat treatments under a range of humidity environments. Table 1, samples A–D, show the change in porosity (refractive index),[10] film thickness, elastic modulus, and dielectric constant of similarly treated sets of films exposed to varying amounts of water vapor at ambient temperature following calcination. The data should be considered as four independent sets of data: 1A–4A, 1B–2B, 1C–3C and 1D–3D. Prior to humidity treatment, each set of films was treated identically and exhibited similar porosity (refractive index 1.14–1.15).[10] The film thickness was also recorded with the elipsometric measurements. Following the water vapor treatment the porosity (refractive index) and film thickness were measured again. The films were then treated with hexamethyl disilazane (HMDS) at 425 °C, to ensure complete or near complete dehydroxylation and passivation.[11] After treatment, the moduli and dielectric constants were measured.[12] For each set of samples, a significant increase (≥0.5 GPa) in modulus is obtained with increasing exposure to water vapor. The thickness and porosity of the films decrease with increasing modulus, and a corresponding increase in dielectric constant is observed. To shorten exposure times, higher water vapor concentrations, *e.g.* > 20,000 ppm, were used. This resulted in cracked films. The data demonstrates that post-calcination treatments of 2000 to ~ 10,000–15,000 ppm water vapor for 3–40 h at ambient temp. produces porous ceramic films with a modulus greater than 4 and a dielectric constant ≤2.2.

The effect of water vapor on the mechanical integrity of the porous ceramic after calcination is enhanced at elevated temperatures. Heating the porous ceramic films to a minimum of 50 °C and up to 450 °C allows the film to be exposed to water vapor concentrations exceeding 35,000 ppm without detrimental effects to the film. The upper thermal limit was maintained at 450 °C to be consistent with the microelectronic applications of these films. However, in principle much higher temperatures can be employed. The high temperatures and water vapor concentrations greatly reduce the exposure time required to obtain a high modulus. Table 1, samples E–G, demonstrate the increase in modulus with increasing water vapor concentrations at a treatment temperature of 425 °C. Again the data should be viewed as independent sets of samples: 1E–3E, 1F–3F, and 1G–3G. Each set of samples was treated identically up through the calcination step. The data show a decrease in film thickness with increasing modulus. However, the dielectric did not change significantly.

Table 1, sample H, shows the data for one set of films that was treated with the same concentration of water vapor for varying times. These data indicate that an exposure time of only 15 min can result in increased modulus. Other samples generated in our laboratory show significant increase in moduli (> 4.0) with exposure times as low as 10 min. Even shorter times (1–2 min) are possibly adequate for obtaining significant improvements in the elastic modulus.

The mechanism(s) involved during the humidity treatments which result in increased film strength without increasing the dielectric significantly is not known. The calcination step is relatively fast and may result in inadequate cross-linking and the formation of strained silicon–oxygen bonds creating sub-nanometer scale porosity within the walls of the porous silica. The humidity treatments may allow for more complete cross-linking to occur within the ceramic network by partial or very slight dissolution and re-precipitation of the silica. This might also facilitate the breaking of strained Si–O bonds resulting in relieve of stress within the wall structure. A related mechanism is discussed by Ozin *et al.* on moisture aged sols.[13] More detailed studies of the pore and wall structure using small angle

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Table 1 The effects of humidity treatments at varying temperatures, exposure times, and water vapor concentrations on calcined mesoporous silica films

Film identity	Heat treatment	Film thickness pre-humidity exposure (μm)[a]	$[H_2O]$ (ppm)	Time of humidity exposure. (h)	Refractive index post-humidity exposure[b,10]	Film thickness post-humidity exposure (μm) E/P[c]	Modulus (GPa)	k′ At 200 °C
Humidity treatments with increasing concentrations and varying exposure times at ambient temperature								
1A	5 min 425 °C N_2 5 min 375 °C air	1.15	0	0	1.15	1.15/1.08	2.0	2.03
2A	″	1.18	2600	19	1.17	1.08/1.01	3.1	2.16
3A	″	1.24	3800	48	1.21	0.96/0.96	4.9	2.20
4A	″	1.24	3800/8300	48/3	1.23	0.87/0.86	6.1	2.15
1B	6 min 375 °C air	1.15	0	0	1.15	1.15/1.15	2.9	2.01
2B	″	1.17	7200	20	1.18	1.05/1.04	4.0	2.12
1C	10 min 375 °C air	1.29	0	0	1.15	1.29/1.28	2.0	1.98
2C	″	1.25	10000	3	1.17	1.18/1.16	3.0	2.10
3C	″	1.25	9300	18	1.18	1.13/1.13	3.5	2.01
1D	1 min 180 °C air 10 min 375 °C air	1.26	0	0	1.15	1.26/1.23	2.6	1.97
2D	″	1.26	10000	3	1.19	1.05/1.03	4.4	2.10
3D	″	1.26	9300	15	1.20	1.00/0.97	4.8	2.22
Humidity treatments with increasing concentrations with constant exposure time at high temperature (425 °C)								
1E	10 min 375 °C air	1.18	0	0	NA	1.16	3.0	1.99
2E	″	1.17	4000	0.75	NA	1.13	3.7	2.00
3E	″	1.18	15000	0.75	NA	1.08	4.6	2.04
1F	1 min 180 °C air 10 min 375 °C air	1.14	0	0	NA	1.11	3.5	2.15
2F	″	1.15	4000	0.75	NA	1.07	4.2	2.07
3F	″	1.15	15000	0.75	NA	1.00	5.3	2.21
1G	1 min 180 °C air 10 min 375 °C air	NA	0	0	NA	0.90	3.5	2.03
2G	″	NA	4000	0.75	NA	0.90	3.7	2.05
3G	″	NA	15000	0.75	NA	0.85	4.5	2.04
Humidity treatments with constant concentration with increasing exposure times at high temperature (425 °C)								
1H	10 min 375 °C air	NA	0	0	NA	1.03	2.2	1.93
2H	″	1.00	15000	0.25	NA	0.99	2.7	1.96
3H	″	1.01	15000	0.75	NA	1.01	2.8	1.90

[a] All films had similar pre-treatment porosity (refractive index = 1.14–1.15)[10] following calcination. [b] NA not available. [c] E = elipsometry and P = profilometry.

neutron/X-ray scattering and positron annihilation spectroscopy is anticipated, in order to better understand the relation between the fine structure within the film and the elastic modulus.

In conclusion, we have demonstrated that the treatment of porous ceramic films with water vapor at concentrations up to 35,000 ppm at temperatures ranging from ambient to 450 °C, and for exposure times ranging from a few minutes to several days, can greatly enhance the mechanical integrity of the film without significantly changing the dielectric constant of the material. The result of such humidity treatments is a much stronger film with elastic modulus increases of more than 0.5 GPa, while maintaining a high degree of porosity which results in dielectric constants at or near 2.0. The procedure could be applicable to a porous silicate or organosilicate film. The films in this study contained disordered porosity, but the procedure might be as effective on films with ordered porosity. Further variations in temperatures, exposure times, and water vapor concentrations during the drying and calcination processes of the green film may have beneficial effects on the mechanical and dielectric properties of ceramic films.

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9 Selected samples in this study were sent to CHEMTRACE, of Freemont, CA for analysis to confirm the presence of less than 50 ppb metals in the sol.

10 Refractive indices measured using a Gaertner elipsometer model L116A. Films in this study with refractive index ≥ 1.20 will have porosity $< 50\%$. A refractive index of 1.170 indicates 60% porosity and 1.150 indicates 70% porosity. Porosities were calculated from refractive indices (D. J. Taylor, *Thin Solid Films*, 1998, **332**, 257–261). Surface area of the films averages ~ 900 $m^2 g^{-1}$, av. pore diam. 35 nm (range 28 to 42 nm) and av. pore vol. 0.8 cc g^{-1}.

11 Following humidity treatments but prior to silylation all samples were heated to 425 °C under vacuum for 3–5 min.

12 For each film, the dielectric constant at 1 Mhz was inferred from the film capacitance measured with a precision LCR meter (HP 4284A), using metal dots on the film deposited on a highly doped conductive p-type silicon wafer. The film capacitance was measured at 200 °C in dry air. Dielectric constant values were measured using four different dots on the film, and the average is reported in the table. Film thickness needed for dielectric calculations were measured using a Zygo NewView (model 200) non-contact optical profilometer. The elastic modulus was measured by indentation using a Hysitron Pico indenter with a Berkowich diamond tip. Indentation depths were < 0.1 μm to avoid substrate effects.

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