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Effects of trace metals and organic additives on porosity and dielectric constant of high purity mesoporous silica films†

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The beneficial effects that alkali metal and alkylammonium salt additions to molecularly templated silica sols have on the resulting mesoporous silica films formed from evaporative-coating methods with respect to porosity, elastic modulus, dielectric constant, and film surface uniformity were investigated and identified.

Porous ceramic films are potentially useful as low dielectric constant interlayers in semiconductor interconnects.[1–6] A key challenge with advanced dielectric films in interconnects is the need for extremely low dielectric constants (≤ 2.0) in very high purity materials (< 50 ppb metals). This communication describes film properties as a function of metal content in molecularly templated porous films, and a specific family of additives that may be used with highly pure alkali-metal-free ceramic precursors for such dielectric films. This enables better control of the film porosity and quality, maintains the film's structural integrity and lowers the dielectric constant.

The precursor solution used to prepare mesoporous thin films is typically composed of TEOS (tetraethylorthosilicate), a surfactant, and water dissolved in a polar organic solvent (typically an alcohol).[2] The sol is aged under a specific set of conditions to allow for the formation of a specific range of silicate oligomers. The hydrolysis and condensation chemistry is typically catalyzed by a small amount of acid or base, and a surfactant is used as a pore former in the deposition sol mixture. After evaporative-coating onto a silicon wafer, the wafer has a green film deposited on it composed of structurally templated oligomeric silicic acid units. The film is dried to remove residual solvent and facilitate condensation of the structure. The film is then typically calcined to drive the condensation chemistry of the silicic acid subunits. In addition to cross linking the oligomeric silica fragments, the calcination process also serves to remove surfactant from the porous silica framework, revealing the nanometer scale porosity. Following calcination the film is chemically treated (typically silylated) to replace surface hydroxyl groups with hydrophobic alkyl silyl groups.

We have observed that the presence of trace, 0.01–1000 ppm, amounts of alkali metals has a significant effect on the properties of mesoporous silica films. Alkali metal impurities resulted in a more stable film after calcination, with uniform thickness, and with a specific porosity (as determined by refractive index measurements).[7] Without the trace alkali metal contamination, the film produced had a very spotty, non-uniform surface, and had significantly lower porosity. As shown in Table 1, the addition of potassium systematically lowered the refractive index of the calcined film (the refractive index is inversely proportional to the porosity).[7] The deposition sol contained TEOS, water, ethanol, nitric acid, and the nonionic surfactant, polyoxyethylene-10-lauryl ether ($C_{12}H_{25}(OCH_2)_9OCH_2CH_3$), in a 1:5:5:0.05:0.17 molar ratio respectively. The sol was aged for 20–24 h at ambient temperature, and spin coated onto the wafer at a spin rate of 2000 rpm. Using specific treatments involving air calcination summarized in Table 1, the addition of more than 0.3 ppm potassium resulted in smooth uniform films with refractive indices less than 1.17, elastic modulus values near 4.0 GPa, and dielectric constants close to 2.0. Films prepared in an identical manner without the added potassium typically had higher elastic moduli (> 5.0), but were considerably less porous (refractive index > 1.20),[7] had non-uniform spotty surfaces, and much higher dielectric constants (> 2.50). A similar effect was noted for nitrogen calcined films (Table 1).

In semiconductor applications, alkali metal contamination is detrimental to the electrical properties of the device. In the absence of alkali metal cations, smooth, consistent, uniform, films can be difficult to achieve. The impact that alkali metal cations have on this chemistry has not been determined. It is possible that they affect the viscosity of the spun-on film, or perhaps the phase transition temperature of the template during drying/calcination. Exactly how these properties are influenced by the alkali contamination is not known. However, we postulate that they play a highly mobile, ionic role in which their strong interaction with hydroxyl groups within the matrix allows the transient formation of more nucleophilic Si–O$^-$ K$^+$ ion-pairs. These short-lived ion-pairs could undergo a series of addition/elimination reactions traveling through the silica framework driven by strain relief within the matrix (eqn 1)). The highly mobile alkali cations simply follow the migrating charge as it diffuses through silica walls around the surfactant aggregates.

$$\text{Si–O}^-\text{K}^+ + \text{Si–O–Si} \rightarrow \text{Si–O–Si} + \text{Si–O}^-\text{K}^+ \qquad (1)$$

The above proposed mechanism can be thought of as a low temperature stress-relief annealing process that allows for the healing of defects within the silica matrix. In the absence of the stabilizing alkali cations, this process would be much slower as it would involve the much less nucleophilic Si–OH group, ultimately resulting in a higher defect density in the film. This proposed low temperature annealing process would be a continuous one occurring throughout the aging, spin-coating, drying, and calcination stages. However, the non-volatile alkali

Table 1 Effect of potassium additions to deposition sols on the refractive index (porosity) of resulting films

[K$^+$] ppm added to deposition sol	Refractive Index[7] Drying/Calcination 375 °C (6 min.) in air	Refractive Index[7] Drying/Calcination 150 °C (2 min.) + 425 °C (2 min.) in nitrogen[8]
0[a]	1.280	1.240
0.033	N.A.	1.223
0.050	1.300	1.225
0.100	N.A.	1.192
0.150	1.206	1.185
0.300	1.170	1.173
50.0	1.156	1.168

[a] Sols with no added alkali metals may still contain trace (< 50 ppb) levels of total alkali metal contamination from trace amounts present in chemicals used to prepare the sol.[9] N. A. = data not available (not measured).

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† Electronic supplementary information (ESI) available: nitrogen adsorption/desorption isotherm and pore distribution chart. See http://www.rsc.org/suppdata/cc/b3/b304903e/

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metal cations remain in the film after calcination is complete. This is detrimental to the electrical performance of semiconductor devices containing such films. It is, therefore, highly desirable to use organic additives that can substitute for the alkali metal cations, and leave no ionic inorganic residue behind.

The addition of trace amounts of alkyl ammonium salts to highly pure (<50 ppb total metals) deposition sols for films prepared as described in Table 2, result in films with significantly greater porosity (*i.e.* lower refractive indices). Parts per million levels of tetramethyl ammonium chloride resulted in the production of films with smooth, uniform surfaces, refractive indices of less than 1.17, elastic moduli between 3.0 to 4.0 GPa,[10] and dielectric constants from 1.9 to 2.2 after silylation (similar to the effect of potassium doping).[11] These salts were completely removed from the film *via* calcination. Thus, the desired film properties were obtained without inorganic ionic contamination. We believe that the alkylated ammonium cations play a similar role as that postulated for the alkali metals during the aging, spinning, drying, and calcination stages in film production.

To further investigate this hypothesized "mobile cationic effect" an additional set of experiments was conducted using cetyl (cetyl = $C_{16}H_{33}$) trimethyl ammonium ion as the cationic species. Originally, the cetyl trimethyl ammonium cation was used as the surfactant template for mesoporous ceramics.[1] Perhaps the much larger cetyl trimethyl ammonium ion was also performing as a mobile cationic species? Deposition sols containing the non-ionic polyoxyethylene 10-lauryl ether surfactant (as described in Table 1) were prepared with varying levels (300–30,000 ppm) of cetyl trimethyl ammonium chloride (CTAC). The films were calcined in air as before. Film quality was improved relative to undoped films. The films had a less spotty, more uniform surface and were significantly more porous (refractive indices ranged from 1.13 to 1.16). The films also had low dielectric constants (*k* values ranged from 1.9 to 2.2). However, film strength in these CTAC doped films was low (elastic modulus values ranged from 1.5 to 3.0) and film quality was still less than desired, with some visible spottiness and striations. The relatively poor film quality of the CTAC doped films is possibly due to the reduced mobility of the much larger cetyl-substituted ammonium ion relative to the methyl-substituted ammonium ion. Also although solubility of the CTAC was not a problem, the CTAC ions may be aggregated primarily as micelles and unable to migrate in this form. However, it is important to note the improvement in film quality when the cetyl ammonium ion is used *versus* sols not containing any cationic stabilizing species. This observation suggests it is possible that slightly smaller cationic surfactants such as dodecyl or octyl substituted trimethyl ammonium ions might fulfil both functions, as a pore former, and as a catalyst for refining the silica structure in the pore walls providing greater porosity and high uniformity with consistent mechanical integrity.

In conclusion, the presence of tetraalkyl ammonium cations in the as-spun film provides a mechanism for enhancing the cross-linking of the silicic acid structural units. Including tetraalkyl ammonium cations in the deposition sol results in a film with greatly improved surface uniformity and films with a high degree of porosity (*i.e.* low dielectric constants), and no contamination resulting from added alkali metal cations or other inorganic species. This is postulated to occur through a low temperature, catalytic annealing process of the mesoporous ceramic film that is facilitated by the tetraalkyl ammonium cation.

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Table 2 Effect of tetramethylammonium nitrate additions to deposition sols on refractive index (porosity) and dielectric constant of resulting films

$[(CH_3)_4NNO_3]$ ppm[a] added to deposition sol	Refractive Index[7] Drying/Calcination Treatment 375 °C (6min) in air	Dielectric Constant Measurement at 200 °C
0	1.240	$>$ 2.4
0.91	1.178	2.27
1.61	1.167	2.20
2.97	1.162	2.17
5.93	1.158	2.09
11.9	1.153	1.99

[a] For equal ionic strength, 1ppm potassium requires 3.5 ppm tetramethyl ammonium nitrate.

Notes and references

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7 Refractive indices measured using a Gaertner elipsometer model L116A. Films synthesized in this study having a refractive index of 1.20 or higher will have porosity less than 50%. A refractive index of 1.170 indicates 60% porosity while a measurement of 1.150 indicates 70% porosity. Porosities were calculated from refractive indices. (See D. J. Taylor, P. F. Fleig and S. L. Hietala, *Thin Solid Films* 1998, **332**, 257.) Surface area of the films averages about 900 $m^2 g^{-1}$, average pore diameter 35 nm with a range of 28 to 42 nm, and average pore volume is 0.8 cc g^{-1}. All films measured in this study for thickness were between 0.91 and 1.16 µm.

8 Films calcined in pure nitrogen atmospheres had greatly improved surfaces but incomplete removal of surfactant.

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 X. Li, J. Birnbaum, R. E. Williford, G. E. Fryxell, C. A. Coyle, G. C. Dunham and S. Baskaran, *Chem. Commun.*, 2003 (in press, DOI: 10.1039/b304843h). Although high quality films were obtained using the tetramethyl ammonium salt in the deposition sols, structural integrity of the resultant films was less than desired (*i.e.* elastic moduli ranged from 3.0–4.0). However, humidity treatments following calcination but prior to silylation improved film strength.

11 Silylation is the final dehydroxylation and hydrophobation chemical treatment conducted on the film to obtain low dielectric constant films. An activated silane is introduced into the film to react with hydroxyl groups, replacing them with alkylated silyl groups throughout the mesoporous structure. P. J. Bruinsma, N. J. Hess, J. R. Bontha and J. Liu, S. Baskaran, *MRS Symp. Proc.* 1997, **Vol. 445**, 105.