Effects of H$_2$O on structure of acid-catalysed SiO$_2$ sol–gel films

M.A. Fardad $^a$, E.M. Yeatman $^{a,*}$, E.J.C. Dawnay $^a$, Mino Green $^a$, F. Horowitz $^b$

$^a$ Optical and Semiconductor Devices Section, Department of Electrical and Electronic Engineering, Imperial College of Science, Technology and Medicine, London SW7 2BT, UK

$^b$ Instituto de Fisica, UFRGS, Campus do Vale C.P. 15051, 91501-970, Porto Alegre, RS, Brazil

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Abstract

Thin silica films were deposited on silicon wafers by the sol–gel technique, using spin coating. The sols were prepared by HCl catalysis of tetraethylorthosilicate (TEOS) diluted in ethanol, using different molar ratios, $R$, of H$_2$O:TEOS. The films were then baked at various temperatures, and characterised using ellipsometry, profilometry, optical scattering and infrared spectroscopy. It was found that the thickness, shrinkage, porosity and pore sizes all decrease with increasing $R$. It was also found that high water levels yield films of higher homogeneity and finer texture, and less tensile stress.

1. Introduction

The fabrication of glass films by the sol–gel technique has attracted considerable attention in microelectronics, optics and other fields. We are interested in silica-based glass films of thicknesses in the range 2–30 $\mu$m, for application in integrated optics on silicon substrates. Possible deposition techniques for this application include thermal oxidation, sputtering, chemical vapour deposition and flame hydrolysis. However, the sol–gel technique offers some potential advantages over these techniques; in particular, sol–gel can be used to produce films with a great variety of composition and structure. High shrinkage inherent in the process produces tensile stresses, which make the fabrication of crack-free films beyond 1 $\mu$m in thickness very difficult [1].

Glasses fabricated by the sol–gel route are typically microporous, and the capillary forces associated with solvent evaporation from the pore surfaces are believed to be the main cause of shrinkage and stress [2]. The porosity of these glasses is also of interest because it may allow the insertion of a dopant species into a host glass; for example, semiconductor microcrystals for third-order optical non-linearity [3].

The characteristics of sol–gel films are determined by a large number of process parameters, and it is important that the effects of these parameters are well understood to make sol–gel a reliable and practical technology for device fabrication. We investigated one of the most important parameters, the amount of water used for hydrolysis and condensation of the sol before spinning. In order for the hydrolysis and condensation reactions to convert silicon alkoxide completely to SiO$_2$, two moles of water are needed for each mole of Si precursor. However, an excess of water can be used, and it is the effect of this excess that is reported here.

* Corresponding author. Tel: +44-71 589 5111. Telefax: +44-71 823 8125. E-mail: e.yeatman@ic.ac.uk.
Many attempts have been made to investigate the effects of water on bulk silica gels [1,2] and on some aspects of the structure of films [4-7]. Klein and Garvey [2] observed that, in bulk gels, increased water increases the hydrolysis rate in both acid- and base-catalysed solutions. They also found that in acid-catalysed solutions water has a strong effect on surface area and porosity, while acid addition has little effect. Glaser and Pantano [4] found a monotonic increase in refractive index with water concentration for spin-coated silica films. They consequently observed that the density of silica spin-coated films increases with increasing molar ratio, \( R \), and that film shrinkage during thermal treatment is reduced. They concluded that the high density results from the absence of a liquid phase during the polymerisation of films after spinning; thus, the coarse low density microstructure associated with the growth and gelation of highly condensed silica structure in bulk gels is eliminated. Brinker et al. [5] showed that, as the excess water is increased from 0.5 to 6.0 vol.\%, the refractive index of silica films deposited by dipping increases from 1.34 to 1.43, corresponding to a reduction in porosity from 22 to 7\%, but that further increases in excess water content cause a reduction in refractive index. They concluded that water increases both the surface tension, which compacts the structure, and condensation, which stiffens the structure, increasing its resistance to compaction. Also, Matos et al. [6] found that the thickness of as-deposited silica spin-coated films decreases with increasing \( R \) due to lowering of the condensation rate. This study is the first, to our knowledge, to report the effects of excess water on the pore size distribution, porosity and stress of silica spin-coated films.

2. Experimental procedure

Equal volumes of tetraethylorthosilicate (TEOS) and ethanol were mixed and stirred vigorously for 10 min at room temperature. Then 0.1M HCl was gradually added to the solutions, until a water to TEOS molar ratio of \( R = 2 \) was attained. Additional deionised water was added to give solutions with \( R = 3, 4 \) and 5, so that for all solutions the molecular ratio TEOS:HCl was maintained, as summarised in

<table>
<thead>
<tr>
<th>Sample (R ratio)</th>
<th>TEOS ml</th>
<th>ethanol ml</th>
<th>H₂O ml</th>
<th>HCl (0.1M) ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R = 2 )</td>
<td>5.0</td>
<td>5.0</td>
<td>0.0</td>
<td>0.81</td>
</tr>
<tr>
<td>( R = 3 )</td>
<td>5.0</td>
<td>5.0</td>
<td>0.41</td>
<td>0.81</td>
</tr>
<tr>
<td>( R = 4 )</td>
<td>5.0</td>
<td>5.0</td>
<td>0.81</td>
<td>0.81</td>
</tr>
<tr>
<td>( R = 5 )</td>
<td>5.0</td>
<td>5.0</td>
<td>1.21</td>
<td>0.81</td>
</tr>
</tbody>
</table>

Table 1. The solutions were placed in the refluxing bath immediately after mixing, and the temperature of the bath was increased to 70°C in 15 min, while stirring, and kept there for 2 h. The solutions were then aged for 24 h at room temperature, before being diluted with an equal volume of EtOH and stirred for 10 min, to give the solution used for spin coating. All the chemicals were obtained from Aldrich Chemical Ltd.

The sols were dispensed on p-type, 75 mm diameter silicon wafers, through a 0.1 \( \mu \)m filter (PTFE Whatman, obtained from BDH Merk Ltd), and thereafter the substrate was spun at 2000 rpm for 15 s. The coated substrate was baked at 100°C for 5 min, and then cleaved into 10 pieces. Each piece was baked in air at a different temperature, in the range from 100 to 1000°C, for 30 min. The samples were kept in covered petri dishes for a few days in room conditions before the experiments were continued; this allows the completion of surface hydroxylation, and gave reproducible ellipsometer results when water is used as an adsorbate.

The thickness and refractive index of the samples were measured using a Rudolph AutoEl III ellipsometer, with an operating wavelength of 633 nm, and precisions of about \( \pm 0.002 \) and \( \pm 3 \) Å in index and thickness, respectively. For microporous films, the measured index is strongly dependent on relative humidity, because of condensation of water in the pores. By measuring the dependence of index on humidity, information about porosity can be obtained. We have extended this technique to the use of different adsorbate species, in order to probe pore sizes [3]; this, for the sake of brevity, we call molecular probe ellipsometry. In this technique, the film is placed in a sealed chamber on the sample stage of the ellipsometer; first dry \( N₂ \) gas is passed through the chamber to empty the pores of any condensed
adsorbate, and then N₂ having been bubbled through the liquid adsorbate is passed over the sample to fill the pores; in each case the refractive index is measured. By assuming that all the accessible pores in dry and saturated atmospheres are completely empty or filled with adsorbate, respectively, the pore volume and index of the solid skeleton can be determined by an extension of the Lorentz–Lorenz relation [8]:

\[
\frac{(n^2_f - 1)}{(n^2_f + 2)} = (1 - \nu_p) \left( \frac{(n^2_s - 1)}{(n^2_s + 2)} \right) + \nu_p \left( \frac{(n^2_p - 1)}{(n^2_p + 2)} \right),
\]

where \(n_f\), \(n_s\), and \(n_p\) are the refractive indices of the film, solid skeleton and pores, respectively, and \(\nu_p\) is the volume fraction porosity. Measurement of \(n_f\) for both the dry and saturated films allows both \(\nu_p\) and \(n_s\) to be determined with the assumption that \(n_p\) has the same value as that of the bulk adsorbate in the saturated case, and of air \((n_p = 1)\) in the dry case.

In order to empty the pores, an initial high flow rate of N₂ was used for a few minutes and the rate was then reduced to 1000 sccm (standard c.c. per minute) for 15 min. The flow rate was kept at 100 sccm for 15 min to fill the pores. The low flow rate in this case reduces the likelihood of cooling of the sample surface, which could cause condensation on the external film surface. Comparison of the measured film thickness for wet and dry atmospheres indicated that this did not occur. The temperature inside the chamber was monitored by a thermocouple to ensure that there was no drift or alteration due to gas flow. In each case, the measurement was recorded once repeatable readings were obtained. The adsorbates used are listed in Table 2. Their average diameters were estimated using a combination of bond length data [9] and Van der Waals atomic radii [10]. All were obtained from Aldrich Chemical Ltd, except C₂₄H₄₄O₈ obtained from Fluka Chemie AG.

The optical quality of the films was first studied qualitatively by visual examination, and by optical microscopy. The homogeneity of the films was then investigated quantitatively by measuring the intensity of scattered light resulting from oblique reflection of a laser beam from the film-coated silicon substrate. A helium–neon laser beam, having a wavelength of 633 nm, was directed onto the sample, through a chopping wheel, at an angle 59° from the normal. The specularly reflected beam was absorbed onto a black card, and the scattered light was collected at normal incidence to the sample using a ×10 microscope objective, and measured using a silicon photodiode and a lock-in amplifier. The position of lens and angle of incidence were fixed during measurements.

The film stress, \(\sigma_f\), can be determined by measuring the resulting substrate curvature [11], according to Stoney's formula:

\[
\sigma_f = \frac{E_s t_s^2}{6(1 - \nu_s)} \left( \frac{1}{r_s} - \frac{1}{r_f} \right),
\]

where \(r_s\) and \(r_f\) are the radii of curvature of the bare substrate and substrate with film, respectively; \(E_s\), \(t_s\) and \(\nu_s\) are the Young’s modulus, thickness and Poisson’s ratio of the silicon substrate, respectively, and \(t_f\) is the thickness of the film. Tensile stresses are positive and compressive stresses negative; thus, a positive radius of curvature denotes a convex film surface. Entire 75 mm diameter wafers were used, and curvature was measured from plots of surface profile along 30 mm lines over the central part of the film surface using a Dektak IIA auto-levelling profilometer. To reduce inaccuracy caused by lack of axial symmetry in the wafer curvature, two scans were made, in orthogonal directions, for each mea-

<table>
<thead>
<tr>
<th>Probe molecule</th>
<th>Diameter (Å)</th>
<th>Index, (n_D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water (H₂O)</td>
<td>3.28</td>
<td>1.333</td>
</tr>
<tr>
<td>Methanol (CH₃OH)</td>
<td>4.72</td>
<td>1.329</td>
</tr>
<tr>
<td>Carbon tetrachloride (CCL₄)</td>
<td>6.49</td>
<td>1.460</td>
</tr>
<tr>
<td>Cyclohexane (C₆H₁₂)</td>
<td>7.36</td>
<td>1.426</td>
</tr>
<tr>
<td>1,5,9-Cyclododecatriene (C₁₂H₁₈)</td>
<td>9.30</td>
<td>1.507</td>
</tr>
<tr>
<td>Dicyclohexano-24-Crown-8 (C₂₄H₄₄O₈)</td>
<td>14.00</td>
<td>1.490</td>
</tr>
</tbody>
</table>
surement, and the inverse radii thus obtained were averaged. Care was taken not to use wafers which had a substantially asymmetric curvature before deposition. Wafer thicknesses, measured with a micrometer, were 390 ± 3 μm. Final film thicknesses were measured by ellipsometry and checked by patterned etching and profilometry, and interim thicknesses were estimated by interpolation. Equivalent single-layer thickness measurements indicate that the assumption that final thickness is proportional to number of layers is sufficiently accurate. For $E_s/(1 - \nu_s)$, the value 180 GPa was used [11].

In order to give an indication of the effect of water content on stress, 10 layers were deposited for each $R$ value, using 10 s rapid thermal annealing at 1000°C in all cases.

3. Results

Fig. 1 shows film thicknesses measured as a function of bake temperature for each $R$ value, as described in Section 2. Fig. 2 shows the equivalent evolution of refractive indices (for films under N$_2$ gas), and Fig. 3 shows fractional porosity, measured using water vapour. During measurement, the $R = 2$ film baked at 200°C absorbed water and swelled, giving a 2% increase in thickness. Measurable swelling was not observed in other samples. The degree of shrinkage of films continues to increase with bake temperature up to 800°C, after which there is an apparent increase in thickness. This effect results from substrate oxidation. All 800°C samples show no porosity, indicating that there are no remaining pores accessible to water molecules; however, refractive indices continue to rise until 1000°C, where the $R = 5$ sample had the highest index, 1.464.

Fig. 4 shows the water vapour isotherm of the sample which exhibited the highest porosity measured using water vapour. These samples were those baked at 400°C for $R = 2$ and $R = 3$, and at 500°C for $R = 4$ and $R = 5$ (see Fig. 2). The isotherms are of type I in the Brunauer–Emmett–Teller (BET) classification [12], which indicates micropores of roughly cylindrical shape, with width less than 20 Å [13]. Isotherms become sharper and the plateaus begin at lower relative humidity as $R$ is increased, which indicates that as $R$ is increased the pores are becoming smaller.

The pore size distribution is indicated more clearly in Fig. 5, which shows the measured fractional

![Fig. 1. Film thickness vs. annealing temperature (measured in dry nitrogen). For this and following figures, lines are for ease of viewing only.](image1)

![Fig. 2. Film index vs. annealing temperature (measured in dry nitrogen).](image2)

![Fig. 3. Film porosity vs. annealing temperature (from measurements in dry and water vapour saturated atmospheres).](image3)
porosity vs. adsorbate size, measured by molecular probe ellipsometry. The pore size distribution is broad in all cases, and the extent of this distribution drops with increasing bake temperature and with increasing \( R \). For example, for films baked at 400–500°C, the \( R = 2 \) and \( R = 3 \) samples have substantial pore volume accessible to adsorbates of Van der Waals diameter greater than 14 Å, while the \( R = 4 \) and \( R = 5 \) samples do not. After 700°C baking, all the available pores in \( R = 4 \) and \( R = 5 \) samples are smaller than 4.7 Å, while for the \( R = 3 \) and \( R = 2 \) samples some pores are still accessible to the 14 Å probe molecules.

The instrumental precision of the above results, based on ellipsometry, result in error ranges that are too small to be indicated in the figures. The precision in the indicated values of relative humidity and process temperature are approximately ±1% and ±5°C, respectively.

All films appeared highly transparent to the naked eye, and the transparency was enhanced by increase of water ratio. Striations, very small radial variations in thickness typically obtained in spin coating [14], were clearly visible under optical microscopy for all films, but they became more difficult to see with the naked eye as \( R \) was increased.

For each value of \( R \), optical scattering of the
seven films baked in the range 400–1000°C was examined and the results were averaged. No systematic variation was observed with annealing temperature. The results given in Fig. 6 show the mean values obtained and the vertical bars indicate the standard deviation. The figure shows clearly that, as \( R \) increases, the intensity of scattered light decreases, and the variation in scattering intensity also decreases. Scattering will result from both surface roughness and bulk inhomogeneity, and the reduction of either of these quantities is of value for optical applications. The results are in agreement with what has been found in the production of bulk gels [15] where, with increasing \( R \), finer texture was reported.

The stress results given in Fig. 7 show compressive stress, and the magnitude of this stress tends to increase with \( R \). For the first few layers, the results are less reliable. This is because an important source of error is the lack of circular symmetry in the wafer curvature, and this asymmetry tends to decrease with increasing total film thickness. Beyond the fifth layer, we estimate the precision in total film stress to be about 10%. In this range, more systematic variations of stress with number of layers is seen. This can be related to the fact that, as each new layer is annealed, previous layers undergo an additional anneal period, resulting in a variation of film stress with depth. However, accurate measurement of this variation requires film thickness to be measured after each coating, rather than interpolated as we have done.

At the annealing temperature there is an additional tensile stress component applied to the film because of the larger thermal expansion coefficient of the silicon substrate. It has been demonstrated that, in order for thick, crack-free films to be fabricated, the tensile stress in each layer must be eliminated at the annealing temperature; this results in compressively stressed films at room temperature [11]. The stress due to thermal contraction is given by

\[
\sigma_{th} = \frac{E_f}{(1-\nu_f)}(\alpha_s - \alpha_f)(T - T_A),
\]

where \( T \) and \( T_A \) are the measurement and annealing temperature, respectively, \( \alpha_s \) and \( \alpha_f \) are the thermal expansion coefficients of the substrate and film, respectively, and \( E_f \) and \( \nu_f \) are the Young’s modulus and Poisson’s ratio of the film, respectively. We have used the values \( E_f/(1-\nu_f) = 85 \text{ GPa} \), \( \alpha_s = 2.6 \times 10^{-6}/\text{K} \) and \( \alpha_f = 0.55 \times 10^{-6}/\text{K} \) [11]. For the annealing temperature of 1000°C, this gives \( \sigma_{th} = -170 \text{ MPa} \).

The intrinsic stress, defined as \( \sigma_i = \sigma_f - \sigma_{th} \), is also plotted in Fig. 7. Recently, Parrill [16] has reported in situ measurements of stress during annealing of sol–gel silica films on silicon which show a considerably larger stress reduction during cooling (about 450 MPa from 900°C to room temperature). However, the cooling time was several hours as compared with several seconds in our measurements; thus the difference may be accounted for by a significant contribution in Parrill’s case from viscous relaxation.

Fig. 7 shows that only the \( R = 5 \) film has approximately zero intrinsic stress. As \( R \) decreases, the
amount of intrinsic tensile stress increases. This shows that increasing the water content decreases the formation of tensile stress due to shrinkage, and therefore lowers the temperature at which the films must be processed to produce thick multilayers without failure.

Fourier transform infrared spectroscopy (FTIR) results are plotted in Fig. 8. The films examined were the thick multilayers deposited using rapid thermal annealing. One object was to determine whether excess water would cause an increase in the amount of OH remaining in the thick structure. Si–OH bonds, reported to give an absorption peak at about 950 cm$^{-1}$ [16,17], were absent in all cases, but there is a small shoulder in this region for the $R = 2$ and $R = 3$ films which does not appear for $R = 4$ and $R = 5$. The main peak at 1070 cm$^{-1}$, caused by the Si–O–Si stretching vibration, systematically increases with increasing $R$; this could be caused by increasing densification, which can give a large reduction in surface-to-volume ratio.

4. Discussion

The silica films shrink during thermal treatment first due to removal of trapped water and solvent within the structure and subsequently by continuous condensation and combustion of unreacted alkoxyls (–OR) and uncondensed hydroxyls (–OH). The shrinkage is constrained in two dimensions by the substrate; consequently, each of these two mechanisms is accompanied by a distinct increase in tensile stress [16], and an increase in porosity, as shown in Fig. 3. The densification indicated by reduction in thickness, as shown in Fig. 1, is gradual, as it is dependent on collapse of the pores by viscous relaxation of the film structure.

Figs. 1–3 show that the thickness, shrinkage and pore volume all decrease, and refractive index (before full densification) is increased, as the molar ratio of water to TEOS, $R$, is increased. The figures also show that the variations of the indices and porosities with the thermal treatment temperature become more gradual as $R$ is increased. These results, indicative of more complete hydrolysis and higher density with increasing $R$, are in agreement with other results [4].

Some workers [18,19] maintain that addition of excess water in weakly acidic silica sols speeds hydrolysis, thus producing a more highly branched polymeric network, but that it also slows condensation. Thus, we should expect that increased $R$ will result in lower sol viscosity, because of both the greater dilution and the lesser degree of condensation, and therefore in reduced film thickness before thermal treatment. We also expect reduced shrinkage and porosity formation during thermal treatment, because there are fewer unreacted –OR groups to be removed from the film.

Klein and Garvey [2] found that, in acid-catalysed solutions, increased water produces bulk gels with higher surface area and porosity. Fig. 3 shows that, as $R$ is increased, the porosity is reduced and, since the accessible pore volume drops for every adsorbate size, the total surface area is also less. This difference can be explained by the very large differences in the amount of time spent during the gelling, aging and drying stages of bulk gels and films. Aggregation, gelation and drying, and the related shrinkage, occur in seconds to minutes during film deposition, rather than days or weeks as in the bulk systems; therefore, less aging (cross-linking) results in a more compact structure in films compared with bulk gels [20]. Frye et al. [21] found that the isotherm for a bulk gel and a film prepared under the same conditions indicates pore sizes on the micrometre scale for the bulk gel, and on the nanometre scale for the film.

Simple models of shrinkage during formation of sol–gel glasses relate the large tensile stresses that
cause shrinkage to the capillary pressure associated with solvent drying from pores of very small radii of curvature. However, our results show that films produced using excess water, while having smaller pores that collapse at lower temperatures, actually show reduced shrinkage stresses. This correlates with the in situ stress measurements of Parrill [16], which show that the largest build-up of tensile stress during heat treatment is in the temperature range associated with removal of organics, i.e., 400–500°C. We conclude that the reduction in unreacted –OR groups resulting from more complete hydrolysis before spinning is the main factor in reducing stress formation during heat treatment.

5. Conclusions

Excess water yields a film with lower thickness per spin, and reduced shrinkage, porosity and pore size, and consequently with higher density. For porosity and pore size, the result is opposite to what has been observed in the production of bulk gels; the difference essentially results from the huge differences in the relative duration of the gelation, aging and drying stages. Increasing the amount of water yields films with higher homogeneity and surface uniformity, and thus reduced optical scattering. Higher water also reduces the tensile stresses resulting from shrinkage, and thus produces material more suited to crack-free thick multilayer films. We found no evidence that excess water results in increased optical absorption due to residual OH groups; in fact, the reverse appears to be the case.

Excess water gives significant improvement in film quality and ease of processing, except when substantial porosity is desired.

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References