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Effect of solution chemistry and speciation on shelf-life of silica sols and characteristics of deposited mesoporous thin films

J. C. Birnbaum,* X. Li, C. R. Yonker, G. E. Fryxell and S. 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 effects of storage temperature and time on deposition characteristics of molecularly templated silica sols, used in synthesis of mesoporous silica films, were investigated by preparing acid catalysed water–ethanol–TEOS sols with surfactant and analysing by silicon-29 NMR spectroscopy over a period of multiple days, and by producing films after specific storage times corresponding to collection of NMR spectral data, and analysed for thickness and porosity.

Over the last several years, development of low dielectric-constant (*k*), high modulus, porous silica thin films has been intensely investigated due to the demand for reduced interconnect RC delay, power consumption, and cross talk in integrated circuitry.[1–5] The desired properties of such films typically include dielectric constants $k \leq 2.0$, elastic modulus ≥ 5.0 kPa, and hydrophobicity in the film to ensure no moisture uptake and stability in dielectric constant. It is highly desirable that the sol formula be stable for long-term storage (*e.g.* up to six months) in order to obtain highly reproducible film properties (*e.g.* porosity and thickness) over large manufacturing runs. During the development of this deposition solution, we conducted a shelf-life study on four different sol formulations to determine their potential for long-term storage and use. This communication describes this study.

All solutions tested were based[2,4] on a water–ethanol solvent system, used tetraethyl orthosilicate (TEOS) as the sol precursor, employed a non-ionic polyoxyethylene surfactant as a template, and used dilute nitric acid as a catalyst for TEOS hydrolysis and oligomerization. Solutions were stored at 3 °C initially and then at 30 °C for up to 70 days. Periodically during this time frame, portions of the stored solution or sol were removed to conduct ^{29}Si NMR analysis and to prepare films. Films were prepared by spin coating the solutions on 100 mm diameter silicon wafers, and heat-treating the films for drying and calcination. The films were analysed for thickness and porosity (refractive index). The four sol formulations investigated contained; TEOS : water : ethanol : surfactant : acid; in molar ratios of: sol **#1**, 1 : 5 : 5 : 0.17 : 0.05; sol **#2**, 1 : 10 : 10 : 0.17 : 0.05; sol **#3**, 1 : 2 : 10 : 0.17 : 0.05; and sol **#4**, 1 : 5 : 5 : 0.17 : 0.05. Sols **#1** and **#4** contained the same molar ratio of constituents but differ in the order the reagents were mixed. With sol **#1** the TEOS was added last after the other reagents were well mixed (sols **#2** and **#3** were made in this fashion). With sol **#4** all reagents except surfactant were mixed and stirred at 30 °C for 1 h, surfactant was then added followed by 3 °C storage. Table 1 lists selected Si-29 NMR integration results, and thickness and porosity data obtained from the films made from these sols, which reflect the general trends observed for each sol during the course of the investigation. With the exception of sol **#3** which produced very low porosity films from the start, the remaining sols exhibited similar trends, the most noteworthy being a significant decrease in porosity with time. Our standard sol (sol **#1**) will be discussed in detail. Sol **#4** having the same formulation as sol #1 yielded quite similar results. Sol **#2** being more dilute resulted in considerably thinner films but followed the same general trend of decreasing porosity with time.

Fig. 1 depicts the silicon-29 NMR spectra on sol **#1**. The spectra are referenced to TMS (0.00 ppm). Our standard procedure for film preparation is employing this sol and aging it at 20–25 °C for 20–24 h. Depending on drying and calcination procedures employed, this sol produced films close to the physical and chemical properties described above. It is therefore desirable to maintain this mixture of oligomers and have the aging process cease at this point. The first three spectra represent the formation of silica oligomers within the first 24 h at 3 °C. The fourth spectrum is of the sol stored at 3 °C for 48 days. The last two spectra are the same sol stored at 3 °C for 26 days followed by 30 °C storage for 8 and 44 days, respectively. The spectra demonstrate that the silica precursor is completely hydrolysed (TEOS, −82.4 ppm[6]) in the first 2–4 h and undergoes the majority of oligomerization (water and alcohol condensation reactions[7]) within the first 24 h. At this point the sol consists primarily of Q3 species ($\approx$0.7 mol fraction, $\sim$−100 ppm) and Q2 species ($\approx$0.2 mol fraction, $\sim$−90 ppm). Q4 species are present in low concentration ($\approx$0.1 mol fraction, $\sim$−110 ppm), which is near the detection limit of the analysis. The spectra do not distinguish between hydrolysed Q3 species and esterified Q3 (or condensed versions of these species)

Table 1 ^{29}Si integration data reported in mol fraction. Film refractive index, and thickness data for sols #1, #2, #3 and #4

Days at (temp/°C)	NMR int.[a] Q0[b] (TEOS)	Q1	Q2	Q3	Q4	Refractive index	Thickness/ μm
Sol **#1**							
1 (3)	< 0.01	< 0.01	0.2	0.7	0.1	1.165	1.07
7 (3)	< 0.01	< 0.01	0.17	0.67	0.16	1.167	1.08
14 (3)	< 0.01	< 0.01	0.17	0.67	0.16	1.168	1.16
26 (3)	< 0.01	< 0.01	0.17	0.7	0.13	1.167	1.13
48 (3)	< 0.01	< 0.01	0.15	0.71	0.14		
26 (3), 8 (30)	< 0.01	< 0.01	0.17	0.69	0.14	1.166	1.1
26 (3), 14 (30)	< 0.01	< 0.01	0.07	0.64	0.29	1.175	1.14
26 (3), 22 (30)	< 0.01	< 0.01	0.11	0.67	0.22	1.182	1.17
26 (3), 38 (30)						1.19	1.26
26 (3), 44 (30)	< 0.01	< 0.01	0.11	0.64	0.25		
Sol **#2**							
1 (3)	< 0.01	< 0.01	0.25	0.59	0.16	1.158	0.59
9 (3)	< 0.01	< 0.01	0.25	0.66	0.08	1.158	0.6
16 (3)	< 0.01	< 0.01	0.23	0.77	0	1.166	0.59
22 (3)	< 0.01	< 0.01	0.14	0.68	0.18	1.162	0.58
30 (3)	< 0.01	< 0.01	0.14	0.63	0.23	1.16	0.59
38 (3)						1.168	0.59
38 (3) 15 (30)	< 0.01	< 0.01	0.12	0.63	0.25	1.17	
Sol **#3**							
1 (3)	0.01	0.05	0.07	0.53	0.34	1.26	
8 (3)	< 0.01	0.04	0.03	0.42	0.51	1.24	
14 (3)						1.25	
45 (3)						1.24	
Sol **#4**							
1 (3)	< 0.01	< 0.01	0.16	0.63	0.21	1.165	1.03
7 (3)	< 0.01	< 0.01	0.17	0.61	0.22	1.165	1.09
13 (3)	< 0.01	< 0.01	0.13	0.63	0.24	1.167	1.03
21 (3)	< 0.01	< 0.01	0.06	0.66	0.28	1.167	1.04
26 (3), 3 (30)						1.172	1.09
26 (3), 30 (30)						1.192	1.13

[a] NMR integration normalized. [b] All Q species reported in mol fraction.

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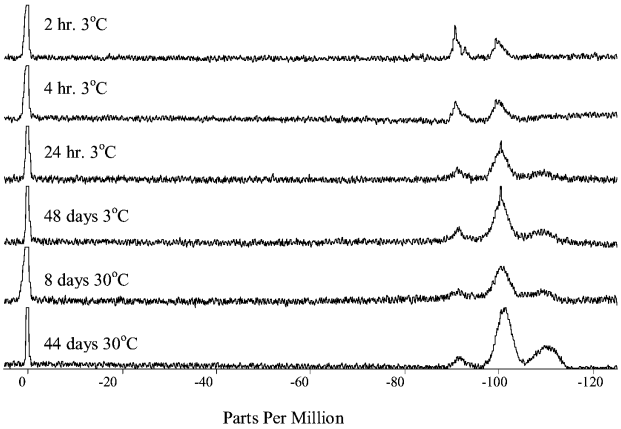

Fig. 1 ^{29}Si NMR spectra of sol **#1**.

because most Q3 species are partially hydrolysed and partially esterified (Q3 species hydrolysed $EtOSi(OH)_3$, Q3 species completely esterified or condensed $EtOSi(OSi\equiv)_3$).[7] However, as more hydroxyl groups undergo condensation or esterification the Q3 peak is observed to shift up field slightly (*i.e.* observed shift of Q3 peak from first to last spectrum, −98 to −101 ppm). Storage at 3 °C from 1 to 48 days does not appear to show dramatic changes of the sol in the NMR spectra. However, upon closer inspection of integration data and of film thickness and porosity data during this time frame, significant changes are recognized. Fig. 2 shows the results of the NMR analysis of sol **#1** and the film thickness and porosity data in graph form. Silica oligomers are plotted as mol fraction of Q2, Q3, and Q4 species versus days stored at 3 or 30 °C. Typically TEOS and Q1 species are consumed within the first couple hours and are therefore not plotted. In this same time frame Q3 species become the dominant form of silica and remain so throughout the course of the experiment. For sols stored at 3 °C, Q3 and Q4 species gradually increase in concentration as Q2 species gradually decrease. Although the rate of increase in Q3 and Q4 species is slow, the overall change in sol composition is fairly drastic. Over the 48 day period of sol storage at 3 °C, Q3 species increase ~3.5% in mol fraction and Q4 species increase ~6.9%.[8] This increase is at the expense of Q2 species which decreases ~18% in mol fraction.[8] Upon examination of the films, this net change in oligomeric ratio results in a net increase in film thickness of >10% and a decrease in film porosity as indicated by a 1.8% increase in refractive index.[8,9] Increases in Q3 and Q4 concentrations indicate continued alcohol and water condensation reactions resulting in further growth of oligomeric species (branched, cyclic, or linear) within the sol.[7] As oligomeric species increase in size and complexity, wall thickness in the resulting film is likely to have increased, thus decreasing the amount of porosity measured in the resulting film, and increasing the film thickness. Also as the average size of oligomeric species present increases, sol viscosity also increases resulting in thicker films (spin coating speeds and temperatures remained constant throughout the study).

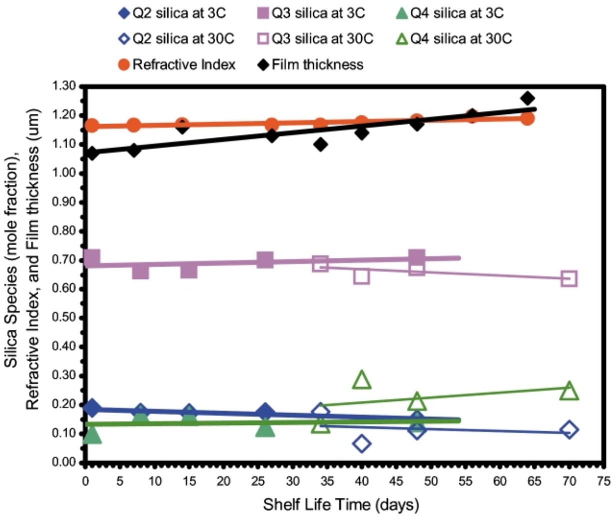

Fig. 2 ^{29}Si NMR integration data and film thickness and porosity data for sol **#1**.

The sol discussed above was also stored at 30 °C for 44 days. As might be expected the rate at which the sol changed was increased. Fig. 2 shows that although the rate of decrease in Q2 species remained fairly constant at 3 to 30 °C, the rate of Q4 formation was increased by about an order of magnitude. The large increase in the rate of Q4 formation is due to Q3 species decreasing in concentration. Over the 44 day, 30 °C storage period, the mol fraction of Q4 species increased well over 50%. This large increase in Q4 species resulted in an 8% increase in film thickness and a decrease in film porosity as measured by a 2% increase in refractive index (*vide supra*)[8,9]

Our results indicate potential advantages with 3 °C storage over that of ambient. However, it is also evident that with sols synthesized from the recipes employed in this study, storage times of more than a few days is detrimental to the physical and chemical properties of the resulting film produced by the sol. Silica sols based on the water–ethanol solvent system do not appear to have stable speciation characteristics over long periods of time for this intended low-*k* thin film application. Colder storage temperatures (*i.e.* −10 °C) could most likely increase sol storage times to perhaps a few weeks without significant negative effects. Alternate solvent systems and mixtures of silica precursors may offer opportunities for engineering a deposition solution with better shelf-life.

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8 Due to relatively high variance in individual readings from the elipsometer and of NMR integration results, percentage increases and decreases in silica species present, refractive index, and film thickness were calculated using the trend line equation (least squares) generated from the graph.

9 In producing thin films, we have observed that small decreases in film porosity have very large negative affects on our ability to treat the films after calcination for dehydroxylation and hydrophobicity. For example, increases in refractive index of 1% typically result in an increase in dielectric of $\geqslant 0.2$ and an increase in Δk (k_{25}–k_{200}), which is practical inverse measure of hydrophobicity, of $\geqslant 0.2$.