Sol-gel fabrication for applications in photonic communications

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Chapter 4 Development of thick film by multilayer spin-coating process

An overview of the achievements presented in this chapter is provided below:

- A unified thermo-stress evolution is described. Organically modified silane was used to increase the compliance of the gel structure, leading to an increase in critical crack thickness. After rapid thermal annealing, a single-layer thickness of $\leq 0.45 \mu\text{m}$ was achieved without cracks. An alternative method is proposed to identify the zero-stress point by correlating with available data of the glass transition point of bulk glasses from the literature. This knowledge was used to successfully fabricate crack-free thick-film ($\sim 4 \mu\text{m}$) by multiple-deposition spin coating on 4" Si substrates. This work contributes to one manuscript in preparation;
- Particle-inclusions have been significantly suppressed by a simple solvent technique. The findings of this work may contribute to a patent;
- A striation suppression process has been developed without compromising the single-layer thickness of the film by using butanol as a replacement co-solvent. By modification of the Birnie's plot, a more robust co-solvent strategy is presented. This work on striations results in two manuscripts in preparation [1];
- Radial thickness non-uniformity observed using the in-house spin coater was eliminated. A hypothesis was proposed to explain the efficacy of lidless spinning. This work will contribute to one manuscript ; and
- By a simple optimization scheme, with the necessary construction and modification of the spin coating system and the entire station, thick films of 4-microns $\text{GeO}_2\text{:SiO}_2$ were synthesized in only **10 repetitions**. The propagation loss of the films fabricated as estimated by the prism-coupler method is $< 0.6 \text{ dB/cm}$. The improved mSC-RTA process described in this chapter is capable for synthesizing purely inorganic films from the alkoxide sol-gel route with much less iterative cycles, improved film uniformity and better optical film quality (i.e. reduction of inclusions) than reported in the literature. This result will be communicated through another manuscript .

In the previous chapters, the aspects of low-cost and composition flexibility of the sol-gel derived films were discussed and the ease of tailoring the composition was shown in Chapter 3 to be beneficial in a few photonic applications. The characterization of microstructural and optical properties of the $\text{GeO}_2\text{:SiO}_2$ thin films provide a basic process requirement for the development of the multiple spin coating deposition process.

Encouraged by the possibility of further improvements (see §2.4.9), the multilayer SC-RTA process was adopted for the fabrication of micron-thick germanosilicate film as the core layer of the waveguide structure. Since a substantial amount of the propagating optical power is confined in the core of the waveguide structure (for instance, the confinement factor, as determined by beam propagation simulations, is $\sim 80\%$ for a $4 \times 4 \mu\text{m}$ buried channel waveguide with $\Delta n = 1.315\%$, i.e. $x \approx 0.160$), a large part of this chapter deals with the synthesis of the core layer which was deposited on commercially available Si wafers with 10 microns of thermal oxide (thickness uniformity is $\pm 5\%$). This thick thermal oxide is used as a lower cladding for the planar or channel waveguide. Because of the high-temperature processing, most loss-bearing constituents were effectively removed to yield near ideal amorphous silicate films, thus allowing low-loss waveguides to be made. In the work of Syms *et al.* [2-6], while a number of aspects regarding the film defects was documented, namely, striations, particle-inclusion and uniformity [2, 3, 5-7], but none has been treated with significant improvement.

This chapter reveals the work undertaken by the author that addresses issues of film defects arising from spin coating,

- cracks—by increasing the critical thickness of cracking,
- comets and particle-inclusions—particle re-deposition,
- edge beading—film thickness that is significantly higher at the periphery of the substrate,
- thickness non-uniformity across large wafers—a thickness profile that is thicker at the centre, and
- striations—surface undulations.

Aside from cracking, the rest of the defects listed above is universal to all spin-coated gel films. In general, the effect of other defects, except striations, can be suppressed if the number of repetition can be reduced. Because of the lack of commercial dedicated equipment for high quality spin coating and the incomplete understanding of defect mechanism in some cases, the author believes that further work in these aspects can only be beneficial.

A glance at similar work previously reported shows a large variation on the single-layer thickness and, in many cases, no effort was dedicated to increase the single-layer thickness (Table 4-1). As discussed below, one reason that explains the

general reluctance to work with a more viscous sol is the fact that most defects tend to be more severe. Some recent understanding about the mechanisms of the above defect generation and suppression techniques [8-23] prompt a second look at the SC-RTA in an attempt to optimize the process for better quality films.

From the results of preliminary fabrication of the relatively large footprint of the arrayed waveguide structures (cf. §2.3 and §5.3), no transmission was observed. This was partially attributed to the growth of micro-cracks in the films (several hundred microns) that were mostly caused by inclusion of gel particle and glass flakes, thickness non-uniformity ($> 30\%$ across 4" wafers) and striations (tens to hundreds of nanometers). As suggested in Section 2.3, the quality of the core layer critically affects the functionality of essential photonic components such as an AWG. Strategies and techniques for mitigating the aforementioned defects developed in this work are presented in this chapter to enable the fabrication of practical AWGs.

Table 4-1. Comparison of the single-layer film thickness (measured after thermal treatment unless otherwise stated) for multilayer coated inorganic waveguides reported in the literature. Dip coating process is characterized by the withdrawal rate in $\text{cm}\cdot\text{min}^{-1}$; whereas spin coating process is noted by the spin speed in rpm.

Composition	Coating condition	Single-layer thickness, nm	Ref.
$\text{TiO}_2\text{:SiO}_2$	$3-11\text{ cm min}^{-1}$	160 – 300	[24]
$\text{GeO}_2\text{:SiO}_2$	10 cm $\text{min}^{-1}/\text{RH}60\%$	210	[25]
$\text{GeO}_2\text{:SiO}_2\text{ (Er}^{3+}\text{)}$	4 cm min^{-1}	10	[26]
$\text{GeO}_2\text{:SiO}_2$	$2-7\text{ cm min}^{-1}$	< 37	[27]
$\text{TiO}_2\text{:SiO}_2$	2500 rpm/20 s	300 (as-dep.)	[28]
$\text{GeO}_2\text{:Al}_2\text{O}_3\text{:SiO}_2\text{ (Er}^{3+}\text{)}$	3000 rpm/30 s	126	[29]
$\text{GeO}_2\text{:M}_x\text{O}_y$	2000 rpm/20 s/ $<\text{RH}30\%$	~ 166	[30]
$\text{TiO}_2\text{:SiO}_2$	1000 rpm/30 s	< 230	[3]

Each topic in this chapter begins with a brief summary of the initial observations of each of the defects. Since no comprehensive texts exist that deals with many of the topics of this chapter, rather detailed overviews of the existing available knowledge of the underpinning physical mechanisms are reviewed, then the solutions or improvements implemented are evaluated. A summary of the latest understanding of the correlation between defects and spin-coating parameters will be

first provided; a holistic approach is used to identify parameters that yield defect-free film, across the entire 4" wafer and larger, while maximizing the single-layer thickness.

4.1. The multilayer spin-coating—rapid thermal annealing (mSC-RTA) process and equipment

The original SC-RTA process as developed by Syms *et al.* [2-4] requires the *a priori* knowledge of the zero-stress annealing temperature for a particular silicate composition. Owing to the single-layer thickness limitation, practical dielectric layers were fabricated by multiple coatings of the sol-gel solutions and subsequent intermediate annealing to avoid an accumulation of stress at large thickness (c.f. §4.3.1.1). Syms *et al.* [2, 3] ingeniously made use of a rapid thermal processor to treat each coating up to an annealing temperature (700°C to 1100°C) that continuously yielded a near stress-free film as the repetition progresses. A thickness of $> 30 \mu\text{m}$ of borophosphosilicate ($\text{B}_2\text{O}_3\text{:P}_2\text{O}_5\text{:SiO}_2$) films was claimed to be achievable. An extended period of heat treatment at a temperature higher than the annealing temperature was performed to ensure that the inherent graded density profile of the dielectric stack converges to a plateau state.

The fabrication of optical-quality microns-thick $\text{GeO}_2\text{:SiO}_2$ films by the mSC-RTA process was preformed with addition and modification to the process flow as shown before in Figure 3.1 for the deposition of single-layer thin films. The buffered Si wafers or substrates were mostly used directly out of the box. When cutting was required¹, the substrates were then subjected to a solvent-water wash and blow-drying by N_2 . Before deposition, a prolysis cleaning step was done either by electric air furnace with a 5-hour ramp to 550°C, then hold for 30 minutes or rapid thermal processor (RTP) in O_2 for 2 mins at 600°C [31]. The mSC-RTA process employs a RTP to carry out high temperature annealing $> 900^\circ\text{C}$ in less than a few minutes² after the spin-coating of each layer of pristine and dried xerogel film. Once the target thickness is achieved, a consolidation heat treatment is imposed at an elevated

¹ Precautions were exercised to prevent any scratching of the oxide surface by scattered Si debris; or Si debris landing on the oxide surface. For debris of an appropriate size, it is difficult to remove once it chemically adheres on the oxide surface.

² The RTP has become a standard tool in the microelectronic/semiconductor industry [32]. Typically, the entire RTA recipe takes less than a minute to execute; however, the system cooling rate may vary from system to system and depends on the highest temperature and duration of the recipe.

temperature for an extended duration to further allow the multli-layer films to form a homogeneously dense film. A schematic of the process flow can be visualized in Figure 4-1.

Figure 4-1. The mSC-RTA process flow for slab waveguide synthesis.

In the RTP system, a set of halogen lamps is used to heat the Si wafer (c.f. interband and free carriers absorption of silicon). A pyrometer (MODLINE4 with a pass band of 4.8 to 5.2 μm) is used to measure the temperature. As shown in ref. [33], a pyrometer with a pass band centered around 5 μm avoids interfering radiation from the halogen lamp source (whose cut-off is around 4.0 μm due to the absorption of quartz used). The pyrometer has been calibrated to the 4” buffered Si wafer that is used as a substrate for the deposition of the GeO₂:SiO₂ films to a tolerance of ~ ±8°C. A temperature variation across the 4” Si wafer has been found to be < 40°C. A schematic of the RTP setup is shown in Figure 4-2. Adopting from the ref. [3], a quartz cover was used to prevent condensation of vapourized residues on the chamber quartz window. A simple recipe was used, comprising several seconds of ramp to 500°C, hold for 10 seconds, and ramping again to 950°C for 20 seconds of holding then cooling for 100 seconds to ~ 25°C. The 500°C hold is to allow ample of time for

any organic constituents to be decomposed and removed via the exhaust before densification takes place. The above step also serves to avoid overshoot of the hold temperature at 950°C due to slow system response. Considering the wavelength spectrum of the halogen source tails off at $\sim 4\ \mu\text{m}$, the xerogel film and buffer SiO_2 ($> 10\ \mu\text{m}$ thick) absorb very little of the IR radiation³; hence, the Si substrate acts as a heating element for the annealing of the xerogel film. Assuming a thermal diffusivity that of a $\nu\text{-SiO}_2$ ($\sim 0.0082\ \text{cm}^2/\text{s}$), the heat from the Si substrate can traverse the SiO_2 and the xerogel film in time scale of $\sim 10^{-4}\ \text{s}$ (c.f. ref. [33]). Hence, rapid annealing of the xerogel films is seen to be effective in short durations.

Figure 4-2. A schematic illustration of the JipELEC RTP system used.

³ For wavelength less than $4\ \mu\text{m}$, the absorptivity, α (see section 3.4) $< 0.2\ \text{mm}^{-1}$ which translates to an intensity attenuation of less than 0.2% for a $10\ \mu\text{m}$ -oxide.

Figure 4-3. A schematic illustrate of the in-house designed glovebox for the mSC-RTA process.

Due to the labour intensiveness of the mSC-RTA process, a new in-house sol-gel processing chamber was designed⁴ and fabricated. The chamber comprises of a glove box for solution preparation purpose, one other for spin-coating deposition and another down-stream compartment houses the RTP. The schematic is shown in Figure 4-3. Besides technical and process requirements, the design also incorporated ergonomic considerations⁵. Proper air tight openings were fitted to allow read-through for gas, vacuum and electrical pipes. Rearrangement of the clean room was planned and executed to accommodate the new cluster and in general increase space for human maneuvers and reduce workplace hazards. The glove box compartments were passed the test for class 100 enclosures (i.e. ≤ 100 particles that are of a size $\geq 0.5 \mu\text{m}$, compliant with the US Federal Standard 209E⁶) clean room standards.

The merit of the consolidation step has been validated by the work of Syms *et al.* [3]. As a result of the repetitive RTA cycles for each new xerogel film deposited,

⁴ The original design specifications, proposed by the author, included some advanced features. However, due to some fabrication issues, some features were omitted. The author also supervised the construction of the entire chamber and subsequent modifications.

⁵ The author and other users often experience back problems after prolong usage at the old spin-coating glove box due to a lack of space for human maneuvers and inflexible positioning that forces users to stand.

⁶ New cleanroom standards documents are in the process of formalization by the International Organization for Standardization (ISO) [34]. These documentations extend the standardization to equipment, facilities, and operational methods for cleanrooms and associated controlled environments.

prior layers are subjected to an increasing number of RTA cycles in an accumulative fashion, hence, a slight increase in refractive index (RI) or density of the film. This RI gradient⁷ contributes to the uncertainty in the determination of RI by the prism-coupling technique (alternatively called m-line scan) and may contribute to polarization dependence of the eventual waveguide. In reference [3], an extensive heat treatment, at a temperature close to the reflow temperature of the core layer, demonstrated that the gradient was effectively smoothened.

4.2. Characterization of thick films and measurements of early planar waveguide slabs.

For most part of the work described in this section, the determination of thickness was carried out by using a reflectometer (Filmetrics F20) for thin films on Si substrates and prism-coupling (PC) set-up (METRICON 2010) for thick films on SiO₂/Si substrates.

The theory, equipment and application of reflectometry or optical reflectance measurement are well-established (c.f. ref. [37]). In general, optical constants such as RI, thickness and sometimes, even surface roughness can be characterized. The F20 reflectometer uses a broadband tungsten halogen source from 600 to 1000 nm. The beam spotsize is ~ 3 mm at normal incidence. With known values of RI estimated from §3.5.7 using the nominal GeO₂ content, x , the specified working range of thickness from the manufacturer is ~ 20 nm to 50 μ m. The thickness determination uncertainty can be seen to be less than ~ 10 nm on average (see comparison in the Table 4-2). The uncertainty can be improved (or closer to the specified precision of 0.1 nm by the manufacturer [38]) if the film structure is better known (c.f. §3.5.7). For thickness profiling of the radial thickness non-uniformity (RTNU) across substrates or wafers, a steel ruler fixed to the stage was used as a position gauge.

⁷ This gradient can be qualitatively evaluated by the P-etch method [3] or quantified by spectroscopic ellipsometry [35, 36].

Table 4-2. Comparison of thickness measurement of single-layered films deposited on Si by the reflectometer (FM) and spectroellipsometer (SE). The standard deviation (SD) is given for the difference values.

Samples	SE Thickness, nm	FM Thickness, nm	Difference, nm
5a1	111.10	85	26.10
10a1	129.40	125	4.20
20a1	122.30	110	12.30
40a1	106.10	98	7.80
40a2	186.10	185	1.50
5b1	368.10	383	-14.90
10b1	314.00	312	2.00
20b1	368.35	367	1.55
40b1	282.70	278	4.70
40b2	440.60	438	2.60
		SD	10.23

Another thickness measurement method used in the work is the prism-coupling technique (METRICON 2010). This concept was first conceptualized and mathematically formulated by Tien *et al.* [39, 40]. A simple description of the theory is also found in ref. [41]. Today, PC equipment has become a standard characterization tool in many thin-film, optics and photonics laboratories in universities and research institutes. RI and thickness can be readily determined with conventional setups. The film face of the sample is pushed against a high-index prism which is fixed to a rotating stage. As the stage turns, reflection at the prism-film interface is detected as shown in Figure 4-4(a). At certain angles (i.e. condition of phase matching), the effective indices, n_m^{eff} , will match the propagation constants, β_m , of optical modes supported by the film structures, thus part of the incident energy is coupled into the film (via the evanescence wave). A reduction in the reflected intensity of the incident beam was detected as shown in Figure 4-4(b) at phase matching conditions. By the following relationship [42, 43],

$$n_m^{eff} = n_p \sin \left(\sin^{-1} \left(\frac{\theta_i}{n_p} \right) + \theta_B \right), \tag{4-1}$$

where n_p is the RI of the prism and θ_i and θ_B are the angle of incidence and prism base as shown in the schematic diagram (Figure 4-4(a)), the effective index is derived from the angle of incidence (Figure 4-4(b)).

Figure 4-4. (a) The operating principle of a prism-coupling waveguide measurement setup with a propagation loss measurement attachment. (b) The measured reflected intensity from the prism-film interface for both the TE and TM modes.

On the other hand, the theoretical effective index, $\bar{n}_m^{eff}$, for a particular linear polarization (TE or TM) mode can be numerically determined through the waveguide dispersion relationship. Knowing the mode number, m , wavelength of the lightwave in air, λ_0 , RI of medium above and below the film and assuming the extinction coefficient of the film is negligibly small, there is one set of values of the RI and thickness of the film that yields $\bar{n}_m^{eff}$ that is closest to n_m^{eff} [41, 44-46]. Therefore, by determining at least a pair of $\bar{n}_m^{eff}$ and $\bar{n}_{m+1}^{eff}$ for two effective indices of two measured modes, n_m^{eff} and n_{m+1}^{eff} , RI and thickness, can be reliably determined [43]. The accuracy of the values inevitably enhances by taking an average of additional pairs of effective indices. The minimum RI resolution is 0.00009 which is governed by the minimum step size of the θ_i . Data averaging could smoothen out random error due to single-step shift, but it was omitted. Polarizers with axes relative to the prism enable the study of TE or TM modes. When studying the TE and TM modes, the coupling pressure was found to affect the measurements. Caution was exercised to avoid overcoupling (i.e. excessive applied pressure) [43] which would lead to shifts in the TM modes. In fact, the 'dual film mode' available in the METRICON software is capable of taking the supported modes of the SiO₂ undercladding (see Figure 4-4(b)), the RI and thickness of a bilayer system can be determined under ideal conditions [43]. However, in this case, the RI and thickness of the relatively thick 10 μm -SiO₂-buffer layer cannot be resolved after deposition of the film due to effects of stress on the lower-ordered modes of the buffer. Hence, the RIs of the SiO₂ are assumed according to the procedures in ref. [43]. Such assumption leads to additional uncertainty of $\pm$

0.00025. The uncertainty on the thickness values is typically < 20 nm as estimated from a standard deviation of results given by numerical operations done by the METRICON analysis software. Since the planar waveguide was designed to be single-mode at 1550 nm (RI ~ 1.463 and thickness of ~ 4 μm) with one equation and two unknown parameters (i.e. RI and thickness), the thickness value was taken from measurements at 632.8 nm. The uncertainty in the thickness determined at 632.8 nm translates to an uncertainty in RI at 1550 nm of $< \pm 0.00002$. Summing up all the above uncertainties in quadratures, the RI measured by the prism-coupling method is associated with an uncertainty of $< \pm 0.0003$ (accounting for the possibility of single-step shift). Fitted with a He-Ne laser and a semiconductor diode laser, characteristics at 632.8 and 1550 nm can be measured.

An approximation of the propagation loss of a planar waveguide can be determined with a loss attachment (Figure 4-4(a)). A collection probe connected to a bunch of waveguiding fibres is placed very close to the surface of the film. The purpose of the probe is to pick up light that is scattered by the film due to any of the following mechanisms:

- Surface roughness,
- Rayleigh scattering from the intrinsic homogeneous glass, and
- Scattering from interfaces of defects (i.e. cracks, inclusions and pores).

The contribution of higher order scattering such as Raman and Brillouin scattering is likely to be negligible at the level of light-source intensity and optics set-up used by METRICON. Assuming that the scattered intensity, I_{scat} , at a certain position is proportional to the confined light intensity (i.e. the integral intensity, $I_{\beta m}$) of a particular propagating mode, I_{scat} can be expressed in an exponential form according to the Beer-Lambert Law,

$$I_{\text{scat}} \propto I_{\beta m} \propto e^{-\alpha z}. \quad (4-2)$$

Therefore, an exponential curve can be fitted to a I_{scat} vs z plot to deduce an experimental coefficient of propagation loss. An example of such plot is shown in Figure 4-5(b). The initial spike in the graph likely reveals a scattering centre (i.e. defects that will be discussed in the following sections) which is visible in Figure 4-5(a) as bright red spots along the streak perpendicular to the prism. Taking the region in the centre of Figure 4-5(b) that is the most exponential-like, an α of 0.06

dB/cm was derived which is below the detection limit of 0.15 dB/cm [47, 48]. Considering the geometry of the loss measurement in Figure 4-4(a), the scanning axis, parallel the substrate surface, is fixed. Thus, if there is severe thickness non-uniformity of the film, there will be additional uncertainty in the determination of α with the above method.

Figure 4-5. (a) Camera view of the prism-coupling setup at phase-matching condition with the TE_0 mode at 632.8 nm. (b) I_{scat} vs z plot from propagation loss measurement using the METRICON using a 1550 nm semiconductor laser with a TE polarizer.

A sample for which $x \sim 0.200$ (20 mol% GeO_2) was measured and summarized in Table 4-3. As evident from Figure 4-5 (i.e. the bright dots along the streak) and Figure 4-6 (the peaks from the beginning; note the non-exponential nature), there is a substantial amount of defects that scatters light from the plane of the film, thus rendering the film undesirable for the device fabrication. Light scattered from the bulk prism is likely able to find its way to the entrance face of the fibre bundle. This problem was later mitigated by the use of a stray light shield mounted between the prism and the fibre bundle. Films synthesized at this stage were far from ideal. Factors affecting the film quality and difficulties in processing are discussed below.

Table 4-3. Characterization of a mSC-RTA planar waveguide, (sample ID.: PWG5; $x \sim 0.200$). The uncertainties accompanying the derived quantities are standard deviations of a number of readings carried out at different locations of the sample.

	21-layer	
	632.8 nm	1550 nm
Thickness (μm)	4.97 ± 0.05	4.97 ± 0.06
Number of modes	4	2
Refractive index (TE)	1.4830 ± 0.0005	1.4687 ± 0.0005
Refractive index (TM)	1.4835 ± 0.0005	1.4694 ± 0.0005
Attenuation coefficient (dB/cm)	$1.27 \pm 0.2^*$	$0.3 \pm 0.2^*$

*Such difference in attenuation between two wavelengths is typically attributed to scattering of the Rayleigh type whose efficiency scales with λ^{-4} [49-55].

4.3. Challenges of forming a defect-free, homogeneous spin-coated sol-gel films

There is no doubt that spin-coating solution deposition is a very simple way to form a film on a rigid substrate (with smooth, rough or even patterned surfaces). However, this simplicity comes at a cost. To form inorganic and amorphous films as desired in optic and photonic applications via a sol-gel route, the solution is first dispensed onto the substrate and it is subsequently spun till a xerogel film remains. An RTA treatment follows. Reiterating points highlighted in Section 2.4.8 and above, during the spin-coating process, striations may develop; comets, particle inclusions or glass flakes can be found on the films immediately after rotation of the substrate stops; the xerogel film may also have macro thickness non-uniformity across the substrate. When the xerogel film is drying at temperatures $< 200^\circ\text{C}$, cracks can be observed if the film thickness exceeds a critical value (see §4.3.1). Even if the film survives the drying stress, it may still crack during RTA due to other reasons. The causes of cracking of the xerogel or the dense multilayer film are well known [16, 56, 57] and

the few available solutions seem to be effective for a number of material system [2-4, 16].

Much work from the academia and the industry has gained much needed insights into the various defect phenomena and different solutions have been proposed [8, 11, 14-16, 20, 21, 58-75]. However, the ways in which some of these spin coating phenomena will affect films synthesized by the sol-gel process are not well-known. In response to the growing interests in sol-gel derived films in recent years, a number of works has been performed on spin coating defects on sol-gel derived films [8-16, 20, 59, 75-78]. Most studies are restricted to experimental observations. Rigorous theoretical analysis is rare due to the limited availability of commercial characterization equipment and limited characterization of the process (i.e. evolution of the film: rheological and mechanical change) [9, 10, 13, 59, 78]. In addition, due to the scarce interest in adopting spin coating for critical processes, state-of-the-art spin coating equipment is not commonly accessible.

Figure 4-6 illustrates a few early attempts to deposit the core $\text{GeO}_2:\text{SiO}_2$ layer by the mSC-RTA process. Three types of the above-mentioned defects are clearly visible (hence, not acceptable for any optical or photonic functions): surface striations accountable by the 'Marangoni effect' (Figure 4-6(a)); micro-cracks are indicative of comets and particle inclusions (Figure 4-6(b)) and circular fringes are typical of a thickness variation (Figure 4-6(c)). In particular, the effect of the crack micro-clusters (for simplicity, these clusters and inclusions are collectively referred to as point defects hereafter) in Figure 4-6(b) have on the fabrication of AWG devices can be easily visualized when a device design is superimposed onto the samples (Figure 4-6(d)). There is no way to avoid these point defects ranging from a few microns to a few hundreds of micron in size; and these clusters will scatter most of the incident propagating optical signal rendering the device useless. The extent to which these point defects have on the operation of an AWG is discussed in detail in Section 5.5. From the early attempts to fabricate multilayer thick films, such task was apparently not trivial. Even though, satisfactory results have been published by the various groups, results are not readily reproducible as film quality also depends on environmental conditions and equipment which are likely different. Effort in studying these defects was indispensable to demonstrate functional AWG devices.

Figure 4-6. (a) A fresh 10 μm SiO_2/Si wafer about 6 cm in the lateral dimension; earlier thick films (~ 3 to $4 \mu\text{m}$) samples by mSC-RTA with particle/debris induced localized cracks, the white reflecting specks (b) and thickness non-uniformity with decreasing thickness from centre to side due to non-newtonian flow of the sol (c). Such thickness variation can be as much as $\sim 30\%$ (PWG16/17). (d) An AWG schematic drawing adjusted to approximately the same scale as the film samples.

While there is still much to be known about these defects of spin-coated films, to date, there is a lack of comprehensive collection and critical review of all types of defect phenomena discussed above. In an attempt to summarize the work of his group on film stress, cracking and striations of sol-gel derived films, Prof. H. Kozuka has contributed a chapter in the latest 'Handbook of Sol-gel Science and Technology' [16]. As yet, many existing solutions suggested for suppressing striations and thickness non-uniformity involve more diluted or (significantly) less viscous sols that ultimately compromise the single-layer thickness. Based on some trends, observations and possible hypotheses of the various defect mechanisms reported recently, experimental work was carried out aiming to suppress these defects under a condition which may allow increased single-layer thickness, defect-free films to be synthesized.

4.3.1. Stress mechanisms and cracks

Out of all the coating defects highlighted above, the most detrimental is cracks. Undoubtedly, cracks were observed in many forms in the author's experiments. For the purpose of optic or photonic applications, cracked films are essentially useless due to the significant scattering of light. And for this reason, this aspect of sol-gel derived films is most well studied and well known. The phenomenon of thickness-limited crack-free films in elevated temperature deposited on a rigid substrate has been well-documented in the past [16, 56, 79, 80]. One common aspect in many of these cases (particularly true for sol-gel and CVD dielectric films which are porous as deposited) is that shrinkage of the film occurs progressively at higher temperatures. When a film is first deposited on a rigid substrate, it is bonded to the surface of the substrate so that any relative movement at the interface is restrained subjected to the adhesion force. When the film is subjected to high temperature annealing (for the purpose of densification), volume shrinkage may freely proceed in the direction perpendicular to the substrate but *not* along in the plane (i.e. in-plane) of the substrate [56, 81]. As a result, an in-plane tensile stress exists through the thickness of the film. To compound this effect, the rigid substrate used in many applications (e.g. silicon and III-V compounds) has a relatively high thermal expansion coefficient. Under this circumstance with the in-plane film-dimension attempting to shrink (called an in-plane strain) and substrate dimension expanding, the substrate bows biaxially (a perpendicular deflection to the plane of the substrate) towards the film-side enduring a substantial tensile stress which increases with temperature. This effect is graphically shown in Figure 4-7. For a gel-film, the change in microstructure at elevated temperatures as presented in Figure 4-7 (§2.4.7) inevitably causes volume shrinkage via the various mechanisms (e.g. osmotic, disjoining and capillary forces etc. [80]). From Figure 3.21, a significant shrinkage of the film occurs till the temperature is beyond 700°C. Typical shrinkage of film (i.e. reduction in film thickness) can be ~30% [80, 82, 83]. To understand cracks as observed in the mSC-RTA process, consider the change in the microstructure of the gel films with temperature (Figure 4-7). Since a planar tensile stress component is required to initiate crack growth, it is likely to take place during heating up and isothermal hold when film shrinks and substrate expands rather than during the cooling cycle. Since the dominant factor

causing mechanical failure is stress (σ_f in Eq. 2.12). In the next section, the change of stress with temperature is discussed.

Figure 4-7. Illustration of the structural evolution at different temperatures in molecular, microscopic and macroscopic scales (respectively from top to bottom). Bowing of the substrates is caused by the tensile stress (biaxial) in the film. (a) represents the as-deposited xerogel film state. (b) refers to the state close to the maximum tensile stress primarily caused by the shrinkage of the gel film. (c) is at a state close to the glass transition temperature of the film.

4.3.1.1. Thermo-stress relationship of gel films

Due to the change in microstructure of the gel-film (intrinsic stress) and elastic mismatch (thermal stress) of the film and substrate, the total film stress can be expected to change with temperature. Any increase in the stress shall increase the propensity for cracking (c.f. Eq. 2.12). A study of the stress evolution⁸ of a gel film at incremental temperature (Figure 4-9, c.f. [2, 3, 15, 16, 84, 85]) reveals the few hazard zones where cracking may occur. The construction of Figure 4-9 is discussed in the

⁸ Note that positive stress typically represents stresses with tensile nature and conversely, negative values for compressive stresses.

figure caption. There is typically a peak of the stress curve at a temperature $< 100^{\circ}\text{C}$ which strongly suggest the dominance of the capillary force during the evaporation of free volatile solvents (stress regime I^{S} in Figure 4-9). Beyond 150°C , tensile stress increases in the film to a rather short plateau $\sim 400 - 500^{\circ}\text{C}$. The film stress will continue to rise to a peak ~ 700 to 850°C (stress regime II^{S}), after which stress is relaxed viscoelastically as the viscosity reduces while approaching the glass transition temperature, T_g at $> 900^{\circ}\text{C}$.

In I^{S} , nearly 30% of the total thickness reduction occur in this region. Such thickness reduction is primarily caused by the capillary force as the solvent(s) within the gel is evaporated from the film. The shrinkage that is purely due to the loss of volume occupied by solvent after solidification may accumulate stress as observed by Croll [86] on thermoplastic polymers. A crude analysis using Croll's equation for sol-gel-derived films revealed that cracking can be observed for xerogel films thicker than 3 nm (see Appendix H). However, from the author's experience, no cracking was ever observed for as-deposited films with thickness $< 0.6 \mu\text{m}$. The various reasons why Croll's equation may fail to describe the drying of sol-gel-derived films are presented in Appendix H. One possibility is that at the definition of solidification as defined by Croll, the gel body has assumed an elastic property that will resist shrinkage due to the loss of solvent. At a later stage of drying when the menisci of the solvent begins to enter pores of the gel, significant amount of pressure builds up due to the capillary force as discussed below.

Brinker and Scherer [56, 80, 81] have argued that capillary force is the dominant force driving shrinkage in bulk gels; and recently, by modeling the xerogel film as a viscoelastic network under biaxial external loading of thermal stress and syneresis shrinkage and interaction between capillary pressure and hydrostatic pressure within pores, Wang and Xiao [87] obtained agreement to a certain extend with the experimental results of [88] in terms of temporal stress relaxation at room temperature and stress evolution in a temperature range up to 500°C . Kozuka and Parrill's results [16, 85] (e.g. increased water ratio the sol leads to increased film stress and density) also suggest that capillary force is clearly observable.

The capillary force begins to take effect as soon as the receding gel liquid (viz. solvents, water and solutes) interface enters the gel body (i.e. meniscus are inside the gel; c.f. Brinker [56] and Figure 4-8). This force originates from the hydrophobicity

of the inorganic glassy network. At the liquid-solid-vapour interface, a contact angle, ϕ , exists according to the Young's equation,

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos(\phi), \quad (4-3)$$

where γ_{SV} , γ_{SL} and γ_{LV} refer to the specific surface energies at the solid-vapour, solid-liquid and liquid-vapour interfaces, respectively. The balance of forces is visually illustrated in the inset of Figure 4-8. Eq. (4-3) is derived most self-consistently from a thermodynamic consideration [80, 89].

From Figure 4-8, a component of γ_{LV}/δ (δ refers to a unit length) perpendicular to the pore wall can only be balanced by the toughness of the network structure. Hence, for a compliant⁹ network, there would be a net force pointing towards the centre of the pore, hence, the pore either collapse or shrink. The capillary pressure on the network is at maximum when network

Figure 4-8. A schematic drawing illustrates evaporating solvent(s) in a gel cavity of dimension, r_p . The free-body diagram is superimposed on the magnified triple-interface point. See text for explanation of the various parameters.

is withstanding the tension in the liquid which is characterized by the Laplace's equation [81],

$$P_{\text{cap}}^{\text{max}} = \frac{2\gamma_{LV} \cos(\phi)}{r_p} \quad (4-4)$$

where r_p is the radius of the pores. Brinker and Scherer [80] have derived analytically¹⁰ that the biaxial in-plane stress of a film (viz. imposing zero strain boundary condition at film/substrate interface) can be as large as the capillary pressure. Adopting the approach of Beuth [90], the normalized depth of a surface crack (a/H) can be assumed to be > 0.8 with $H = 0.8 \mu\text{m}$, a typical tensile stress on an as-deposited TEOS-derived xerogel film (TXGF) of $\sim 30 \text{ MPa}$ [15, 16, 84], the D_a (one of the two, Dunbar parameter) $= -0.7$, $Z = 3.2$, $\nu = 0.2$ [80, 91], the G_c is estimated at 0.12 J/m^2 . This G_c estimation is indeed very close to twice of the surface energy of a TXGF $\sim 0.055 \text{ J/m}^2$ [92-95]. Furthermore, from a tensile stress of 30 MPa ,

⁹ Elastic compliance is defined as the inverse of elastic modulus.

¹⁰ The analytical treatment involves the different interactions (i.e. giving rise to a hydrostatic pressure to the pore liquid [80]).

the expected pore diameter from Eq. (4-4) (assuming $\varphi \approx 0^\circ$ and an average surface tension of the liquid solvents of $\sim 0.023 \text{ J/m}^2$ or mN/m) is $\sim 1.5 \text{ nm}$. The pore size of a gel film that is still partially saturated with solvents is relatively difficult to measure. As soon as the condensed solvent within the xerogel film starts to be forced out, capillary pressure of higher magnitude is likely to drive shrinkage of pores. However, by performing surface modification¹¹ on the pore walls or supercritical drying¹², the pore size may be preserved. Data from several sources reported pore size of a TXGFs (r_p) ranging from 1.5 to 40 nm [98-101]. The above comparison indeed may show the dominance of the capillary force that could lead to cracks as observed in the laboratories for as-spun TXGFs.

Taking some typical values $\gamma_{LV} = 0.072 \text{ J/m}^2$ (since water is the least volatile sol constituent), $\varphi \approx 0^\circ$ and $r_p \sim 3 \text{ nm}$, $P_{\text{cap}} \sim 50 \text{ MPa}$. Such pressure yields a typical tensile film stress at $\sim 100^\circ\text{C}$ (see Figure 4-9). Kozuka [16] has noted during *in-situ* video observation that most films begin to show cracks between 100 to 400°C . At this low temperature regime, the film is relatively thick and compliant (i.e. small E_f), hence, the strain energy release rate, G_f may exceed the critical level (G_c) at relatively low film stress. In the II^{Sa} regime, residual organics (i.e. SiOR) are being decomposed by pyrolysis and further polycondensation ensues causing a sharp rise in the tensile stress (c.f. [56, 80, 81]). Despite the increase in the modulus and reduction in thickness, a sufficiently high film stress leads to crack growth as observed commonly in experiments [15, 16, 102]. In general, cracks that are formed $< 500^\circ\text{C}$ appear to be non-directional as presented in the inset of Figure 4-10(a) and [16].

At temperatures beyond the plateau in regime II^{S} (i.e. regime II^{Sb}), tensile stress increases again due to continual condensation, sintering for which the rate is inversely proportional to the pore size and thermal stress. Cracks on a single-layered alkoxide gel films are seldom observed due to increased modulus and reduced thickness. In the cases of a relatively thick hybrid gel film (e.g. TEOS-MTES) and multi-layer inorganic films, when cracks are activated they are dependent upon the mechanical properties of the substrates (see the inset of Figure 4-12 and ref. [3, 84,

¹¹ The surface of pores modified by trimethylchlorosilane (TMCS) or hexamethyldisilazane (HMDS) via infiltration or spin-coating is known to retain pore size by an elastic 'spring-back' response [96, 97] that counteracts the compressive capillary pressure.

¹² By drying in a supercritical condition (i.e. pressure and temperature), the gaseous and liquid state of the solvent coexist in a single phase (i.e. mixture), hence abolishing the phase boundary between the states, rendering $\gamma_{LV} \rightarrow 0$.

103, 104]). When $\langle 100 \rangle$ are used¹³, cracks are found along the directions of $\langle 010 \rangle$ or $\langle 001 \rangle$ due to a higher compliance than modulus of (110) planes [103]. This substrate dependence is likely to be a result of the increasing differential in the thermal expansion coefficients and the thermal strain at the film/substrate interface (Figure 4-9).

Figure 4-9. A representation of the change in the mechanical state of the gel films (silica-based) at different temperatures. This graph is constructed based on a collection of data from the various sources [15, 80, 83, 84, 91, 105]. The elastic modulus (E) for film is estimated by applying the porosity-modulus relationship (ref. [105]) on the porosity determined in Figure 3.21 (c.f. §3.5.7) and the value at room temperature is approximated from refs. [106, 107]. The elastic modulus for bulk is taken from data of ref. [91]. The film stress curve, σ_1 , is modeled after refs. [15, 16, 84, 85] where data was measured *in situ* and σ_2 is modeled after refs. [2, 3]. Since the data of film stress for σ_2 done *ex situ*, at room temperature, the σ_2 curve corresponds to the values of intrinsic stress as calculated in refs. [2, 3].

Interestingly, at temperatures higher than $\sim 800^\circ\text{C}$, the intrinsic stress begins to relax. In the fabrication of t-SiO₂, a stress-free oxide can be produced $\sim 1000^\circ\text{C}$

¹³ Alternatively, when $\langle 111 \rangle$ wafers are used, cracks are non-directional as the mechanical properties are isotropic on the plane of (111).

[108]. This has been attributed to the viscoelasticity of the glass in the vicinity of the T_g and above. The temperature dependence of viscosity of silicate glass can be represented in the Vogel-Fulcher form [80],

$$\eta = \eta_0 e^{\left(\frac{A}{T-T_0}\right)}, \tag{4-5}$$

where η_0 , A and T_0 are constants, T is the absolute temperature and η_0 has units of Pascal-seconds. Hence, below a certain viscosity, viscous flow begins and permanent deformation in the film occurs to relax the film stress. The stress relief behaviour can be represented by [109], for the case of a biaxial stress,

$$\sigma(t) = \sigma_0 \left[\bar{c} e^{-\bar{p}_1 t/\tau_s} + (1-\bar{c}) e^{-\bar{p}_2 t/\tau_s} \right], \tag{4-6}$$

where $\bar{c}$, $\bar{p}_1$ and $\bar{p}_2$ are functions of material constants, the shear relaxation time and dilatational retardation time, respectively. The shear relaxation time is defined as

$$\tau_s = \eta / G_0, \tag{4-7}$$

where $G_0 = \frac{E}{2(1+\nu)}$ is the instantaneous shear modulus, with E being the elastic modulus and ν the poisson ratio. This stress mechanism is likely the cause of the reduction in stress shown in σ_2 of Figure 4-9.

Sym *et al.* have found that at a compositional-dependent temperature [4], the intrinsic film stress is reduced to zero at which crack-free multilayer (up to $> 10 \mu\text{m}$) sol-gel-derived films can be synthesized repeatably. Each time when a new layer is deposited on the multilayered film, it was treated at high temperature $> 800^\circ\text{C}$ in a rapid thermal processor for about 10 seconds. At the temperature of zero-intrinsic-stress, T_{0is} , the relaxation should be characterized by a time constant of a few seconds. This is in fact the case for t-SiO₂, the relaxation time is $\sim 4 \text{ s}$ [111]. With a viscosity at T_g of 10^{12} Pa-s and $E \sim 70 \text{ GPa}$ and $\nu \sim 0.23$, using Eq. (4-7) and taking

Table 4-4. Estimation of relaxation time constant of a t-SiO₂ at different temperatures.

Temp., °C	Viscosity, Pa-s*	$\tau_s/\rho_{1,s}$
800	9×10^{14}	4×10^4
900	6×10^{14}	3×10^4
1000	2×10^{13}	9×10^2
1100	4×10^{12}	2×10^2
1200	1×10^{12}	5×10^1

* see ref. [110]

the more dominant term of Eq. (4-6), an order of magnitude estimation of the biaxial relaxation time can be obtained as ~ 46 s (i.e. $\tau_i/\bar{\rho}_i$). It reduces further (see Table 4-4) as the temperature increases beyond T_g that consequently lowers the viscosity. However, the T_{0is} for t-SiO₂ is known to occur at $\sim 970^\circ\text{C}$ and according to the approximation in Table 4-4, biaxial relaxation time could be ~ 30 mins, which is comparable with the duration of a typical oxidation routine. Due to dopant-oxides such as GeO₂, B₂O₃ or P₂O₅ that lower the effective T_g , and due to the inherent OH or porous content in the sol-gel derived films which has the effect of decreasing the viscosity [80, 112], a relaxation time that is comparable to the RTP hold time of ~ 10 s can be achieved [2, 3]. One can expect the tensile in-plane stress to be completely relaxed at T_g or slightly above it. Therefore, a cross-over to compressive film stress (Figure 4-9) after the T_{0is} should be in the vicinity of the T_g .

4.3.1.2. Observations of cracks and solutions

F48 (Figure 4-10(a)) is a single-layer film which was crack-free when dried in room ambient, but, cracked after a furnace treatment at 1000°C . Cracks were found only in the center region on the substrate. The single-layer silicate-based (or any thin transparent film) coating deposited on a Si substrate (i.e. a high-RI, reflective material) with a thickness of less than $1\ \mu\text{m}$ is known to exhibit characteristically visible colour as a result of the thin film interference [113] (see more details in §4.3.4). Consequently, different colours (viz. wavelength of light) reflected off the sample are indicative of different thicknesses. Therefore, a variation of film thickness is vividly apparent as concentric colour bands from the F48 sample viewed under normal fluorescence room light Figure 4-10(a). Such radial variation of thickness can be easily measured by an optical reflectometer. The result is plotted in Figure 4-10(b). The film-thickness measurement of another crack-free film (F35) is shown for comparison. Both films exhibited a consistent radial variation in thickness (decreasing away from the centre) that explains colour bands in the in the adjacent photo. This thickness profile is typical of films made from our equipment and the current recipe. The cause of this profile is discussed in Section 4.3.4. From the thickness profile of F48, a threshold thickness can be deduced beyond which the film (or the part of the film) mechanically fails. By reducing the rate of evaporation during

spin-coating¹⁴ (keeping all other spinning conditions the same), F35 was made thinner and thus prevented cracking after annealing at 1000°C. The cause of the cracking is evidently related to the thickness of the film.

Figure 4-10. Method to determine the single-layer threshold thickness for the 16Ge sol at different spin speed; (a) a single-layer film (F48) showing a typical cracked film after annealing at 1000°C; (inset) an optical micrograph at 50X objective magnification of the central cracked region of the film (b) non-uniformity in the film thickness (note film F35) can be used to determine threshold thickness as in film F48.

In an attempt to increase single-layer thickness, the amount of solvent was reduced to as much as possible but avoiding striations at the same time (see §4.3.3.3). A post-annealing thickness of 0.4 – 0.55 μm was achievable by using a combination of EtOH and BuⁱOH, both at a molar ratio of 2 during the Sol-S preparation (cf. Figure 4-1). However, cracks shown as in Figure 4-11 were observed under an optical microscope. In fact, cracks shown in Figure 4-11(b-e) could be observed in some dried as-deposited films that are generally thicker. These cracks are likely developed during the thermo-stress stage **I**^s or early **II**^{sa} (see Figure 4-9). Thus, capillary force developed during solvent evaporation is likely the cause. According to Eq. (4-4), a liquid of a lower surface tension (γ_{LV}) can be used to replace EtOH and BuOH. However, finding a mutual solvent for both TEOS and water and at the same time with low surface tension and volatility is difficult (see Figure 4-23). Such solvent, for example, is likely to compose of a molecule with a highly polar functional

¹⁴ The method by which the rate of evaporation rate was reduced is shown in Section 4.3.4.

group (OH) and a bulky hydrocarbon group that is not lengthy or a flourohydrocarbon group.

Figure 4-11. Microcracks observed on films with thickness (H) $\geq 0.4 \mu\text{m}$ (a) after an FA at 1000°C , $H \sim 0.46 \mu\text{m}$, (b-d) after RTA 1000°C , $H \sim 0.38 \mu\text{m}$ and (e) after RTA 1000°C , $H \sim 0.41 \mu\text{m}$.

Alternatively, organically modified silane (ORMOSIL) can be used to increase the structural compliance (agility) to the gel film to avoid mechanical failure as capillary force develops a tensile stress on the gel's network. These ORMOSIL precursors typically consist of a TEOS or TMOS molecule with the alkoxy group on one of the Si branches replaced by an inert hydrocarbon group. The meth-triethyloxysilane (MtES) precursor has been shown to effectively delay the sharp increase in tensile stress in the thermo-stress process (i.e. stress rises at higher temperature) and some proven examples of the usage of MtES at lower processing temperature had been reported [114-116]. In this work, then, 60% of the TEOS content was replaced by MtES. A modest increase of the critical thickness to $\sim 0.44 \mu\text{m}$ after RTA of 1000°C was achieved. Therefore, MtES is used in the improved

mSC-RTA process for the fabrication of planar waveguides (c.f. Figure 4-36 in §4.3.5).

Figure 4-12. A multilayer film ($x \sim 0.160$) deposited on SiO_2/Si 4" wafers showing common modes of failure: i) thickness non-uniformity (circular fringes), ii) cracks (inset) and iii) particle/debris inclusions (causing non-propagating cracks). This photo is taken by a high resolution single-lens reflex digital camera fitted with a macro lens at a near-normal angle to the plane of the wafer ($\sim 30^\circ$ off normal).

Directional cracks were noted after several layers of 16Ge-films (see inset of Figure 4-12) at intermediate annealing temperature of 900°C . Similar cracking was noted on samples with smaller substrates when the intermediate anneals were both performed at 900°C after the 3rd to 5th coating (thickness ~ 240 nm/layer). These cracks are similar in nature as those observed by Syms *et al.* [3]. Again, the radial thickness non-uniformity inherent to early samples left the multilayered film with a thicker centre region, hence, more prone to cracking as discussed in Section 2.8.4.3.2. Syms *et al.* [2, 3] showed that the residual tensile stress on the film increases as subsequent layers of sol-gel film were annealed at a temperature below the zero-intrinsic-stress temperature, T_{0is} . The implication of this fact is that each layer of the film must be sufficiently thin to avoid cracking at the peak of film stress as illustrated in Figure 4-9. Due to a lack of a simple scheme to determine T_{0is} , Syms *et al.* [4] ensued to perform some laborious experiments to estimate the value of T_{0is} for different glass compositions.

From the discussion in Section 4.3.1.1, the observed stress relaxation is attributed to the softening of the glass network at high temperature where the T_g is commonly referred to as a point of reference. If T_{0is} were related to T_g of melted-glasses of the same composition, then the need for experiments could be avoided. A comparison of T_{0is} of sol-gel derived films and T_g of melted-glasses from the literature is presented in Figure 4-13. The best fit lines are derived from the data collected from the international glass database (INTERGLAD™) [117]. The data for $\text{GeO}_2\text{:SiO}_2$ are from ref. [4]. The inset in Figure 4-13 shows the best fit lines with the T_{0is} values for which compositions were studied by Syms *et al.* [4].

Figure 4-13. T_g of melted-glasses of different compositions. As before, x refers to the molar fraction of the corresponding oxide in silicate glasses. Data for all melted-glasses were taken from the literature values collected by the INTERGLAD™ database. The data point for which $X = \text{B/P}$ represents a composition of 10% B_2O_3 and 10% P_2O_5 . All lines represent the nonlinear fit lines to the respective data points. The best fit line for the $\text{TiO}_2\text{:SiO}_2$ is likely to be underestimated as a number of the compositions for which T_g are quoted contains small amounts of alkaline & alkaline-earth metals ($< 10\%$). (inset) Correlation between T_{0is} and T_g of melted-glass.

In addition, Syms *et al.* has also indicated that crack-free thick films can be synthesized with an annealing temperature in a window of 100°C around the T_{0is} , with more margins on the upper bound as compressive stress is much less detrimental as tensile. From the inset of Figure 4-13, the T_{0is} of $\text{P}_2\text{O}_5\text{:SiO}_2$ and $\text{TiO}_2\text{:SiO}_2$ match

with T_g of the melted-glasses of the same composition quite well. The fact that the 10 mol%-GeO₂ as studied by Syms *et al.* contains an additional 10 mol% P₂O₅ may explain the T_{0is} is $\sim 150^\circ\text{C}$ below the T_g best fit. And in the case of B₂O₃:SiO₂, the T_g best fit is as much as $\sim 200^\circ\text{C}$ lower than the T_{0is} . A likely explanation can be due to the fact that B₂O₃ is very hygroscopic and test samples from the literature may therefore contain OH or H₂O which will reduce the viscosity. Overall, T_{0is} is seen to be approximately equal to or above T_g .

For the case of 16% GeO₂ in this work, T_g is estimated at $\sim 940^\circ\text{C}$. Henceforth, cracking as seen in Figure 4-12 can be of no surprise as the intermediate annealing temperature was 900°C . The above analysis predicts that an annealing temperature $> \sim 940^\circ\text{C}$ is required to produce crack-free films of 4 μm thickness. Indeed, raising the intermediate temperature to $1000 - 1050^\circ\text{C}$, crack-free films were fabricated (see §4.3.5). The above analysis seems to be able to explain the experimental facts for the one composition (i.e. $x \sim 0.16$) in this work. However, a variety of compositions should be used in the future to validate the universality of the analysis, albeit the crudeness in the approach¹⁵.

4.3.2. Inclusion-induced defects

From Figure 4-6 and Figure 4-12, scattering centres are visibly dispersed throughout the films. Viewed under a microscope, these scatterers typically consisted of defects shown in Figure 4-14. The thickness of the inclusions observed on films ranges from 1 to 10 μm as estimated by the focus knob (1 μm resolution and a depth of focus of 2.5 μm using an M-Plan-F1 50X objective lens). Considering that a typical channel-channel spacing of the AWG in the central arrayed-waveguide region (see Chapter 5) is on the order 127 μm or less, defects of the size shown in Figure 4-14 may affect more than one waveguiding channels. The situation is understandably worse at the input and output of the two free propagation regions where the channels are only microns away from each other ($\sim 14 \mu\text{m}$ at the slab waveguide to arrayed waveguide interface, see Table 5-1).

Figure 4-15 illustrates the accumulation of an abnormally thick gel material surrounding an inclusion. Depending on the size of the inclusion, a certain quantity of fluid sol will be displaced in a ripple fashion forming a hump encircling the inclusion.

¹⁵ T_g is known to be quite sensitive to composition and as well as fabrication conditions.

At the same time, sol from up-stream can be trapped at the ‘windward’ slope causing an accumulation of gel material. This pile-up forms regions of thicker material (visible in Figure 4-15(a)) which is susceptible to cracking and delamination as discussed above (§4.3.1).

The origin of any inclusions is likely from globules of sol ejected from the edge of the spinning substrate during the spin-off stage (c.f. §2.4.7). When the globules subsequently gel (small droplets can probably dry in air and being transported by air flow, while large drops will be splashed to the wall of the spin-coater chamber), mechanical agitation caused by resonating centroids of moving parts and recirculating or turbulent air flow during spinning carries gelled particles back on the undried film. In the work of ref. [118], computational fluid dynamics simulations were used to determine the air flow patterns of a spin coater similar to the Laurell PPE coater used in this work (Figure 4-16(a)). This pattern is schematically indicated in Figure 4-16(b). Note that the aperture on the lid was designed for positioning automatic dispense system; however, only hand-held syringe was used in this work leaving the aperture opened. As long as a negative air pressure is not maintained at the drainage¹⁶, a certain amount of backdraft will be evident during spinning. Such backflow is known to increase with increased spin rate [21, 118]. In this situation, a majority of the air reaches the centre of the wafer and then flows radially away and spirals up along the wall of the chamber. Conceivably, such air flow pattern may brush up droplets, particles, small debris and redeposit them on films during spinning.

¹⁶ Certainly, if there is an adequate amount of pressure gradient between inlet and exhaust, laminar flow has been shown by CFD [118] and other numerical techniques [119].

Figure 4-14. Some examples of defects caused by particle or debris inclusions that are found over the entire area of 3-layered spin-coated films on buffered Si wafers. Note the size of each defect. (a) a flake of gelled glass materials deposited onto the gelling film while it was still wet. Other observed deposits were in the range of $< 30 \mu\text{m}$. (b) An inclusion from the prior layer forms a hump or hill where sol materials accumulate on the slope during spinning. Hence, the abnormally thick gel material on the slope of the hill is then prone to cracking during drying. Delamination was often observed as a result. (c) A crack originated from underlying layers propagated to the top-most layer. (d, e) A more elaborate case of (b) where delamination occurred during the deposition of previous layers and subsequent layers of deposition and cracking. Such clusters grow to about few hundred microns in size as additional processing continues. (d) An image where the focus is on a plane that is atop of (e).

Figure 4-16. (a) The schematic diagram of the PPE Laurell spin-coater. (b) A possible air flow pattern during spinning.

Early practices involved the use of aluminium foils as liner with elaborate flushing (dispensing solvents from squeeze bottles) and cleaning (rubbing using lint-free wipes) after every spin cycle and even changing the aluminium foils regularly¹⁷. The chamber wall was wetted with solvents before each spin cycle. By implementing

¹⁷ The use of aluminium foils and lint-free wipes were later found to contribute to strands of foreign matters inside the films.

a saturated ambient (i.e. sealing the aperture and filling the floor of the chamber with solvents), the number and also the average size of inclusions were observed to be reduced significantly. Unfortunately, a type of surface non-uniformity, *macro-striations*, was consistently observed. Further details of these striations are discussed in Section 4.3.4.3. Alternatively, motivated by the automated bowl flushing system demonstrated by Syms *et al.*[4], a similar solvent flush system was designed and implemented in this work on the Laurell

Figure 4-17. Laurell spin-coater fitted with a customized flush system.

spin coater to wash away spun-off droplets immediately during spinning. A EtOH and PrOH mixed solvent was pumped (magnetic drive pump by Iwaki) and dispensed along the wall of the chamber by a perforated $\frac{1}{4}$ " teflon tube as indicated in Figure 4-17. The flow rate of the mixed solvents is typically ~ 1.2 L/min. Although an improvement was expected, particles were still present on films after spinning. This result suggests that an appreciable quantity of inclusions originates from the edge of the wafer and small droplets that gel in the air and redeposited on the film by the up-lifting air flow shown in Figure 4-15(b).

A method was developed by which sol was prevented from accumulating at the edge of the wafer, thus dramatically reducing particle re-deposition and edge beading together. The efficacy of this method in suppressing particle-inclusions can be evaluated by observing the reduction in scattering sites in the planar waveguides due to particle-inclusions (see discussion in §4.3.6.1 and Figure 4-38).

4.3.3. Surface corrugations

One form of surface defects, radial striations¹⁸, has been known to plague (both inorganic, organic and hybrid) polymeric films [3, 4, 63, 67, 75, 77, 92, 121-126]. Even in films formed from colloidal sols (colloidal suspended in solvents), striations were observed [63, 69]. A number of commercial spin-on-glass precursors is known to yield in typical laboratory condition [2, 10, 123]. Comprehensive summaries of the topic have been given by Kozuka and Larson—Rehg [16, 63]. Inevitably, striations were noted on films fabricated during this work. Typically, they are surface undulations that are on the order of several tens of nanometers in magnitude and microns in length scale [12, 15, 17, 18, 121]. Conceivably, scattered ambient light from these structures are readily visible to the eyes. In the region close to the axis of rotation, the striations manifest as protruding dots and away from the axis of rotation, these surface structures appear to be streaks radiating from the centre (i.e. the axis of rotation) (see Figure 4-18). Although the magnitude of these striations does not multiply during the mSC-RTA process due to the intrinsic nature of each coating layer, the magnitude of 20 nm is enough to cause substantial light scattering ($\alpha_{SR} \sim 7.8$ dB/cm, c.f. §3.5.6) in a typical waveguide geometry.

In Section 2.4.8.2, both theoretical considerations and experimental evidence suggest that the striations as observed on spin coated films are long-wave instability. This instability is likely affected by, but not limited to, the Marangoni effects,

Figure 4-18. The optical microscope (10X objective lens) images of a film deposited from a 50 vol% dilution of PrOH spin-coated at 3000 rpm. Striations in the proximity of the axis of rotation (top) and striation patterns away from the centre (bottom).

¹⁸ Distinction should be made with another type of surface defect known as 'orange peel'. Investigators have report irregular arrangements of dimples across the surface of the films [74, 120, 121].

differential evaporation, viscous effect and capillary force¹⁹. For a lack of a better quantitative measure, striation is observed when disruptive forces overcome the stabilizing ones, if any. A review and critique, in terms of the fluid dynamic concepts introduced in Section 2.4.8.2, of all reported striation suppression techniques are provided below.

4.3.3.1. Suppression techniques

Since that the basic mechanisms of film forming, regardless of nature of the material is quite universal, the following discussion draws on numerical and experimental results of spin coating organic and inorganic polymeric or colloidal solutions. Rehg and Higgins had extended the existing model for colloidal solutions [69]. By using the results of their numerical analysis, they demonstrated conceptually the different protocols that may be employed to suppress Marangoni-driven striations via reduction in the peak instantaneous temperature-induced Marangoni number. From Figure 4-19, adopted from ref. [69], the destabilizing $\overline{Ma}_T$ is clearly shown to be non-constant and positive. The $\overline{Ma}_T$ varies with the change of the temperature gradient (ΔT) and film thickness (H) during the course of spinning. The definition of the modified thermal Marangoni number and solutal Marangoni number is reproduced from Eq. 2-7 and Table 2-6, respectively, to facilitate the foregoing analysis,

$$\overline{Ma}_T^* = \frac{\partial \gamma}{\partial T} \left(\frac{\rho c_p \Delta T H}{\eta k_T} - \frac{\rho^2 c_p \dot{e} \Delta H_{\text{vap}} H^2}{\eta k_T^2} \right) \text{ and} \quad (4-8)$$

$$\overline{Ma}_S \equiv \frac{\partial \gamma}{\partial C} \frac{\Delta C H}{\eta D_M} \quad (4-9)$$

where the parameters are once again indicated in Table 4-5.

¹⁹ This capillary force is to be distinguished from the one of Section 4.3.1.1

Table 4-5. Fluid parameters involved in the determination of the Marangoni number

Symbol	Meaning
$\frac{\partial \gamma}{\partial T}$	Change in surface tension with temperature
ρ	Density
c_p	Heat capacity
ΔT	Temperature gradient between the surface and bottom of the liquid film
H	Thickness
η	Viscosity
k_T	Heat transfer coefficient
ΔH_{vap}	Enthalpy of vaporization
$\dot{e}$	Rate of evaporation (mass loss)
$\frac{\partial \gamma}{\partial C}$	Sensitivity of surface tension with solvent concentration
ΔC	Concentration gradient of the reference solvent between the surface and bottom of the liquid film
D_M	Mass diffusivity

Figure 4-19. An example of the instantaneous Marangoni curves adopted from Rehg and Higgins [69]. The case under study involves a hard-sphere, polymeric colloids in ethanol at a solvent mass fraction of 0.97 and a spinning rate of 5000 rpm.

In Rehg and Higgins' study [69], the finite initial ramping speed of spinning was unambiguously shown to increase the $\overline{Ma}_r$ as much as 5 times for a significantly longer period of time as compared to an impulsively accelerated spinning. The main contributing factor was the sluggishness of film thinning (c.f. thickness dependence of $\overline{Ma}_r$). This finding was in qualitative agreement with the experimental results of Frasci and Saremski [125]. To numerically validate claims of suppressing surface striations by a solvent-saturated chamber ambient [75, 126], Rehg and Higgins showed a notable decrease in $\overline{Ma}_r$ by a solvent saturation of 30 wt% of the ambient. The efficacy of solvent saturation was reasoned to be a retarded evaporation (i.e. evaporative cooling) and prolonged effect of radial drainage leading to a 7% additional loss of thickness. Because the thickness is dependent on the initial viscosity of the solution, an increase in mass fraction of solute (i.e. polymer) was seen to give rise to a higher peak $\overline{Ma}_r$.

In concurrence with many other studies [11, 17, 22, 23, 63], the numerical study of Haas and Birnie [11] shows that less volatile solvents substantially reduce the $\overline{Ma}_r$ (via a reduction in ΔT [9, 127]), hence, the possibility of the formation of striations. Furthermore, an initially thick liquid layer will lead to an increase in peak $\overline{Ma}_r$ and the spin speed has a relatively weak influence on the peak $\overline{Ma}_r$. Recognizing that many sol formulations contain a mixture of solvent components, especially when a multicomponent oxide is involved²⁰ and the interplay between thermocapillarity and solutocapillarity under such a situation, Birnie proposed a methodology to select multiple solvent systems to hinder the occurrence of striations [8]. The principle is to select a co-solvent so that the $\partial_C \gamma(T, C) < 0$ and $\Delta C > 0$ (treating C as the concentration of the main solvent and the co-solvent as a solute) to yield a negative $\overline{Ma}_s$ (c.f. the solutal Marangoni number in Table 2-6) for at least a substantial part of the initial stage where $\overline{Ma}_r$ is likely to peak due to a initial thickness and evaporation (cf. Figure 4-19) [69]. In fact, solvent combinations that

²⁰ Although in many cases one would prefer to have all the metal precursors to contain the same organic species to adhere to a homogeneous solvent system, in practice, not all metal oxide precursors are available commercially in all the different organic species. And one may like to obtain precursors with different organic constituents to tailor the chemical reactivity (c.f. §2.4.6).

yield systems with $\partial_C \gamma(T, C) > 0$ and $\Delta C < 0$ could be stabilizing but such combinations are difficult to find for typical sol-gel processing (cf. Figure 4-23). Although the methodology has been shown to work in one material system [128], the universality is questionable [17, 22, 23].

Experimentally, Kozuka had contributed a comprehensive study of the effect of many of the parameters of the alkoxide-route sol-gel process on wavelength and magnitude of striations [16]. Neither the magnitude nor the wavelength of striations was sensitive to the amount of sol deposited on the substrate (this result is contrary to the numerical results of Haas and Birnie [11]). The ramp rate, at which the experiments were conducted, was likely set to the highest. The centrifugal drainage to evaporation transition (SET) is likely to take place at a similar instance in time, regardless of the initial volume of sols dispensed on the substrate. Therefore, the films are at similar thickness as instability takes place, leading to similar characteristic features of the striations [13]. Haas and Birnie predicted that the peak Marangoni numbers are higher for larger dispensed volumes, thus, a larger striation magnitude is expected. Albeit some simplifications made in the model, the above discrepancy may suggest that using the Marangoni number alone is not sufficient to determine the onset of striations.

Both magnitude and wavelength increased with the sol viscosity (or aging time²¹) [15, 18]. This characteristic is in agreement with the prediction of Rehg and Higgins with respect to the initial weight fraction of the solution content (alternatively the dilution), but experiments have not demonstrated such a clear correlation for a polystyrene-solvent system [23]. In fact, Rehg has shown experimentally for a polymethylmethacrylate (PMMA)-1,2-dichloroethane system that a 'viscosity inoperability' (0.001 – 1 Pa·s) within which striations were observed [63]. The viscosity is likely to be adjusted by varying amount of solvent dilution. Rehg's reasoning was that viscous damping acted to stabilize the film at high viscosity and at low viscosity (also moderately high Reynolds number), dynamic thinning affected more pronounced centrifugal thinning at an earlier instance. In other words, an increase in viscosity and decrease in film thickness help to reduce the Maragoni number.

²¹ Bearing in mind that the composition of the sols (viz. the solvents content) change with aging time, hence the effect of solutal effects may also change.

Kozuka *et al.* observed a modest reduction ($< 20\%$) in striation magnitude with an accompanying decrease in wavelength by increasing spin speed up to 6000 rpm in two material systems of titania and silica [15, 16]. Similar trend is found for the phosphosilicate films by Haas and Birnie [12]. And most recently, Kozuka reported the reduction of striation magnitude and the increase in wavelength by using less volatile solvents [17]. Such effectiveness of striations suppression using less volatile solvents is in agreement with a number of studies [14, 22, 129]. Another brut-force approach is to immobilize the surface by the use of surfactants [130, 131].

Recently, some analytical methods have been reported to control thermally-induced instability. Oron and Peles [132] proposed the use of internal volumetric heating while an alternate method of using an opposing temperature gradient to actively suppress the thermocapillary effect on stagnant films has been conceived [133, 134]. Even more advanced, a negative feedback control system with radiative substrate heating was proposed by Grigoriev [135]. Although such system is readily realizable for quiescent pure liquid film, in order for the technique to be applicable for spin-coating, the evolution equations of the system must be adequately modelled. In addition, Grigoriev foresees that the control algorithms to suppress solutal effects can be extremely complex.

Due to the complexity of the problem, no mathematical formulation is yet available to describe the formulation of the formation of striations involving effects such as temperature-induced and composition-induced Marangoni effect, differential evaporation, inertial effect and surface tension. Although there have been plenty of studies that demonstrate the effect of any one of these factors on the resulting magnitude of striation, no studies have dealt with the intercorrelation of the different factors on the formation of instability. A comprehensive multi-variable analysis is performed on the experimental observations collected in this project. The details are presented below.

4.3.3.2. Micro-striations

The execution of the above suppression techniques is, in general, laborious as there is no mathematical scheme available to characterize the onset of striations, albeit some consistent trends. In addition, many of the protocols such as high dilution, high

spin speed and high solvent-saturated ambient all contribute to a lower thickness which is undesirable in the present context.

In an attempt to evaluate a number of the passive techniques to suppress striations for the recipe developed in Section 3.2. The effect of dilution, spin speed and solvent substitution were studied. As the solvent-saturated spin (SSS) protocol reveals a similar effect on the instantaneous $\overline{Ma}_r$ curve [69], the dilution experiment can be used as a representative case for the SSS. Five sols were prepared according to Figure 3.1 with 16 mol% GeO₂ for six types of samples listed in Table 4-6. Since solvents of different nature may have an effect on the relative rate of reaction between the test sols, this solvent effect can lead to a difference in viscosity of the sols at the time of deposition and ultimately affect the observation of striations [16]. To minimize the solvent effect, instead of adding the dilution before the Ge precursor as in Figure 3.1, the dilution solvents are added after one hour of aging of the Sol-SG (without any prior dilution) and one hour before coating. The dilution solvents tested were acetone, ethanol (EtOH), isopropanol (PrⁱOH) and isobutanol (BuⁱOH). The ramp rate was set ~ 3000 rpm/s. Again, the spinning was performed under controlled RH (< 20%) and at room temperature on Si substrates. After deposition, films were dried in ambient for at least 3 days. Optical microscopic images were taken and surface profiles were recorded at a radial distance of ~ 1.5 cm from the centre of rotation. The surface profiles are presented in Figure 4-20 with the corresponding microscopic images on the right column.

Table 4-6. Experimental matrix for striation suppression study. The as-deposited thickness of the films indicated is an average thickness value derived from reflectometry.

Samples	Sol dilution	Spin speed, rpm	Thickness, nm
STR1	150 vol% EtOH	1500	203
STR2	50 vol% EtOH	5000	283
STR3	50 vol% EtOH	1500	385
STR4	50 vol% Acetone	1500	509
STR5	50 vol% Pr ⁱ OH	1500	422
STR6	50 vol% Bu ⁱ OH	1500	372

As expected, increased dilution, increased final spin speed and solvent selection all resulted in reduced magnitude in surface striations to different extends. The film spun at 5000 rpm did result in a substantial decrease in striation magnitude

from about 22 to < 2 nm which is a remarkable reduction ($> 90\%$) than that reported previously up to $\sim 25\%$ [15, 16, 18, 19]. This result suggests that the efficacy of any suppression techniques is not a simple, single-variable function but a multivariable function involving properties such as viscosity and rate of evaporation. However, dilution and solvent selection prove to be more effective as seen from Figure 4-20. The effect of dilution, as mentioned previously, is to reduce viscosity, hence more significant cumulative centrifugal thinning (i.e. longer) leads to thinner film before the onset of striation development. Nevertheless, the drawback, in the view of the present work, of both increased spin speed and dilution is reduced thickness. Furthermore, at high speed, more turbid air flow may lead to film non-uniformity (c.f. §4.3.4) or particle inclusion (c.f. §4.3.2).

Figure 4-20. Quantification of surface striation resulted from the complex fluidic instability of the sol. In all cases, the Sol-S is prehydrolyzed then is processed with (a) EtOH 50 vol% dilution at spun at 1500 rpm, (b) PrOH 50 vol% dilution at spun at 1500 rpm, (c) EtOH 50 vol% dilution at spun at 5000 rpm, (d) EtOH 150 vol% dilution at spun at 1500 rpm, (e) Acetone 50 vol% dilution at spun at 1500 rpm, (f) BuOH 50 vol% dilution at spun at 1500 rpm. The right column shows the respective optical microscopic views under a 10X objective; scale bar represents 100 μm .

The expectation of the solvent replacement is that striation can be reduced without a compromise in thickness where fluid dynamical forces are used instead of

compromising via changing the spin coating parameters (evident in Figure 4-20 and Table 4-6). In the observation of the effect of solvent replacement, an interesting observation is found. While the use of isopropanol (Pr^iOH) showed no pronounced effect on the striations (Figure 4-20(b)), the use of acetone and isobutanol (Bu^iOH) resulted in marked improvement (Figure 4-20(e-f)). To explain this observation, the fluid properties of the respective solvent component are scrutinized. Some of the pertinent solvent properties²² are listed in Table 4-7 to aid the foregoing discussion. The rate of evaporation is expressed as, assuming a laminar overlayer air flow (c.f. refs. [21, 63]),

$$\dot{e} = K_e \Omega^{1/2}, \quad (4-10)$$

where Ω denotes the rate of rotation in unit of revolution per minute (rpm). The constant of evaporation is taken from experimental values in the literature where available and is otherwise predicted by,

$$K_e = \frac{A_{Sc} D_{air} P_{vap} M}{\nu_{air}^{1/2} \rho_{vap} R T}, \quad (4-11)$$

where $A_{Sc} = 0.386 * (\nu_{air}/D_{air})^{0.462}$, ν_{air} , D_{air} , P_{vap} , M , R are kinematic viscosity and diffusivity of the vapour molecules in air, vapour pressure, molecular mass and the universal gas constant respectively. At the point of striation development, the sol is treated to assume the characteristics of the ones of the solvents. The polymeric precursor molecules are treated only as a hindrance to solvent diffusion. As noted above, the use of solvents of low vapour pressure is effective in suppressing instability. A more in-depth analysis reveals that the situation is rather complex.

By extending the analysis of Zhang and Chao [138] with Eq. (4-8), the relative influence of the thermocapillary and differential evaporation effects can be evaluated quantitatively (Figure 4-21). Zhang and Chao's experiments involved films of thickness of ~ 1 mm where the differential evaporation was much more significant than the thermocapillary effect. At film thickness below $10 \mu\text{m}$, the effect of

²² Since surface tension of the solvent is an important property, the author would like to highlight the fact that there is a considerable spread in values for a particular substance in the literature (a standard deviation between 0.5 to 1 mN/m for solvents used in this study), values were only selected from a traceable source that undertook the measurement under the same condition [136]. Consequently, the values of $\partial_C \gamma$ have standard deviations of up to 0.0087 mN/vol%·m. In general, trends and deduced values are consistent between the different sources with one exception where the approximation of $\partial_C \gamma$ for STR5 is in the opposite sign (i.e. negative; $\gamma[\text{EtOH}]$: 21.99 mN/m; $\gamma[\text{Pr}^i\text{OH}]$: 22.70 mN/m) to what is indicated in Table 4-8 [137].

differential evaporation is negligible (see Figure 4-21(a)). Since no delayed surface flattening was noted, a capillary force is assumed to be relatively insignificant. Therefore, the stability of the film can be considered essentially as a competition between themocapillarity, differential evaporation and solutocapillarity. In order to better describe the solution systems in each of the test solutions, the corresponding properties shown in Table 4-7 should reflect the combined properties of each of the constituent. Using the appropriate mixing rules for each of the property²³ [139-141], the relevant effective properties are calculated and tabulated in Table 4-8 for each of the test solutions, STR3 – STR6. The detail of the calculations is shown in Appendix I. The ΔT values, assumed to be linear with the depth of the film, indicated are worse-case estimates drawn from the previous studies involving evaporative cooling [9]. Known binary azeotropes²⁴ exist only for water and alcohols (i.e. alkanols) for the solutions involved. The azeotropic water concentration in all cases is > 10 mol%. Only in the solution STR3 that the composition between water and ethanol is rather close to the azeotropic point, otherwise the water concentration is well below the azeotropic compositions. Hence, in the discussion of effective rate of evaporation and concentration gradient, only the one of the co-solvents and ethanol are considered. Since no known azeotropes exist for the solvent mixtures, the components in the solutions are assumed to evaporate at their intrinsic rates and a lever-rule method was used to determine the effective rate of evaporation. Also note that the film thickness dependence of the modified Marangoni number (Eq. (4-8)) is presented in Figure 4-21.

Table 4-7. Solvent properties at 20°C [136, 141, 142].

Properties	Acetone	MeOH	EtOH	PrOH	BuOH	H ₂ O
$\partial\gamma$ (mN/K·m)	-0.126	-0.0882	-0.0901	-0.135	-0.190	-0.1515
γ (mN/m)	24.020	22.454	22.386	21.322	22.940	72.75
P_{vap} (kPa)	24.6	12.9	5.88	1.993	0.959	2.34
M (kg/mol)	58.08	32.04	46.07	60.10	74.12	18.02
ρ (kg/m ³)	789.9	791.4	789.5	785.1	810.3	998.2
k (W/ K·m)	0.190	0.202	0.182	0.1399	0.1352	0.5984
η (mPa·s)	0.326	0.431	1.20	2.30	2.95	1.002
c_p (kJ/kg·K)	2.17	2.54	2.47	2.85	2.76	4.18
ΔH_{vap} (kJ/kg)	551	1230	879.0	747	673	2450
$\dot{e}$ (μm/s)	7.58	2.66	1.68	0.606	0.362	--

²³ For most properties, the mixing rule is just a simple lever rule relationship with only one exception of viscosity.

²⁴ The term azeotrope refers to a solution of two or more substances where the boiling point of the solution is lower than the any one of the constituents in their pure form. The boiling point of the azeotrope is lowest at a specific azeotropic composition.

Figure 4-21. Thickness dependence on the Marangoni number. Marangoni number shown for the case of pure ethanol (a) and the representative solvent solution used in STR3 (i.e. a mixture of ethanol and 2-propanol (b). The inset in (a) shows a magnified view for thin thickness.

Within this context, the thermocapillarity and differential evaporation is strictly destabilizing; therefore, the modified Marangoni number of Eq. (4-8) is positive (with a negative $\partial_T \gamma$ and ΔT). The modified Marangoni number can be calculated using parameter values in Table 4-7, say for Ethanol (see Figure 4-21). The corresponding $\overline{Ma}_T^*$ for the solution in STR3 is plotted in Figure 4-21(b) for comparison. The change in the influence of the thermal Marangoni effect and the differential evaporation effect with different thickness of the film is clearly illustrated in Figure 4-21. The $\overline{Ma}_T^*$ values are plotted in Figure 4-22 for STR3-STR6 using the effective fluid properties of the respective solutions as shown in Table 4-8. The decreasing trend in $\overline{Ma}_T^*$ with solvents of low volatility is observed as expected.

Since the test fluids (viz. the sols) are expected to exhibit a number forces and as yet there is no mathematical formulism to quantify the interaction between all the forces, the validity of the critical thermal Marangoni number established in previous works [11, 127, 143] in this context is unclear; and thus, such discussion in this analysis is omitted. For the present objectives, the results shown in Figure 4-22 is phenomenologically useful in demonstrating qualitatively the effect of destabilizing forces: thermocapillarity and differential evaporation; quantitatively, numbers

obtained in Figure 4-22 are in numerical agreement (to the same order of magnitude) with previous studies [11, 127, 138].

Table 4-8. Summary of fluidic properties of the solvent solution systems that are representative of the solution under test.

Sample	STR3	STR4	STR5	STR6
Co-solvent	EtOH	Acetone	Pr ⁱ OH	Bu ⁱ OH
$\partial\gamma$ (mN/K·m)	-0.0844	-0.0812	-0.0692	-0.0697
ΔT (K)	-1.87	-4.01	-1.77	-1.72
$\partial_C\gamma$ (mN/mol%·m)	0.01064	-0.01634	0.01064	-0.00554
ΔC (vol%)	-ve	+ve	-ve	-ve
ρ (kg/m ³)	808.8	810.5	812.0	812.0
k (W/ K·m)	0.218	0.223	0.214	0.210
η (mPa·s)	2.387	1.694	3.106	3.518
c_p (kJ/kg·K)	2.660	2.577	2.796	2.611
ΔH_{vap} (kJ/kg)	785.6	744.9	826.2	833.2
$\dot{e}$ (μm/s)	1.585	4.093	1.252	1.201
Film Thickness (nm)	385	509	422	372
Striation Mag (nm)	~ 22	< 2	~ 20	< 2

Figure 4-22. Marangoni numbers for test solutions STR3 - STR6. The modified (total) Marangoni number is plotted in (a) and the respective components in (b) and (c).

By a suitable design of the solvent system, the solutocapillarity can be tailored to stabilize the disruptive forces (i.e. a negative $\overline{Ma_s}$). The solutal effect is treated as the co-solvent being the solute dissolving in EtOH. Consequently, the $\partial_C\gamma$ is calculated with reference to the surface tension of EtOH (viz. C refers to the

concentration of EtOH). The solutal surface tension coefficient for STR3 is chosen to be the same as the one of STR5, as Pr^iOH is present in Sol-SG as a solvent in Sol-G (cf. Figure 3.1). The concentration of Pr^iOH (including the amount released by the TPOG precursor in hydrolysis, alcoholic condensation or ligand exchange, c.f. Sections 2.4.4 and 2.4.6) in every sols is less than 9 mol%, the effect of which is hence neglected except in the case of STR5. In contrast to the study of Kozuka *et al.* [17], the selection of solvents, in this work, having surface tension and viscosity restricted to a very close range, attempts to isolate the effect of solvent volatility. At present time, no effort was dedicated to derive some good estimates for values of ΔC and that no relevant data is available to the author to provide any quick estimates. In the foregoing discussion, only the sign of ΔC will be used to determine the nature of the solutocapillarity (viz. whether stabilizing or destabilizing).

The occurrence of striations is explained using both Table 4-8 and Figure 4-22. Striations were noted for STR3, in which the co-solvent added at the dilution stage was EtOH. $\partial_C \gamma$ is taken from the case of STR5 to reflect the fact that small residual amount of Pr^iOH is present from previous steps. The solutocapillarity of STR3 is, in fact, similar to the nature of the one of STR5. Treating the similar cases of STR3 and STR5, where the only difference is mostly the relative concentration of EtOH and Pr^iOH , they both incurred striated surface due to the themocapillarity and differential evaporation. Although solutocapillarity (as shown in Table 4-8) is stabilizing (i.e. $\partial_C \gamma(T, C) \times \Delta C < 0$) but the magnitude of ΔC can be small which can be understood as the similar rate of evaporation between EtOH and Pr^iOH (c.f. Table 4-7). Another possible reason that gives rise to instability is that $\partial_C \gamma(T, C)$ taken from the values of surface tension for EtOH and Pr^iOH from one reference [137] is negative, which is contrary to values from five other sources [136, 140-142, 144]. In such case, the solutocapillarity is destabilizing.

Due to a lower $\overline{Ma}_\tau^*$ (Figure 4-22), instability is suppressed in the case of STR6. Although ΔC is likely to be larger than in STR3 and STR5, $\partial_C \gamma$ is smaller by half; the overall effect is still inadequate to amplify disturbances. In fact, according to the rationale of Birnie (viz. the use of the Birnie's plot as referred to later)[8], Bu^iOH would be considered as a 'bad' co-solvent and yet striation is much suppressed. One reason for the effectiveness in striation suppression is likely due to a weak disturbance

that may not exceed the critical Marangoni level. Another possible explanation is that the viscosity of the sol may slow down the interaction for the destabilizing forces in a way that either the Marangoni number is reduced due to the viscosity dependence (see Table 2-6 or Eqs. (4-8) and (4-9)) or the peak Marangoni number is delayed beyond the duration of the spin cycle. Against the conventional perception that the more volatile solvents yield more pronounced striation [17, 22, 75, 129, 145], very little can be seen on STR4. This striation suppression is very reproducible for the STR4 recipe in our laboratory. Striation suppression of two solvents of similar relative nature as the pair in STR4 had also been reported by others [128]. From the final as-deposited thickness, STR4 is actually thicker (likely due to higher ϵ). Therefore, the lower viscosity which leads to substantial cumulative convective thinning (i.e. from centrifugal drainage) does not play a prominent role in striation suppression. The elaborate thermal and evaporation destabilization is clearly seen in Figure 4-22. However, unlike the other cases, the STR4 system has a relatively high and negative $\partial_C \gamma$ and a positive ΔC that is likely to be much higher due to the difference in the rate of evaporation between acetone and EtOH (Table 4-7). In this case, the stabilizing solutocapillarity is large enough to suppress thermocapillarity and differential evaporation.

The thickness of film produced by the sol in STR4 has been noted earlier to be substantially thicker than the rest. Supposing then, for a weakly destabilizing solutocapillarity, the $\overline{Ma}_s \sim Om(10^1)$, $D_s \sim Om(10^{-10})$ [139, 146] and $H \sim Om(100 \times 10^{-6})$, an estimate of ΔC is in the order of $< 10^{-2}$ vol%. Assuming evaporation is the main mechanism for the concentration gradient, this small ΔC especially for STR6 suggests that the peak of instantaneous $\overline{Ma}_t^*$ occurs much earlier than the SET point; whereas, for STR4, due to the higher rate of evaporation of the mixture (Table 4-8), the SET point may take place at an early instance closer to the peak $\overline{Ma}_t^*$. In this case, the film may have developed a substantial mechanical property (i.e. solidification) to resist the disrupting forces in the case of STR4.

The above analysis can be extended to explain the results of Kozuka *et al.* [17]. The sol systems in their work involved TEOS/H₂O/EtOH/co-solvent. Although EtOH was not in the starting recipe, it is likely to be present in the aged sols due to hydrolysis of TEOS (cf. Eq. 2.1 in §2.4.4). Therefore, C is used again as

concentration of EtOH. Their results showed that there is a quasi-linearly decreasing striation magnitude with co-solvents of higher boiling points (i.e. lower vapour pressure in general). Methanol (MeOH) was found to yield the highest striation magnitude. The properties of MeOH are provided in Table 4-7. The MeOH system is in fact very similar to STR4 in the nature of all of the acting forces, only differs in that $\partial_C \gamma$ is small ($-0.00068 \text{ mN/vol}\% \cdot \text{m}$) and ΔC is likely to be small and positive with an $\dot{e} \sim 2.66 \text{ }\mu\text{m/s}$ when closely compares with the one of EtOH. The stabilizing effect of the solutocapillarity can be conceived to be inadequate to counteract the destabilizing effects. Methoxyethanol (MOE) has properties close to Pr^iOH except for a significantly higher surface tension of 33.16 mN/m [136]. The use of MOE as a co-solvent should yield a very destabilizing system with the relatively high $\partial_C \gamma = -0.0895 \text{ mN/mol}\% \cdot \text{m}$ and a negative ΔC if only the effects of Marangoni and differential evaporation were considered. By the use Birnie's plot [8], MOE is again considered as a 'bad' co-solvent. Yet, an unambiguous reduction in striation magnitude was noted by Kozuka.

The improvement in striation over the EtOH case deserves scrutiny. In this case, the only observable stabilizing force acting against the combination of thermocapillarity, differential evaporation and solutocapillarity is likely to be the surface tension (cf. the Capillary number in Table 2-6). The capillary force was clearly observed in the case with the co-solvent of 1,2-propanediol (also known as 1,2-propylene glycol) which has a high sol viscosity ($19 \text{ mPa}\cdot\text{s}$), surface tension ($\sim 36 \text{ mN/m}$) and very low vapour pressure ($\sim 0 \text{ kPa}$). The high viscosity effectively slowed the damping or stabilizing capillary action to after the spin cycle where the magnitude of the striations reduced with drying time under ambient condition. Similarly, surface tension in the MOE case could take place but on a much faster time scale due to a lower viscosity ($2.7 \text{ mPa}\cdot\text{s}$). Due to a much lower surface tension, the stabilizing effect of capillary force is not pronounced in the test samples of STR3 – 6.

At this point, a noteworthy reminder may be important regarding the above analysis. In the above analysis of the films STR1 – STR6, the solutocapillarity due to water was omitted for the following reasons. In most sols used in this work, the content of water in the overall Sol-SG is only $< 4 \text{ vol}\%$. The effect is either insignificant when comparing to body forces exerted between each solvent and co-solvent pairs or the moment at which the water concentration becomes substantial due

to the loss of volatile solvents may take place well after the SET point where the viscosity or mechanical property of the films resist any deformation or body forces. The effectiveness in striation suppression of STR4 validates the above statement, where both acetone and ethanol would yield destabilizing solutocapillary forces with respect to water, if the concentration of water had been significant. In the above analysis, no quantification for the solutal Marangoni number was performed due to the unavailability of ΔC . With the time evolution of the thermal Marangoni number as shown in Figure 4-19, the time evolution of ΔC should be considered to provide a more accurate evaluation of the competition between the destabilizing and stabilizing forces. A full hydrodynamic calculation would be needed to accomplish the above. For the purpose of this work, only the nature of the soluto-capillarity has been considered in an attempt to provide further improvement to previous models or guideline for co-solvent selection (i.e. Birnie's plot).

Figure 4-23. Birnie's plot for the selection of co-solvent in alkoxide-based sol-gel. This plot has been drawn from a solvent-centric point of view, and is ethanol in the current work. Hatched area refers to region of poor co-solvents; shaded areas indicate conditional co-solvents and unshaded areas are locations of desirable co-solvents. Square data points are solvents used in this work; squares with asterisks are good co-solvents. The dark band below the abscissa shows values of surface energy exhibited by as-deposited gel films. The block arrows points towards directions of co-solvent with favourable qualities.

From a practical standpoint, a vapour pressure-surface tension ($P_{\text{vap}}-\gamma$) plot proposed by Birnie [8], hereinafter referred to as the Birnie's plot, can be used to illustrate guidelines for co-solvent selection for striation-free films. A Birnie's plot is shown in Figure 4-23 with solvents used in common alkoxide-based sol-gel indicated. The plot is orientated about the main solvent, EtOH in this case. During spin coating, the reduction of thickness occurs in a short time and especially for sol-gel processing, the composition (i.e. concentration of solvents and water) changes as well due to evaporation and the on-going sol-gel chemistry through the different stages (cf. Eqs. 2.1 – 2.4). The Birnie's plot serves as a map for choosing co-solvent that could provide a stabilizing solutocapillarity, if not throughout the entire sequence but during the part where the film is prone to instability (i.e. time around the SET and before during the spin-off stage; also see Figure 4-19). First, the four quadrants are marked with the appropriate sign of $\partial_C \gamma$ and ΔC , yielding either positive (destabilizing) or negative (stabilizing) solutocapillarity. The unshaded areas (i.e. Quadrant 1 & 3) are where a favourable co-solvent can be found for EtOH to yield striation-free films. However, not all substances located in the entire quadrants are effective as co-solvents. These are substances in the vicinity of EtOH. Their properties are likely similar to the ones of EtOH so that only a weak solutocapillarity is present. Pr^iOH has been shown to have little effect on stabilizing the film (cf. STR3 and STR5). The use of ethyl acetate and MeOH has led to striated films [22]. As shown in this work (STR4, acetone), the co-solvent must not only have an appreciable $\partial_C \gamma$ with EtOH but also a large difference in P_{vap} or initial relative volumes with EtOH to create a substantial ΔC . Co-solvent selection from quadrant 3 (lower left) can be difficult as most are long-chain ethers or heavy aliphatics including hydrofluorocarbons. Some Hydrofluoroethers and perfluorocarbons substances were studied by the author. They were immiscible with the sol and water. Dibutyl ether and n-butyl acrylate have been shown to be compatible and shown striation-free films. On the other hand, volatile substances in quadrant 1 (upper right) are not the most advisable for coating applications due to an increase thermocapillarity, different evaporation, skin effect [76, 119], film non-uniformity (c.f. §4.3.4 and ref. [9]), short time window for handling²⁵ and safety concerns (viz. low flash point).

²⁵ From the experience of the author, using the sol recipe from STR4 for depositing films on a 4" wafer, the thinner portion of the liquid film (e.g. at the periphery of the wafer) tend to gel even before there is

Quadrant 2 is evidently shown in cross-hatched, showing unsuitable substances for co-solvents. Likewise, solutocapillarity in quadrant 4 is disruptive. However, experiments (both in this work and others: IBA, MOE and 1,2-propanediol [16]) have shown that substances further away from EtOH on the Birnie's plot yield stable films. The reduced thermocapillarity and increase in surface tension seems to contribute to the stabilization. Note that substances in the far corner of the quadrant 4 are likely to be highly viscous and hence a suitably longer cycle time is required for the slow surface tension to effect stabilization. With all the observation and analysis presented above, the additional information of viscosity and capillary force is added to the Birnie's plot as originally proposed in ref. [8]. Borders as shown in Figure 4-23 are by no means absolute boundaries in rigorous sense as time evolution of thickness, ΔT and ΔC is not considered. In any case, Figure 4-23 provides guidelines for solvent and co-solvent pairs that are probably effective in suppressing striations.

4.3.3.3. Macro-striations

From the above section, the solvent-saturated spinning (SSS) was not a preferred coating protocol in this work, in terms of the yield of the single-layer thickness. However, SSS does have one advantage. The inclusion-induced defects were noticeably less severe, namely, a smaller size. This is likely due to the fact that the saturated ambient reduces the solvent evaporation, hindering the gelation process; hence, the particles originated from the respective sources are smaller. Also, the magnitude of turbulent air is likely to be less severe as in a case with open-lid. By making use of the above STR6 recipe with an attempt to maintain a desirable thickness, a thickness of ~ 270 nm after FA1000°C could be achieved. Additional work was performed, as discussed below, to evaluate the feasibility and the improvement that could be achieved.

Spin-coating was now done with a partially-saturated ambient. Striations of the type noted in the preceding section was not noted but a type that is consistently shown to have a longer wavelength by about $Om(10^2)$ was seen. At such length scale, the surface structures can be readily resolved with eyes and cameras (Figure 4-24). Such macro-striations exhibit similar characteristics, namely, the cellular patterns at

enough time to allow the completion of liquid dispense to fill the entire surface of the wafer and pressing the button to start the spin coating routine.

the centre and radial striations in off-centre region. This is the first known observation of striation at such length scale.

In these cases, the sol typically consists of 16 mol% GeO_2 without the dilution step as in Figure 3.1 but a co-solvent is added to Sol-SG. The initial dilution step for the preparation of Sol-G used MOE instead of IPA. MOE was used to improve thickness uniformity as discussed in the following Section 4.3.4.3. Films were spin-coated at 1000 rpm under an RH of $< 30\%$. Under the SSS protocol, the thickness of film is not so sensitive as before as the rate of evaporation is significantly reduced. However, the preference to select a lowest possible spin speed is to achieve a thicker film. In general, the edge bead on film under SSS is broader than non-SSS protocol. The edge bead is broader as spin speed is reduced (~ 1 cm for 1000 rpm after multilayer deposition, see Figure 4-24 for single-layer films). The lid aperture (Figure 4-16) was sealed and solvents were used to wet the walls and filled the bottom of the coating chamber.

This dramatic increase in length scale of the instability can be explained by the surface tension of the solution. Due to the long-wave nature of the instability, surface tension tends to resist curvature by preferentially selecting the longer or increasing the length scale of the disturbance. Experimentally, Haas and Birnie [12] and Kozuka [16] found that the wavelength increases with lower spin speed. Haas and Birnie measured the elapsed time between the onset and the settling of striation and found that it was longer also at lower speed [13]. Also, Kozuka found an increase of wavelength when MOE is used to reduce striation magnitude as discussed above. MOE has a relatively high surface tension than the other co-solvents used in Kozuka's experiments. This observation unambiguously indicates that surface tension is in effect and it broadens length scales of the instability in time. For the films synthesized in this work, the solvent-saturated ambient slows the evaporation, prolonging the time from SET to the freeze-in point. Such delay of freeze-in of the film allows for the fluidic motion to occur in a longer period of time. Less diluted sols are likely to be higher in surface tension. Hence, the instability grows into striations of longer wavelengths.

Figure 4-24. Macro-striation observed on films deposited in solvent saturated ambient. The sols composed of 16 mol% GeO_2 with no solvent dilution. (a) and (b) are made from the same recipe at different time.

Similar to above section, stabilizing solutocapillarity was used via addition of co-solvent. Both acetone and isobutanol failed. The effect of thermocapillarity, differential evaporation and solutocapillarity are likely to be suppressed by the slow evaporation. Film instability observed under SSS is in contradiction to results found in refs. [75, 145]. Effort to elucidate the source of instability is left for future work.

To summarize the results in the section, the following inferences are drawn. When dealing with fluidic instability in spin-coating sol-gel-derived films, the evaporation of solvent is a very important process. It may lead to either stable film formation (i.e. with flat surface) or unstable film formation where striations are observed on surfaces of dried films. Hence, the choice of solvent or solvent system is important for forming striation free films, without having to compromise a reduced

single-layer thickness (Table 4-6). Isobutanol is now used as the co-solvent in sols that produce striation-free films.

Using the volatility of the solvent as a sole selection criterion to avoid instabilities is inadequate. The details of the film evolution and multiple acting forces must be considered. Not only the nature of the forces (whether it is stabilizing or destabilizing), the magnitude is important as the forces compete. From the current analysis and previously studies, a univocal conclusion is that the onset of instability is likely to take place before the SET where inertial forces are substantial. In addition, Figure 4-22 predicts the onset of instability (i.e. Marangoni number exceeding the critical level) to be at least $Om(100\ \mu\text{m})$ which is 2 orders of magnitude above the thickness at which striation is observed on sol-gel films. This discrepancy and the fact that the onset of instability is before SET both suggest that the approximation of dimensionless numbers of $\overline{Ma}_r^*$, $\overline{Ma}_s$ may not be adequate in describing the film system under spin coating. These numbers are ratios of the respective forces against viscous damping and have traditionally been used in linear analysis of stationary and slowly moving films. This work is a call for further work in hydrodynamical-mechanical modeling of spin-coating of sol-gel films and the subsequent linear analysis to provide a more formal mathematical description which has numerical predictive power for the occurrence of film instability.

Macro-striations were observed for the first time when spin-coated under the SSS protocol. Such elaborate length scale was explained by surface tension of the sols. Despite the success of SSS in the experiments of Du *et al.* [75] and Daniels *et al.* [145], at rather low dilution, significant film instability may still occur in sols.

4.3.4. Thickness uniformity

During preliminary experiments, the thickness of spin-coated films was found to be non-uniform over the area of the substrates. In Figure 4-10(a), concentric colour bands, caused by thin-film interference, are indicative of a continuous thickness variation from the centre to the edge of the substrate as shown in Figure 4-10(b). At a condition for constructive interference and a zero relative phase difference of each reflected rays, the thickness of the film, H , approximately follows the relationship [147],

$$H = \frac{m\lambda_m}{2n_f(\lambda) \cdot O}; \quad O = \cos \left[\sin^{-1} \left(\frac{n_a}{n_f} \sin \phi_0 \right) \right], \quad (4-12)$$

where O is an off-normal factor, λ_m is the wavelength at a particular interference peak and $m = 0, 1, 2, \dots$. The parameters n_a , n_f and ϕ_0 are the refractive indices of the ambient and the film and the angle of incidence, respectively. The relationship is plotted in Figure 4-25 and the colours can be seen to cycle continuously (for instance, the path indicated by the white arrows) the visible spectrum as thickness increases from ~ 100 nm²⁶ (c.f. Figure 4-10(a)). The intensity of the reflected colours fades as thickness increases and thus the order of interference, m , increases. In fact, a simple digital camera system has been shown to determine the thickness of thin-films of known refractive indices, from the colour components [113] using existing calibration values.

When depositing thick film using mSC-RTA process on a 10- μm -t-SiO₂/Si wafer, the degree of radial thickness non-uniformity (RTNU) generally worsens as the sol ages and solvents are depleted during the

processing. Such variation with thickness clearly produced an circular fringes that are not observable either with only the t-SiO₂/Si wafer (thickness uniformity from the product specifications: < 5%) or with a uniform GeO₂:SiO₂ film (< 6%) (c.f. Figure 4-6 (a) and (c)). This interference effect is a result of interactions between a number of interfaces: ambient/GeO₂:SiO₂ film, GeO₂:SiO₂/t-SiO₂ and the t-SiO₂/Si. The entire spectrum, in this case, are visibly limited only to yellow, green and red as shown in Figure 4-12, where $H \sim 1.8$ μm ; and the spectrum reduces to only yellow and red for the film shown in Figure 4-6(c) where $H \approx 3.4$ μm .

Figure 4-25. Mapping of reflected colour bands as thickness of the film changes for the case when $\theta_i = 0^\circ$.

²⁶ For thickness of film of 50 to 100 nm, the sample typically looks dark due to destructive interference. And below 50 nm, the sample seems reflective again.

A quick check with the coherent length condition would be instructive. For a typical fluorescence lamp (FL), its mean wavelength ($\bar{\lambda}$) is ~ 550 nm and a spectrum bandwidth ($\Delta\lambda$) of ~ 300 nm [148]. The coherence length of the source is given by [147]

$$l_c^{FL} \sim \bar{\lambda}^2 / \Delta\lambda \quad (4-13)$$

which is about $0.83 \mu\text{m}$. At normal incidence, Eq. (4-13) would suggest that $l_c^{FL} \sim 2n_f H$. For $n_f \sim 1.485$ (see Figure 3-19 for $x \sim 0.16$), no interference should be observed beyond a film thickness of $0.28 \mu\text{m}$ and yet interference is clearly observable in films with thickness as large as $4 \mu\text{m}$ (e.g. Figure 4-12). In fact, because the detection of the interference is from the film filter and not directly from the FL; hence, the effective coherence length of the film filter (TF) should be used for the coherence length condition [149],

$$l_c^{TF} \sim \frac{(m + 1/2) \bar{\lambda}^2}{2n_f \Delta H}, \quad (4-14)$$

where ΔH refers to the thickness non-uniformity over an area of the film. The effective coherence length can be in excess of $100 \mu\text{m}$ due to the small ΔH . Considering, in this case, the width of a circular band that appears as red on the film (Δw_{CB} in Figure 4-26), in the small angle approximation, can be expressed as

$$\Delta w_{CB} \sim \frac{(m + 1/2) \lambda_{red}^2}{2n_f \phi l_c^m} \quad (4-15)$$

where m an order that shows strong red peak where $l_c^m \ll l_c^{FL}$. Eq. (4-15) predicts that as the degree of RTNU (ϕ) is increased, the width of each of the colour band will decrease. This trend was, indeed, experimentally observed.

The consequence of this RTNU has been briefly mentioned in Section 2.3 and will be further elaborated in Section 5.6. This issue must not be

Figure 4-26. Schematic diagram of parameters relevant to the RTNU. See text for explanations.

compromised for device fabrication and commercially competitiveness (c.f. Table 2.1). The origin of this RTNU as discussed below stems from an uneven rate of evaporation across the liquid film during spin coating. A number of different attempts in reducing RTNU were studied. The efficacy of each method, in fact, revealed more information about the mechanism that leads to RTNU.

4.3.4.1. Spin program

At a first glance, the RTNU is likely to have caused by a radially dependent effect of which the centripetal force is obviously one such effect. Hence, a few different spin programs were experimented (Figure 4-27). Sols, prepared according to Figure 3.1 with $x \sim 0.160$, were deposited on 4" Si wafers. Spin coating was done in room temperature and RH of $< 20\%$. The idea was to investigate the effect of ramp rate, final spin rate and hold spin rate on the RTNU. Despite the rather extreme values used for the spin parameters, no marked changes in the thickness profile were noted by visual inspection. In fact, Haas and Birnie [13] have found that centripetal-force-driven thinning typically give way to evaporation-dominant thinning during spin-coating at an elapsed time of < 5 s which decreases for higher spin rate. From the above argument, the similar thickness profiles resulted from spin programs A, E and F can be understood as the ramp rate is quite similar before the SET time. For the program D, a substantially slower ramp rate may allow a lower RTNU to form during centripetal²⁷ drainage. However, no visibly remarkable improvement was noted. Therefore, the author concluded that the major cause of the RTNU was not the centripetal force.

Figure 4-27. Spin programs attempted to counteract the RTNU.

²⁷ In the frame of reference of a rotating object, the centripetal force is the body force that directs radially outward from the centre of rotation.

4.3.4.2. Off-centroid spinning

With the unresolved RTNU profile, an attempt was performed to reduce the degree of RTNU at least in the central area that would be large enough for one AWG device. By spin-coating with the planar centroid of the sample displaced from the rotational axis (Figure 4-28), the RTNU profiles with approximately equal offsets in different radial directions are superimposed. During the mSC-RTA, the first layer was spin-coated with the rotational axis placed at position 1, then subsequent layers at 2, 3, 4, and 1 again Inherent limitation of this technique is that large wafers or samples cannot be used; hence, a typical substrate of $\sim 5 \times 6 \text{ cm}^2$ was used and that the total number of layer is required to be multiples of the maximum number of offset positions.

Figure 4-28. (a) Placement of off-centred positions on the spinning wafer to mitigate RTNU. (b) Illustration of the spinning geometry of the off-centroid spinning (e.g. position 1 in a).

Table 4-9. Summary of resulted RTNU (in percentage) by spin-coating under different coating conditions. Diameter of samples are from 4 to 6 cm unless otherwise stated in the coating condition. PI-suppression refers to the protocol in which particle-inclusion was suppressed. The thickness is measured by the prism-coupling technique.

Sample	Coating condition	Avg. Thickness, μm	Error on Avg.	RTNU, %
PWG16	Centroid/closed lid with opened central aperture	3.28	NA	17.36
PWG14	Off-centroid/closed lid with opened central aperture	3.56	0.01	9.23
PWG19	Off-centroid/closed lid with opened central aperture	4.32	0.02	6.92
PWG20	Off-centroid/closed lid with opened central aperture	4.27	0.01	4.47
PWG21	Centroid/Closed lid/partial solvent saturation	3.97	0.01	2.58
PWG23	Centroid/Open lid/solvent flush	4.01	0.01	3.56
PWG24	Centroid/Open lid/solvent flush	4.08	0.01	4.13
PWG26	Centroid/Open lid/solvent flush/ 4" wafer	3.78	0.01	< 3%
PWG28	Centroid/Open lid/solvent flush/PI-suppression/ 4" wafer	3.76	0.00	2.26%
PWG29	Centroid/Open lid/solvent flush//PI-suppression 4" wafer	3.81	0.02	3.07%

Thickness of films was measured by the PC technique. The RTNU is quantified as,

$$RTNU[\%] = \frac{(L_{\max} - L_{\min})}{L_{\max}} \times 100, \tag{4-16}$$

where $L_{\max}$ and $L_{\min}$ are typically the thickness in the centre and edge respectively. Comparing the RTNU of spin-coated films (PWG14, 19, 20) with centroid-axis-matched spinning (PWG16), a notable improvement was achieved from $\sim 18\%$ to $\sim 6\%$. Correspondingly, the spacing of the circular fringes increased. Although this method was rather successful in reducing the RTNU, the off-centroid spinning caused substantial vibration even at a low speed of 1000 rpm. This vibration leads to

mechanical agitation on the sample, spin bowl and turbulent air flow while spinning; all of which, ultimately contributed to an increase in the number of flakes of glasses and particles of gel to be deposited on the gel film while spinning. These deposits are expected to cause detrimental optical scattering sites and are not removable by N₂ gun as they are chemically bonded to the gel film before it dries. Alternative solutions without the use of off-centroid spinning would be beneficial.

4.3.4.3. Chelation

An observation was made when TEOS was replaced by 3,3,3-trifluoropropyltrimethoxysilane (tFPtMOS). Uniform films were consistently formed. The chemical structure of tFPtMOS is represented by the schematic diagram shown in Figure 4-29. An elaborate inert organic structure in the ORMOSIL

Figure 4-29. A comparison between the molecular structure of the TEOS (a) and 3,3,3-trifluoropropyltrimethoxysilane (b).

precursor is known to retard the condensation reaction sterically [150]. In the spirit of synthesizing uniform films while maintaining a reasonable thickness (i.e. high sol-viscosity), chelating agents were used while any dilution of the sol can be minimized. Certain molecules are known to undergo a chemical process of alcohol exchange or transesterification (c.f. §2.4.6). After modification, typically due to increased steric effect, the rate of hydrolysis and condensation is reduced [151, 152]. While both methoxyethanol (MOE) and acetylacetone (AcAcH) are two well-known stabilizing agents for reactive alkoxide precursors, only the use of methoxyethanol has been reported for germanium alkoxide [27, 153].

From the discussion above, the chemical activity of the sol seems to have an effect on the uniformity of the film. Hence, the experiments below were designed to study the effects of dilution, chamber configuration, aging time and chelating agent on the thickness uniformity of the film. The sample preparation follows that described in Figure 3-1 where Sol-G is a mixture of TPOG and IPA for sample F81-F89. Within this group of samples, the volume of dilution was varied from 50 to 150 vol% (as a

percentage of Sol-S); the aperture on the lid of the chamber was either opened as before or closed (with the bottom of the chamber filled with EtOH) to assimilate a solvent-saturated ambient and the aging time was varied. All films were spun at 1000 rpm in room temperature and RH < 20%. The thickness was measured by a reflectometer after a furnace annealing of the samples for 15 minutes at 1000°C. The design of experiment is summarized in Table 4-10. The thickness profiles are shown in Figure 4-30(a) and re-plotted on normalized scale in Figure 4-30(b-c). The normalized scale can be useful in a sense that the non-uniformity is expected to be, if not worse, at least the state of what is shown for the multi-layer film. Samples of 50 vol% are grouped in Figure 4-30(b); the ones of 150 vol% and open aperture are grouped in Figure 4-30(c) and the ones of 150 vol% and closed aperture are grouped in Figure 4-30(d).

Table 4-10. Experimental matrix to study the affect of chemical activity to RTNU. The chamber ambient was controlled by leaving the chamber aperture (Figure 4-16) open or closing it to achieve a partially solvent-saturated ambient. Aging period refers to the one for the Sol-SG.

Sample	Dilution, vol%	Chamber ambient	Chelation agent	Aging period
F81	50	Open-apt	IPA	2 hrs
F82	150	Open-apt	IPA	2 hrs
F83	50	Closed-apt	IPA	2 hrs
F84	150	Closed-apt	IPA	2 hrs
F85	50	Closed-apt	IPA	7 hrs
F86	150	Open-apt	IPA	7 hrs
F87	150	Closed-apt	IPA	7 hrs
F88	150	Closed-apt	IPA	2.5 days
F89	150	Open-apt	IPA	2.5 days
F1	0	Open-apt	AcAc	2 hrs
F9	0	Closed-apt	AcAc	2 hrs
F27	0	Open-apt	MOE	2 hrs
F25	0	Closed-apt	MOE	2 hrs

F81 (50 vol% dilution; open aperture; 2 hours of aging) shows a RTNU²⁸ of > 20%. This figure is in accord with the RTNU of the earlier slab-waveguide (multi-layer) samples of PWG16 of the Table 4-9. In general, a trend of progressive non-uniformity is observed in Figure 4-30(b-d) with aging time, albeit the lesser change in Figure 4-30(c). No sample was prepared for 50 vol% (open aperture) for longer aging time as F81 shows an intolerable RTNU and such sample would only deteriorate further with aging time. This trend is mainly due to the increased sol viscosity with age and the reason will be apparent when Eq. (4-17) is considered in the later part of the discussion (see §4.3.4.4). In Figure 4-30(a), the profiles of the 150-vol% samples (F82-open aperture and F84-closed aperture) both exhibit better uniformity than the corresponding 50-vol% samples (F81-open aperture & F83-closed aperture), albeit a sacrifice in film thickness in the 150-vol% samples. Also, the closed-aperture (curves with filled markers) spin had consistently produced more uniform films. Comparing Figure 4-30(c) and (d), the RTNU of the samples by the closed-aperture spin appear to be more sensitive to aging time. This observation is an evidence for the lengthening of the time scale that is allowed for reactions (i.e. slower evaporation rate leads to a longer time to the SET point). Therefore, a more pronounced difference is noted between the thickness profiles of films spun at different aging times. Although the RTNU for all films spun with closed aperture seem to be of little concern in Figure 4-30(a), when plotted on the normalized axis, a remarkable non-uniformity was resolved (Figure 4-30d)) The above results show that a dilution and a solvent-saturated ambient are capable of improving film uniformity to some extent. The dilution could affect the improvement by reducing the chemical activity or reduced viscosity while solvent-saturated ambient decreases the rate of evaporation. The best RTNU of ~ 5% was achievable with 150-vol% dilution and a closed-aperture spin (Figure 4-30(d)), at a pitiful thickness of ~ 110 nm. From the results shown in Figure 4-30, a relatively thick, crack-free and uniform film is difficult to make with the current sol and fabrication condition.

²⁸ The radial thickness non-uniformity (RTNU) is quantified by $\{1 - (\text{Minimum Normalized Thickness})\} \times 100$.

Figure 4-30. Thickness profiles of single-layered films made from TPOG diluted in anhydrous IPA, Sol-G(IPA). (a) Dotted, dash and solid lines refer to films made at a sol ageing time of 2 hrs., 7 hrs. and 2.5 days respectively spin coated at 1000 rpm and after an FA-1000°C annealing; triangle and circle markers denote sol with 50 and 150 vol% dilution of EtOH; open and filled markers indicate whether the aperture on spin coater lid is opened or closed respectively. (b) – (d) The respective thickness profiles are replotted with normalized thickness to facilitate the evaluation of uniformity.

In order to study the chelating effect of MOE and AcAc on TPOG, the IPA is replaced at the same molar ratio of TPOG:CHA = 1:4. Dilution was kept at a constant 50 vol%. One set of samples were processed under opened aperture and another under closed aperture as above. The aging period for the Sol-SG was 2 hours. The thickness profiles of the resultant films are graphed in Figure 4-31 with the corresponding plots on normalized scales. A quick check of the relative chemical activity is by monitoring the gel time of the sols. The estimation, shown in Table 4-11, reveals a certain hindrance of the chemical activities as a result of the addition of the chelating agents.

Although the AcAc has a certain effect on the reactivity of TPOG, judging from the much reduced thickness of F1 and F9 and the longer T_{gel} , there is no improvement of RTNU observed (Figure 4-31(a) and (c)). There is no clear explanation at the moment. On the other

Table 4-11. An estimation of the gelation time or gel time (T_{gel}) with sols containing different chelating solvent of Sol-G.

Sol-G Composition	Get time (T_{gel}), days
TPOG/IPA	~ 2
TPOG/AcAc	~ 3 – 4
TPOG/MOE	~ 4 – 5

hand, a remarkable improvement was achieved by the use of MOE. The RTNU of F27 (open-aperture spin) is $\sim 8\%$ which is better than the RTNU of centroid-matched spin (PWG16) and quite comparable to the quality of the film produced using the off-centroid spinning technique (c. f. PWG14, 19 & 20 in the Table 4-9). As expected, by performing a closed-aperture spin (F25), the RTNU is further reduced to $< 5\%$ (Figure 4-31(c)). Based on this improved RTNU, a multilayered film, PWG21, was synthesized to evaluate the feasibility of this process. A promising RTNU of $< 3\%$ was achieved over a 6-cm sample following the procedures of F25. Another advantage of the closed-aperture spin procedure is that the inclusion-induced defects are less in number and in size. However, macro-striation was observed on the films (discussion in §4.3.3.3). Neither that any satisfactory solution was found by the author for avoiding these striations without sacrificing thickness nor that there were any solutions in the literature. Therefore, the use of the closed-aperture spin procedure was not pursued further. For all subsequent experiments, the original solvent of Sol-G, IPA, had been replaced by MOE due to its ability to stabilize reaction rate and provide a moderate improvement in thickness uniformity.

Figure 4-31. Improvement on thickness uniformity due to chelating agents on TPOG. The aging time of the combined Sol SG (T_A) and the multiplicative factor (M) referring to the number of average layers for respective single-layer film to achieve $4\ \mu\text{m}$ thickness are indicated in the parenthesis. (a) and (b) are films spun at 1000 or 1500 rpm with spin coater aperture opened after annealing of 1000°C ; (c) and (d) are films spun with aperture closed.

4.3.4.4. Open spin with partial-saturated ambient

To further gain information about the origin of the RTNU, another crucial experimental observation was made. A sol of $R < 2$ was aged for one or two days, spin-coated on a Si substrate at 1000 rpm with an opened aperture spin. The as-deposited film with visible RTNU but the film was truncated (discontinued) at a certain radial distance from the centre. This observation clearly suggests that the RTNU noted on the films is likely caused by a positional dependent rate of evaporation. The rate of evaporation is controlled by the air flow immediately

above the substrate. Therefore, the air flow in the chamber during the spin is likely to be complex with a substantial flow at the centre of the substrate and decreasing away from the centre. The air flow in the chamber during spinning is then likely to resemble the anticipated pattern shown in Figure 4-16(b). Air saturated with solvents can be trapped in regions away from the centre of the substrate, consequently contributes to a decrease in the rate of evaporation.

From the work of many authors [61, 70-72, 119, 154], the thickness of the dried films derived from spin coating can be predicted in the form,

$$H_f \propto \dot{e}^m \nu_0^{1/3} \Omega^{-2/3}, \quad (4-17)$$

where the exponent, m , is theoretically determined to be $1/3$ and ν_0 is the initial kinematic viscosity of the solution. Factoring out the $\Omega^{1/2}$ dependence of $\dot{e}$ (Eq. (4-10)), H_f attains the ubiquitous $\Omega^{-1/2}$ dependence. Experimentally, Chen [62] found an equivalent m to be 0.60 after factoring out the spin-speed dependence from $\dot{e}$. Just above the evaporating liquid film, a boundary layer (whose thickness $\sim \text{Om}(\nu_{\text{air}}/\Omega)$) was found numerically by Bornside *et al.* [21]. This boundary layer transports the vaporized solvent radially along the surface of the film directed toward the wall of the chamber. In order to account for this, the rate of evaporation is expressed as follows [70],

Figure 4-32. The relationship between critical dimension and spin speed predicted for simple laminar boundary layer flow atop of the surface of the film.

$$\dot{e} = k_m (C_s^{\text{air}} - C_{\text{inf}}^{\text{air}}), \quad (4-18)$$

where the coefficient of mass transfer, k_m is $A_{Sc}D(\Omega/\nu_{\text{air}})^{1/2}$, C_s^{air} is the vapour concentration of the solvent in the boundary layer and $C_{\text{inf}}^{\text{air}}$ is the vapour concentration in the ambient far above the spinning substrate. When $C_{\text{inf}}^{\text{air}}$ is taken to be negligibly small, then Eq. (4-10) is recovered. However, in the case where the air above the substrate is saturated by the vapour of the solvent(s), $\dot{e}$, and consequently, H_f is reduced.

For a laminar and steady flow above an infinite spinning disk, the rate of evaporation is said to be constant [155, 156]. From the numerical results of Bornside *et al.* [21], the mass transfer along the surface of the film is fairly uniform, radially, in a wide range of conditions (viz. spin speed and exhaust rate for the particular coater chamber geometry), providing the dimension of the substrate is smaller than the condition beyond which turbulent transients begin to develop and radially dependent mass transfer can be expected. Such critical limit is [21],

$$R_c = \left(\frac{\nu_{\text{air}} \overline{Re}}{\Omega} \right)^{1/2}, \quad (4-19)$$

where the Reynolds number, $\overline{Re}$, at this transition is taken as 0.6×10^5 (c.f. ref. [21], both experiments and theory dictate a range between $0.6 - 0.8 \times 10^5$). Taking ν_{air} and Ω as $0.158 \text{ cm}^2/\text{s}$ and 1000 rpm (104.7 rad/s), respectively, R_c is approximately 9.51 cm . Substrate used in this work is typically $\leq 4 \text{ inch}$. (i.e. $R = 5 \text{ cm}$), thus most experiments are done well below this limit. Exhaust flow is known to reduce the critical $\overline{Re}$ number to as low as 0.25×10^5 where increased film thickness (i.e. increased mass transfer) is observed on the periphery of the substrate. This type of thickness non-uniformity has never been observed in the current work using an exhaustless system, except for the common edge bead formation at the outer rim of the substrates [21].

Judging from the characteristics of the RTNU profile observed in the films fabricated with the spin coater shown in Figure 4-16 (i.e. thicker in the centre) and considering the numerical simulations of Bornside *et al.* [21] and Zhu and Liang [118], a prediction about the air flow pattern in two dimensions can be conjectured for what is likely to take place in the coating chamber of this work (see Figure 4-33(a)).

Due to the restriction on the air influx posed by the lid aperture, relatively more fresh air streams in through the aperture. Upon arriving at the surface of the film, the air flow is displaced radially away from the centre. In the absence of an exhaust (i.e. negative pressure gradient that forces the solvent saturated air to exit the chamber), the air flow approaches the wall of the chamber and a portion moves up along the wall and across back to the central influx stream below the aperture, thus, forming recirculation loops (Figure 4-33(a)). The air trapped in this recirculation zone is conceivably more saturated with the solvent vapour. In other words, the effective C_{inf}^{air} above the centre of the substrate is lower than at the edge of the substrate; thus, leading to progressively thinner film away from the centre according to the Eqns. (4-18) and (4-19).

Figure 4-33. A schematic illustration of the effect of lid on air flow that ultimately determines the thickness uniformity of spin coated films. The air flow pattern is shown with the lid (a) and without the lid (b).

In the light of this hypothesis, the entire lid was removed. With the solvent flush attachment (Figure 4-17) operating, extremely uniform films can be produced consistently (RTNU < 1%) at a spin rate of 1000 rpm (see Figure 4-34). The thickness profiles of the multi-layer films as shown in Figure 4-34 are plotted from results measured from a reflectometer (§4.2). The multi-layer films of PWG25 and PWG26 were fabricated according to Figure 4-1 with the open-lid protocol; and an improvement to < 5 % was achieved. PWG25 and PWG26 were fabricated using most of the defect suppression techniques above (summarized in Figure 4-36) with the

only exception of the inclusion suppression technique. PWG25 contained 45 mol% of ORMOSIL (MtES) and PWG26 contained 60 mol% of ORMOSIL (ethyl-triethoxysilane or EtES). Other details of the samples PWG25 and PWG26 can be found in Table 4-16. The improvement of the deposited film is likely due to the more uniform downward air flux as shown in Figure 4-33(b).

Figure 4-34. Improvement of radial thickness non-uniformity (RTNU) by the open-lid spinning protocol shown in absolute thickness (a) and normalized thickness (b). Note that sample PWGN2 was shown previously in Figure 4-12.

4.3.5. Achievement of uniform films by spin-coating

To facilitate the choice of the optimal spin coating protocol (i.e. process parameters), the process of defects forming caused by the above sol-gel/spin coating parameters are summarized, based on the author's work and the literature, in the Table 4-12. To achieve maximal thickness within the crack-prone limit established in Section 4.3.1 ($\sim 0.45 \mu\text{m}$ for a single-layer film after high temperature annealing), the effect of each of the spin-coating parameters on film thickness and film defects has been used as a guideline. The effects resulted from an increment in the respective sol-gel parameter are indicated in Table 4-12. The effects of increased thickness and reduction in defects are desirable and shown in green-solid arrows and red-dotted arrows represent

the contrary. Therefore, based on the various constraints and to achieve repeatability of the results, the strategy adopted for the improved mSC-RTA is as follows:

- to minimize humidity at a controlled level of < 20 %RH,
- to minimize the water ratio as water may increase the capillary force during drying, surface striation and particle-inclusion,
- to achieve low-moderate condensation rate and aging time (~ 2 – 4 hours),
- to minimize dilution (achieved by a low condensation rate and the use of striation suppressive co-solvent),
- to minimize spin speed (1000 rpm), and
- to maximize evaporation rate (open-lid spinning).

Table 4-12. Summary of the parameters of sol-gel films synthesized by spin coating and their effects on the quality of the deposited film. Up and down arrows indicate an increase or a decrease seen in the film quality in the columns for an increase in the corresponding parameter or effect. Arrows in green/solid tail are desirable and red/dotted tails are bad effects on the overall quality of the film. Dashes indicate no significant effect is caused by the parameter and C, conditional, refers to an effect that may depend on other parameters.

Parameters\Effects	Film thickness	Film cracking	Particle generation	Surface striation	RTNU
Humidity	↑	↑	↑	--	--
Water ratio	↑	↑	↑	↑	↑
Condensation rate	↑	↓	↑	↑	↑
Dilution	↓	↓	↓	↓	↓
Aging time	↑	C	↑	↑	↑
Spin speed	↓	↓	↑	↓	↑
Evaporation rate (air flow)	↑	↑	↑	↑	↑

Based on the above studies and some optimizations, the following recipe was adopted, in terms of molar ratios:

- Sol-S: 1 TEOS : 2 EtOH : 2 Bu'OH : 2 H₂O (HCl) and
 - Sol-G: 1 TPOG : 4 MOE.
- }

A brief 3 hours were allowed for hydrolysis of Sol-S and 2 hours for aging of Sol-SG. No further dilution was added. In view of striation avoidance, EtOH content from the original recipe should be replaced by BuOH as much as possible due to its lower vapour pressure. However, the BuOH has poor solubility with H₂O (Table 4-13)

which leads to phase separation and stoppage of hydrolysis; hence, it is only added after prehydrolysis of TEOS with EtOH in a 1:2 molar ratio.

The effectiveness of this co-solvent technique can be visualized in Figure 4-35. Figure 4-35 shows surface profiler scans for multi-layer samples (4 to 5 μm in film thickness)

after the entire process in Figure 4-1 (similar to Figure 4-20 for dried single-layer films before any annealing). Samples, PWG24-PWG26, were fabricated without observable striations using the above co-solvent technique with the open-lid spinning protocol (for details of the films, see Table 4-9 and Table 4-14); whereas samples PWG4, PWG5 and PWG14 were prepared from a sol composition to STR3 in Table 4-6, §.4.3.3.2, with the closed-lid spinning and the aperture opened.

Table 4-13. The water solubility of butanols. Empirically, liquids with similar Hildebrand solubility parameter are likely mutually soluble.

Substance	Hildebrand sol. param., $\text{cal}^{1/2} \text{ cm}^{-3/2}$	H ₂ O Sol., g/kg
H ₂ O	23	Infinity
Ethanol	12.92	Infinity
1-butanol	11.6	63.2
isobutanol	10.5	85

Figure 4-35. Surface profiler measurement of 16Ge 4- μm films fabricated before the striation suppression adjustment in the sol (a-c) and after (d-f).

Henceforth, the process that implements all of the above defect suppression techniques (§4.3.1.3, §4.3.2, §4.3.3.3 and §4.3.4.4) is summarized in the flow diagram in Figure 4-36, including all critical parameters and spinning protocols. A total of three films were fabricated (on 4" Si wafers with 10- μm t-SiO₂) on different days and two different compositions were attempted (viz. PWG28: 16 mol% GeO₂; PWG29: 5 mol% B₂O₃ and 20 mol% GeO₂). These slab waveguides are crack-free, with little visible particle-inclusions or inclusion-induced cracks, striation-free, uniform and edge-bead-free. Thickness mapping²⁹ was done for PWG28 and PWG29 and the as-received 4" Si wafer with 10- μm thermal oxide for comparison (Figure 4-37). Contour lines are 0.05 μm apart. The uniformity is consistent with profiles of PWG25 and PWG26 as shown in Figure 4-34 and is also seen to be comparable to the one of thermal oxide. Structural characterization has shown that the improved mSC-RTA process provides significant enhancement over any prior attempts in the quality of the multi-layer films. This process has shown to be readily repeatable in terms of the physical attributes of the films. The sol recipe process parameters and protocols used as described above, to the author's knowledge, is the first attempt to optimize the m-SC-RTA process to yield thick high quality silica-based films using alkoxide precursors.

Figure 4-36. Flow diagram of the improved mSC-RTA process.

²⁹ Thickness mapping was done by a reflectometer with an in-house fabricated 2-axis alignment jig (designed by the author).

Figure 4-37. (a) Thickness contour maps of a 10- μm t-SiO₂ on Si; (b) 16Ge 4- μm film on SiO₂/Si (PWG28) and (c) 5B20Ge 4- μm film on SiO₂/Si (PWG29). The dash outline represents the dimension of the 4" wafers; separation between major markings on the axes represents a length of 1 cm.

4.3.6. Optical properties of the multi-layered thick film

Beside the physical qualities of film, stringent requirements are imposed on the optical properties, uniformity and the optical propagation loss characteristics of the film which is to serve as the core layer of the waveguide. An evaluation of these properties is given in this section.

4.3.6.1. Optical propagation loss

Finally, optical propagation loss measurement was performed on PWG28 and PWG29 via the prism-coupler equipment (§4.2). The scans at 1550 nm for both TE and TM polarizations are shown in Figure 4-38. Intensity is plotted in a log scale. Two measurements at different points on each of the PWG28 and PWG29 are shown (Figure 4-38(a-d)). As a result of Eq. (4-2), $I_z^{\beta_m} / I_0^{\beta_m} = I_z^{\text{scat}} / I_0^{\text{scat}}$. A linear region in the loss curves can be found to enable the propagation attenuation coefficient, α_{dB} , in units of dB/cm, to be determined according to the following equation,

$$10 \times \log_{10} \left(\frac{I_z^{\text{scat}}}{I_0^{\text{scat}}} \right) = -(\alpha_{\text{dB}} z + \alpha_0) = f(z), \quad (4-20)$$

where z is the scan direction, α_0 is a constant and $I_z^{\text{scat}} / I_0^{\text{scat}}$ is the measured scattering ratio from the detector of the loss measurement. In general, the first ~ 0.5 cm of the scan is affected by the scattering from prism surfaces (§4.2). However, scattering unexpectedly increased beyond the mid-way point of the scans for curves shown in Figure 4-38(a-d). Since the wafers were not ideally flat, the distance between the surface of the planar waveguide and the aperture of the fibre bundle would change as the fibre bundle was scanned along the waveguide. As a result, the collected scattered light from the surface of the waveguide increased and deviated from the exponential trend with the scanned distance. Since the two regions highlighted above clearly do not follow an exponential decrease with distance (z), only the intermediate region was used in fitting to $f(z)$ in Eq. (4-20). This region can be seen as the portion of the wafer that was nearly flat and not affected by the scattered light from the prism surfaces. From the equations of the linear least square fit, shown in Figure 4-38(a-d) with the respective R^2 values, the attenuation coefficients are < 0.6 dB/cm.

Figure 4-38(e-f) shows measurements of the loss scan for PWG24 which was fabricated without the use of the particle-inclusion suppression technique. Scattering peaks due to scattering inclusions are clearly evident. In comparison, the loss curves for PWG28 and PWG29 are smooth and without any sharp peaks in the exponential region. Therefore, PWG28 and PWG29 exhibit characteristics of low-loss propagation that can be attributed to a reduction of particle inclusions, surface striations and low porosity. In addition, the spread (i.e. standard deviation) of the number of loss measurements of the samples PWG28 and PWG29 is significantly

lower than that of other samples (Table 4-16). The particle inclusion suppression (cf. §4.3.2) was exercised for these two samples only. Such reduction in particle inclusion is reflected in the reduction of optical loss and the aforementioned data spread (uniformity).

Figure 4-38. Loss scan of planar waveguides at 1550 nm for TE and TM polarization: PWG28 (a and b), PWG29 (c and d) and PWG24 (e and f).

4.3.6.2. Uniformity of RI

A common requirement for the fabrication of waveguide devices is that the RI must be uniform to better than $Om(10^{-4})$. For instance, for an AWG device, a shift of about 0.1 nm is caused by a change in RI of 1×10^{-4} [157] which is a substantial fraction of a channel spacing of DWDM systems (§5.3). An evaluation of the uniformity was undertaken by sampling prism-coupling (PC) measurements at different locations on the sample with GeO₂-doped layer on SiO₂ buffer on Si. The results are summarized in the Table 4-14.

Table 4-14. Summary of the optical property measurements by the prism-coupling technique. The uncertainty of the thickness shown is an average out of a number of measurement points. The values in brackets in the refractive index columns are the standard deviation of the respective RI.

Sample (mol% GeO ₂)	Total points	Thickness, μm	n_{TE} (SD)	n_{TM} (SD)	B ($n_{TE}-n_{TM}$)
PWG14 (16)	4	3.56 ± 0.05	1.4645 (0.0004)	1.4654 (0.0003)	-0.0009
PWG21 (16)	3	3.97 ± 0.01	1.4636 (0.0002)	1.4644 (0.0002)	-0.0008
PWG23 (16)	5	4.01 ± 0.01	1.4622 (0.0001)	1.4631 (0.0002)	-0.0009
PWG24 (16)	5	4.08 ± 0.01	1.4623 (0.0001)	1.4631 (0.0002)	-0.0009
PWG28 (16)	6	3.756 ± 0.004	1.46330 (0.00016)	1.46447 (0.00008)	-0.0012

The standard deviation of all the RIs is below the resolution limit of the PC measurements of ± 0.0004 (c.f. §4.2). Indeed, there are data points which fall outside of the standard deviation; however, to give an estimate of the overall uniformity, the standard deviation is used. Hence, taking the full-swing resolution limit of 0.0008, an upper estimate of the uniformity is $\sim 0.060\%$. This value is at the lower range of comparison conducted in Table 2.1. Nevertheless, the upper estimate of the RI-non-uniformity in the same order of magnitude as the finding of Alavian of 0.0004 for a hybrid sol-gel film [157].

4.3.6.3. Birefringence

Birefringence, quantified by the difference in the RI of TE and TM propagating modes, has been found to affect the operation of AWG by inducing a central wavelength shift. Therefore, further discussion on the birefringence is conducted in the next section on the device fabrication. Since the waveguide slabs, formed by the thick $\text{GeO}_2\text{:SiO}_2$ films, are intended to be patterned by dry etching process, the final residual stress state borne by the waveguide channels are likely to differ.

Nevertheless, at this stage, the birefringence can be used as a convenient diagnostic indicator for the fabrication process. The nature of the birefringence (i.e. positive or negative) reveals whether the film is under compressive or tensile respectively [158, 159]. In fact, stress mapping can be done by measuring birefringence. From the Table 4-14, the birefringence, calculated from the average of the RIs, is consistently negative but small, showing that the film is under slight tensile stress. The values of B are slightly above the precision of PC measurements (i.e. 0.0008). If, in fact, the real residual stress state were to be very small, measurements should have a spread of values with some in the positive region. However, no positive values were found in any of the measurements. Therefore, the birefringence shown in the Table 4-14 likely reflects a residual tensile stress that induces a birefringence close to 0.0009.

Referring back to Figure 4-9, the heat treatment process of RTA 1000°C and furnace consolidation at 1100°C yields films that are just slightly below the zero-stress point. This result further supports the validity of the proposed method of locating zero-stress point annealing temperature in Section 4.3.1.2.

4.3.6.4. Other quality engineering issues

Some quantitative estimates of the manufacturability of the solution-based process are given in this section. Using the calibration equation obtained from Figure 3.18, $n_{NIR} = 0.1434(x) + 1.4425$, n_{NIR} (RI at 1.550 μm) is predicted at 1.4654 ± 0.0005 for $x = 0.160$. The samples PWG14 – 24 (Table 4-14) were designed for the same composition of $x \sim 0.16$. The yield RIs for the selected samples are all below the above predicted value, suggesting that $x < 0.160$. A standard deviation of the RI values from the predicted value is noted to be < 0.0050 . This statistical spread can be

traced to uncertainties in the mixing ratio of GeO₂ to SiO₂ using the specific laboratory tools during the critical preparation of the Sol-SG (c.f. Figure 3.1 or Figure 4-36). The uncertainty of the n_{NIR} ($\sigma(n_{NIR})$) is predicted to be < 0.0004 (Table 4-15). This value is much smaller than the deviation from the predicted n_{NIR} . The reason is likely that the robustness of the prediction scheme in Section 3.5.7 should be further enhanced by collection of more samples.

Table 4-15. The variation of process uncertainty resulting in an error in refractive index, $\sigma(n_{NIR})$, with the increase in nominal GeO₂ content (x). Values taken from the curve of Process IV in Figure 4-39(b) for a volume of Sol-SG of ~ 53 mL.

Nominal x	$\sigma(x)$	$\sigma(n_{NIR})$
0	0	0.0005
0.050	0.0009	0.0005
0.160	0.0026	0.0006
0.200	0.0031	0.0006
0.400	0.0047	0.0009

Irrespective of the above discrepancy with the predicted values of RI, the average RI measured for each of the samples shown in Table 4-14 exhibits a statistical spread characterized by a standard deviation of 0.0009. Based on the estimation performed below to quantify the error in the composition of the binary oxide (i.e. error in x), a summary is tabulated in Table 4-15 for a number of nominal compositions. The significant part of the above statistical spread can be attributed to the error in the mixing process (i.e. $\sigma(n_{NIR}) \sim 0.0006$ for a nominal x of 0.160).

The following analysis investigates whether further improvement in the mixing procedure is feasible. Standard error propagation equations (c.f. Appendix J) were used to quantitatively evaluate the effects of the different mixing parameters (i.e. volume of batch and precision of tools) on the uncertainty in the yield RI. Such relationships are illustrated in Figure 4-39. Recall that the mixing sequence of the sols begins with Sol-S and Sol-G separately and an appropriate amount of Sol-G is extracted from the Sol-G batch to be added to the Sol-S to form Sol-SG (c.f. Figure 3.1 or Figure 4-36). The liquid measurement and extraction was carried out using a pipette with markings of a certain precision. Balancing the typical volume of sol and precision, only two types of pipette were used. Type A is a 10 mL capacity pipette with 0.10 mL markings and Type B is a 2 mL capacity pipette with 0.01 mL. Taking process IV shown in Figure 4-39(b), uncertainty is plotted against the batch size of Sol-G and variation of Sol-SG batch size is also calculated. The sawteeth features reflect the limited pipe capacity and draw-dispense repetition required for a specific

volume. In general, the uncertainty reduces with batch size. Typically, Sol-G batches were prepared with about ~ 20 mL TPOG. For earlier single-layer studies, the batch size of Sol-SG was ~ 10 mL and was ~ 45 mL for the multilayer fabrication.

Figure 4-39. Some process parameters that affect the certainty of the final yield RI of the $(x)\text{GeO}_2:(1-x)\text{SiO}_2$ films, where nominal $x = 0.16$. (a) Showing the effect of increase batch volume of Sol-G and Sol-SG. The Process IV is assumed. (b) Improvement in uncertainty by using more accurate dispense tools at different mixing steps. See texts for labels in brackets. Sol-G is taken for a batch with 10 mL of TPOG.

Figure 4-39(b) illustrates the effect of the precision of each pipette used at different mixing step. A 10-mL-TPOG Sol-G batch is assumed. Process I refers to a mixing procedure done strictly with the Type A pipette. Using the Type B at Sol-G step for dispensing TPOG and IPA in Process II, no significant improvement was resulted. Even when the TEOS step employs the Type B pipette (Process III), only slight improvement is obtained. In Process IV, all Type A pipettes are used everywhere with a Type B for the preparation of Sol-SG where some amount of Sol-G is extracted. A clear improvement is noted and hence the Process IV was adopted throughout all the preparation done in this work.

As noted from the curve of Sol-SG volume of 45.3 mL in Figure 4-39(a) and the curve of Process IV in Figure 4-39(b), only very limited improvement can be achieved if the batch of Sol-G or Sol-SG were to be increased any further and that tools of higher precision could be used, considering that the uncertainty in the composition to RI conversion is > 0.0005 in the above analysis.

4.4. Summary of the performance of the $\text{GeO}_2\text{:SiO}_2$ films fabricated throughout this work

The details of the representative films fabricated in this research are summarized in Table 4-16. The relevant experimental coating conditions/protocols are indicated for the preparation of each sample. The centroid spinning refers to aligning the centre of the substrate to the axis of rotation of the vacuum chuck. The off-centroid offsets the centre of the substrate with respect to the axis of rotation to improve thickness uniformity in a closed-lid (with opened aperture) chamber (cf. §4.3.4.2). Refer to Figure 4-17 in §4.3.2 or Figure 4-33 in §4.3.4.4 for schematics of the spin coating chamber used. A solvent flush was later fitted inside the coating chamber, so the solvent flush was used for all coatings after the installation (cf. §4.3.2). PI (particle inclusion) suppression refers to the technique by which the particle inclusion was drastically eliminated and the edge bead was in effect avoided (cf. §4.3.2). MtES and EtES are organically modified silicon precursors that were used to enhance critical cracking thickness (cf. §4.3.1.2). Unless otherwise indicated, the films were fabricated on substrates that are 4 to 6 cm in dimensions. The observed defects on the multi-layer films and any significant improvements due to the implementation of a new protocol are noted under remarks. The solvents used in the initial composition or recipe are also listed. The co-solvents that were strategically employed to suppress striations are printed in bold. The following attributes of the multi-layer films are tabulated to provide quantitative measures of the improvement achieved:

- the average thickness,
- the radial thickness non-uniformity, RTNU (cf. §4.3.4),
- the refractive index for TE mode at the wavelength of 1550 nm,
- the spread of the refractive index of a number of points over the sample or the wafer (cf. §4.3.6.2),
- the magnitude of striations—which is a qualitative estimate of the average peak to peak variations from the results of surface profilometry (cf. 4.3.3),
- the propagation loss of the fundamental mode in the film at 1550 nm, and
- the linear scattering-centre density estimated from the number of scattering peaks in the loss curves (cf. §4.3.6.1).

Cross references are provided for completeness for the locations in the chapter where other results of the samples were shown. The details of how the various

techniques were used to effectively suppress the respective film defects are briefly summarized in the following section.

Table 4-16. Summary of $\text{GeO}_2\text{:SiO}_2$ multi-layer films fabricated in this research with the relevant experimental parameters and resulting film attributes. Significant improvements in the quality of films are indicated under remarks.

Sample (mol% GeO_2)	Coating condition	Solvents in Sol ¹	Remarks	No. of coatings	Anneal. Temp. ² , °C	Avg. Thick., µm	RI (TE) RI (TE)	SD ³ of RI	Striations ⁴ (nm)	TE loss ⁵ (dB/cm)	Particle density ⁶ (cm ⁻¹)	Cross-ref. Fig.
PWG1 (16)	Centroid/closed lid with opened central aperture	EtOH/PhOH	Cracking; particle inclusions; thickness non- uniform; striations	10	900	~3.1	35	—	> 30	—	> 3	Fig. 4-34
PWG2 (16)	Centroid/closed lid with opened central aperture	EtOH/PhOH		10	900	~2.9	32	—	> 30	—	> 3	Fig. 4-12, 4-34
PWG4 (20)	Centroid/closed lid with opened central aperture	EtOH/PhOH		6	900	~1.79	—	—	> 30	—	> 3	—
PWG5 (20)	Centroid/closed lid with opened central aperture	EtOH/PhOH	No cracks; particle inclusions; thickness non- uniform; striations	21	900	4.99	—	-1.4687	> 30	0.3 ± 0.2	> 3	Table 4-3
PWG14 (16)	Off-centroid/closed lid with opened central aperture	EtOH/PhOH		16	1000	3.56	9.23	1.46453	> 25	0.3 ± 0.2	> 3	Table 4-9, 4-14
PWG16 (16)	Centroid/closed lid with opened central aperture	EtOH/PhOH/ Acetone	No cracks; striation suppressed; inclusions	16	1000	3.28	17.36	—	< 5	—	> 3	Fig. 4-6(c), Table 4-9
PWG19 (16)	Off-centroid/closed lid with opened central aperture	EtOH/PhOH/ BuOH	No cracks; particle inclusions; striation suppressed	18	1000	4.32	6.92	-1.4595	< 1	1.0 ± 0.3	> 3	Table 4-9
PWG20 (16)	Off-centroid/closed lid with opened central aperture	EtOH/PhOH/ BuOH		18	1000	4.27	4.47	-1.4638	< 1	0.7 ± 0.4	> 3	Table 4-9
PWG21 (16)	Centroid/Closed lid/partial solvent saturation	EtOH/MoE/ BuOH	Macrostriation; very little inclusions; no cracks	18	1000	3.97	2.58	1.46364	> 40	1.4 ± 0.2	< 0.2	Table 4-9, 4-14
PWG22 (16)	Centroid/Closed lid/partial solvent saturation	EtOH/MoE/ BuOH		11	1000	2.59	—	-1.4633	> 40	—	—	—
PWG23 (16)	Centroid/Open lid/solvent flush	EtOH/MoE/ Butylacrylate	Microcracks; striation suppressed; uniform thickness	10	1000	4.01	3.56	1.46222	< 1	—	—	Table 4-9, 4-14
PWG24 (16)	Centroid/Open lid/solvent flush	EtOH/MoE/1- butanol		10	1000	4.08	4.13	1.46227	< 1	0.6 ± 0.7	> 3	Fig. 4-35, 4-38, Table 4-9, 4-14
PWG25 (16)	Centroid/Open lid/solvent flush/MIES/4 ⁷ water	EtOH/MoE/ BuOH	No cracks; particle inclusions; striation suppressed; film rupture; uniform thickness	9	1050	3.99	—	1.47675	—	—	> 2	Fig. 4-34, 4-35
PWG26 (16)	Centroid/Open lid/solvent flush/EIES/4 ⁷ water	EtOH/MoE/ BuOH		11	1050	3.78	< 3%	-1.4643	< 1	—	> 2	Fig. 4-34, 4-35, Table 4-9
PWG27 (16)	Centroid/Open lid/solvent flush/MIES/4 ⁷ water	EtOH/MoE/ BuOH	No cracks; uniform thickness; no striation	9	1050	3.67	< 3%	-1.4627	< 1	—	> 2	—
PWG28 (16)	Centroid/Open lid/solvent flush/PI- suppression/MIES/4 ⁷ water	EtOH/MoE/ BuOH	Striation suppressed; little inclusions; uniform thickness; no edge bead; no cracks	10	1050	3.76	2.26%	1.48153	< 1	0.1 ± 0.1	< 0.3	Fig. 4-37, 4-38, Table 4-9, 4-14
PWG29 (20) [*]	Centroid/Open lid/solvent flush/PI- suppression/MIES/4 ⁷ water	EtOH/MoE/ BuOH		10	1050	3.81	3.07%	1.46752	< 1	0.57 ± 0.05	< 0.3	Fig. 4-37, 4-38, Table 4-9

* The nominal composition of PWG29 is 20 mol% GeO_2 , 5 mol% B_2O_3 and 75 mol% SiO_2 .

¹ Solvents used in the recipe of the sol. The solvents indicated in bold refer to the co-solvents that were used to suppress striations.

² This annealing temperature refers to the intermediate annealing step performed in a rapid thermal processor. All samples were later subjected to a consolidation step in air furnace at 1100°C for 6 hrs.

³ Radial thickness non-uniformity (cf. §4.3.4).

⁴ Standard deviation of a number of points of refractive index measured across the sample (cf. §4.3.6.2).

⁵ The striation profiles were not rigorously quantified. The numbers indicated should only be used as a qualitative measure.

⁶ Loss figures are averages of 2 to 3 best measurement points across the sample/water.

⁷ Particle density is estimated from the scattering peaks in the loss curves (cf. §4.3.6.1).

4.5. Chapter Summary

This chapter has presented studies related to the fabrication of thick-film (i.e. 4 μm) that is needed to serve as the core layer of planar optical devices. Most of the critical issues on the material properties have been discussed in Chapter 3. Leveraging on the low-cost aspects of the sol-gel technique, the mSC-RTA process was adopted, as previously demonstrated by Syms *et al.* [4]. Using the equipment available in the laboratory, many of the common defects related were observed on spin coated films, namely, cracks, particle inclusions, chuck mark, striations and thickness non-uniformity. These defects are presented in the order of criticality to optical devices. Albeit the plentiful existing literature on these topics, the understanding of each of the defect generation mechanisms is far from complete, especially for the synthesis of sol-gel-derived films. An effort to advance the understanding has been provided here by a critical analysis of a comprehensive collection of the available experimental and theoretical treatments and subsequently using them to explain experimental findings in this work. As a result, a number of significant improvements to the quality of the films was achieved.

Due to the inherently porous nature of the as-deposited gel films, thermal energy was used to drive the film to its full density. Cracking that occurs during heat treatments can be characterized by the stored elastic energy expression which is thickness and stress dependent. The peak temperature determines the stress state of the film via a temperature-dependent evolution (§4.3.1.1). The stress-state peaks at some intermediate temperature and remains tensile below the glass transition temperature. There is a need for a comprehensive model to predict the stress state at the different regimes described in the §4.3.1.1 for sol-gel films, from the onset of tensile stress formation (due to the shrinkage of films) to the relaxation at high temperatures.

The analysis of the experimental observation of striations (§4.3.3) shows that a full Navier-stoke treatment of the spin coating process for sol-gel derived films is needed to establish more appropriate criteria for the onset of instability leading to the formation of striations. The relevant long-wave type of instability is likely not only affected by the Marangoni effect but by a number of hydrodynamics forces during the spinning process, namely, differential evaporation, viscosity and surface tension.

Intensive experimentations were performed by the author to gain information about the elements of spin coating that ultimately led to the characteristic radially thickness non-uniformity (§4.3.4). Many strategies for avoiding or suppressing these defects exist but by no means well-established and rigorously formulated. Strategies that yield a relatively thicker single-layer film were adopted and shown to improve the quality of the film. An effort to enhance the sol-gel process that yields thicker film was undertaken by considering both published results and experiments conducted in this project.

Amidst of all the reported alternative chemical solution techniques (c.f. chapter preamble), which all possess low-cost advantage as the process used in this work, defects discussed in this chapter are likely to affect them.

With the modified mSC-RTA process presented in this chapter, the fabricated films of $(x)\text{GeO}_2:(1-x)\text{SiO}_2$, where $x \sim 0.16$, were deposited in ~ 10 cycles to achieve a thickness $\sim 4 \mu\text{m}$, on a 10-micron t-SiO₂ buffered 4"-Si wafer in a planar waveguide structure. These films were characterized optically and found to be near defect-free, uniform and low-loss (i.e. $< 0.6 \text{ dB/cm}$). The uniformity of the refractive indices, birefringence and manufacturability issues were discussed (§4.3.6). These quality issues will be used in Chapter 5 to evaluate how the quality of the film affects the performance of an AWG.

The major achievements presented in this chapter are outlined below:

- A unified thermo-stress evolution is described. Organically modified silane was used to increase the compliance of the gel structure, leading to an increase in critical crack thickness. After rapid thermal annealing, a single-layer thickness of $\leq 0.45 \mu\text{m}$ was achieved without cracks. An alternative method is proposed to identify the zero-stress point by correlation with available data of the glass transition point of bulk glasses from the literature. This information was to successfully fabricate crack-free thick-film ($\sim 4 \mu\text{m}$) by multiple-deposition spin coating on 4" Si substrates.
- Particle-inclusions have been significantly reduced by a simple solvent technique;
- A striation suppression process has been developed without compromising the single-layer thickness of the film by using butanol as a replacement co-solvent. By modification of the Birnie's plot, a more robust co-solvent selection strategy has been presented;

- Radially thickness non-uniformity observed using the in-house spin coater was eliminated. A hypothesis was proposed to explain the efficacy of lidless spinning;
- By a simple optimization scheme, with the necessary construction and modification of the spin coating equipment and the necessary improvements to the mSC-RTA process, thick films of 4-microns were synthesized in only 10 repetitions. The improved mSC-RTA process described in this chapter is capable of synthesizing purely inorganic films from the alkoxide sol-gel route with much less iterative cycles, improved film uniformity and better optical film quality (i.e. reduction of inclusions) than reported in the literature.

4.6. References

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Chapter 5 Applications in Photonics communications

In this chapter, the major contributions of the author are listed as follows:

- demonstration of the compositional porosity control in $\text{GeO}_2\text{:SiO}_2$ sol-gel films [1],
- demonstration of the bandgap engineering of quantum-well structures by varying the composition of the sol-gel dielectric encapsulant layer. The results on InP quantum-well (QW) structures were published in ref [2] while results on GaAs structures has been submitted for publication [3], and
- evaluation of the fabrication capability of the sol-gel synthesized films in terms the performance of a 16×16 channel arrayed waveguide grating (AWG) device based on buried sol-gel derived waveguide channels. This work will be submitted for publication .

In Chapter 3, a comprehensive characterization has been presented for the $\text{GeO}_2\text{:SiO}_2$ films synthesized by the sol-gel process used in this work. Not only do the optical properties differ with the variation in material composition, other structural properties likewise differ. In particular, the porosity of films decreases with an increase in the GeO_2 content. The thermal expansion of films is likely to be influenced by GeO_2 content. Taking advantage of the above properties, bandgap trimming of different extend was achieved by performing quantum-well (QW) intermixing with sol-gel encapsulant layers of different composition ($x = 0$ to 0.400). A tuning range of the bandgap as high as 64 nm was achieved on InGaAs/InGaAsP^1 QWs.

Once the material characteristics of the sol-gel derived $\text{GeO}_2\text{:SiO}_2$ are known (c.f. Chapter 3), and the necessary processing parameters established (c.f. Chapter 4), planar waveguides (dielectric slabs) could then be considered for the fabrication of arrange waveguide gratings (AWGs). The AWGs are of particular interests to the research community because they are universal components used in many photonic systems [4]. Such demonstration is routinely carried out to demonstrate the capability of a particular AWG fabrication method for planar lightwave photonics [5-12].

¹ The notation used here (i.e. QW/barrier) indicates that the QW is composed of a InGaAs layer and the barrier is a InGaAsP material.

5.1. Dielectric encapsulant layer induced quantum-well intermixing

A typical QW structure used in optoelectronics is shown in Figure 5-1. Quantum wells are made of a well layer that is of the order of few nanometres in thickness sandwiched between two barrier layers that are thicker. The composition of the well typically differs from the barrier material in a way to yield a relatively smaller energy bandgap to provide for electron confinement in one of the dimensions. In general, as-grown QW structures, when subjected to an exposure to high energy dose, will undergo a certain extend of interdiffusion of mobile atoms between the well and barrier layers of different chemical compositions (see Figure 5-1). This interdiffusion, known as quantum-well intermixing (QWI), causes the energy bands to be smoothened, leading to an enlargement of the bandgap (inset of Figure 5-1). By tailoring the properties of the dielectric encapsulant (or simply, a cap) layer deposited on an QW structure, bandgap trimming at a post-growth stage can be performed via QWI. Dielectric cap induced vacancy disordering, in fact, provides a simple and low-cost method to perform QWI as compare to the other means of driving QWI, such as plasma, laser and ion implantation. In addition, dielectric caps can be deposited at spatially specific regions on a wafer to enable spatially selective tuning across a single wafer. This scheme provides a simple platform for photonic integration on III-V-based photonics.

At present, there is a lack of knowledge of the exact defect species (whether simple or complex) that are directly linked to the enhancement of interdiffusion. In general, four observed processes have been reported to affect QWI [13-16]:

- the creation of disordering in the top semiconductor layer of the QW structure via out-diffusion of a mobile atom species, for example, Ga, or by other means,
- interactions between defects or defect and stress fields leading to the annihilation or retention of defects,
- Fickian diffusion of the defects into the active regions (depending on stress and concentration gradient), and
- subsequently, the defect-enhanced thermally-activated inter-layer diffusion of the constituents of the QW layers (i.e. Group III or V ions) leading to a change in the energy profile across the QW.

Figure 5-1. A schematic diagram of a typical p-i-n structured quantum well sample. In the insets on the left column, shows the band diagram for an as-deposited QW structure with abrupt interfaces. Upon exposure to energy capable of causing disorder, the mobile constituents of the well and barrier layer inter-diffuse or intermix.

Some properties of the cap film which are of interests include porosity of film, film stress and composition of the cap. Experimental results have suggested that the out-diffusion of Ga is dependent on the ability of the cap to provide a path for Ga to diffuse via interstitial channels or to provide an appropriate concentration gradient or the oxidation of Ga^2 at the cap/semiconductor interface. A number of reports have demonstrated the effect of porosity to promote out-diffusion of Ga in GaAs/AlGaAs QWs. This process, then, generates Ga vacancies in the barrier layer. The porosity was controlled either one of the following method: the deposition temperature of PECVD SiO_2 [18], prebaking temperature of sol-gel or spin-on glass [19] or oxygen ions exposure of e-beam evaporated SiO_y films or the use of dopant in SiO_2 [20, 21]. Some reports indicated that the oxygen content of the silicon-oxide-based dielectric cap enhanced out-diffusion of Ga [22-24]. On the contrary, by using dielectric caps

² Native oxide of Ga_2O_3 can be formed at 450°C [17].

such as Ga_2O_3 , $\text{Ga}_2\text{O}_3\cdot\text{SiO}_2$, Si_3N_4 , AlF_3 , SrF_2 and the likes, the out-diffusion of Ga has been shown to be suppressed due to the overpressure of Ga in the cap retarding Ga diffusion and the lack of interactions between Ga from the semiconductor and the constituents of the inert cap [14, 16, 17, 25-29].

During rapid thermal annealing (RTA), the process-dependent intrinsic stress and thermal stress between the dielectric and semiconductor layers induce opposing stresses at the interface in static equilibrium. Since the thermal expansion of the dielectric layers is typically much lower than that of the semiconductors (for instance, the coefficients of thermal expansion for SiO_2 and InP are 0.52 and 6.33 ppm/K respectively), at high temperature the semiconductor substrate tries to expand only to be restrained by the dielectric layer at the interface; hence, a tensile stress is induced in the dielectric layer while a compressive stress is cast upon the semiconductor substrate. The stress is largest at the cap-substrate interface of which the QW structures are located in the proximity. Such stress has been shown to affect the intermixing process during RTA [28, 30]. For the GaAs-based system, experimental studies have shown that: 1) stress provides energy for defect-defect reactions as evident from depth-resolved electrical characterization [14, 31] and 2) stress influences the direction and the rate of defects' diffusion [28, 30]. Although, in theory, a tensile stress acting on the semiconductor energetically favours out-diffusion of Ga (c.f. King [32] showed that equilibrium concentration of Ga vacancy increases at a tensile stress $\sim 1\text{GPa}$), there have been various speculations about such stress-dependence out-diffusion [28, 30, 33], but no direct experimental proof has been reported thus far.

Most of the finding above pertains to the QW system of GaAs/AlGaAs; however, some similarities have been found with the InGaAsP system which is widely used in the communications industry. For the InGaAsP system, a blue shift of the photoluminescence (PL) peaks of the QWs is a direct result of intermixing of the group V sublattice [13, 15] (contrasting the group III interdiffusion in the AlGaAs system) [13, 17, 34, 35]. However, group III out-diffusion has been linked to the efficacy of the blue shift for both, the InGaAsP and AlGaAs, systems [13, 15]. Therefore, the above schemes for controlling the out-diffusion and in-diffusion of Group III vacancies are likely to be useful for QWI of InGaAsP-based QWs.

Certainly, the QWs can only tolerate a suitable annealing temperature to promote the intermixing while retaining the crystalline quality. A high annealing temperature may cause the severe surface out-diffusion and dopant-redistribution, which may contribute to significant intrinsic waveguide loss due to free carrier absorption [34, 35]. At this point, the deterioration of the QW structures takes place and PL spectra of the excitonic emission exhibit reduced and broadened emission peaks. Amongst the above techniques, dielectric cap-induced disordering can be seen to be commercially attractive in large-scale production as it only involves the deposition of a dielectric layer which can be applied to large areas as already pioneered by the existing microelectronics industry. The key of this process is the ability to tailor the dielectric properties of the cap layer to spatially control the interdiffusion rate in QW. Hence, the sol-gel process is expected to provide added-values as a low-cost alternative of QWI techniques.

QWI techniques³ (dielectric cap layer as well as other disorder generation schemes such as impurity ion-implantation, laser-induced vacancy defects, plasma-induced vacancy defects) have been successfully demonstrated in GaAs-based systems, on the other hand, InP-based QWI produces low process yield and reproducibility due to the poor thermal stability. In order to avoid the redistribution of highly mobile dopants and undesired modification of material properties, reliable InP-based monolithic integration restrictively demands a relatively low-temperature process, as explored in recent works (i.e. $< 640^{\circ}\text{C}$) [36-38]. In comparison to these approaches, QWI carried out at low temperature is also greatly desirable especially for tuning the strained QWs, where the thermally induced strain relaxation by the generation of misfit dislocations must be avoided. The above limitation of the InP-based QW favours the sol-gel dielectric encapsulant tremendously. A commercially available spin-on-glass cap has been demonstrated to promote QWI in the GaAs-based material [38], and selective intermixing is achievable with the incorporation of P dopant [14]. From the stress analysis in §4.3.1, using sol-gel layer as a cap may induce a significant amount of compressive stress on the surface of the semiconductor during RTA. Such high level of stress serves to increase the interdiffusion kinetics. However, the doping level is limited to less than 5%, as the P-doped silica otherwise becomes hygroscopic and affects the QWI reliability [21]. To date, the work

³ See ref. [34, 35] for a comprehensive review on QWI and the different processes.

described here (also in ref. [2]) can be seen as the first study of its kind on bandgap modification in InP-based QWs using a sol-gel $\text{GeO}_2\text{:SiO}_2$ cap. The effect of the sol-gel-derived germanosilicate encapsulant layer on trimming of the bandgap energy of InGaAs/InGaAsP QW laser structure is examined in this work.

QW samples were provided by H. S. Djie from Nanyang Technological University, sol-gel cap layers were processed by the author, and the rest of the experimental work was distributed evenly. Djie performed the necessary calculations to derive the values of diffusion coefficients as shown in Figure 5-5(b). At least one half of the discussion and analysis below was originated by the author.

5.2. QWI using sol-gel derived $\text{GeO}_2\text{:SiO}_2$ films

An InGaAs/InGaAsP multiple-quantum well (MQW) laser structure as shown in Figure 5-2 was used in this work. Single-layer of $\text{GeO}_2\text{:SiO}_2$ films were applied atop the samples by spin-coating at 2500 rpm with an opened lid aperture (c.f. §4.3.2 for detailed procedures).

1.8×10^{-19} Zn doped	$\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$	100 nm	Contact layer
2.0×10^{-18} Zn doped	$\text{In}_{0.82}\text{Ga}_{0.18}\text{As}_{0.38}\text{P}_{0.62}$	50 nm	
7.3×10^{-17} Zn doped	InP	1400 nm	Upper Cladding
undoped	$\text{In}_{0.90}\text{Ga}_{0.10}\text{As}_{0.21}\text{P}_{0.79}$	80 nm	GRIN
undoped	$\text{In}_{0.82}\text{Ga}_{0.18}\text{As}_{0.38}\text{P}_{0.62}$	50 nm	
undoped	$\text{In}_{0.77}\text{Ga}_{0.23}\text{As}_{0.49}\text{P}_{0.51}$	12 nm	5x Barriers
undoped	$\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$	5.5 nm	5x Quantum Wells
undoped	$\text{In}_{0.77}\text{Ga}_{0.23}\text{As}_{0.49}\text{P}_{0.51}$	12 nm	Barrier
undoped	$\text{In}_{0.82}\text{Ga}_{0.18}\text{As}_{0.38}\text{P}_{0.62}$	50 nm	GRIN
undoped	$\text{In}_{0.90}\text{Ga}_{0.10}\text{As}_{0.21}\text{P}_{0.79}$	80 nm	
2.5×10^{-18} S doped	InP	1000 nm	Lower Cladding
2.5×10^{-18} S doped	InP substrate		

Figure 5-2. The layers of the InGaAs/InGaAsP QW samples used in this work. GRIN: graded refractive index layer.

The MQW laser structures were grown by metalorganic vapor phase epitaxy on (100)-oriented InP substrates, as detailed in Ref. [37]. The active region of the laser structure consists of five periods of 55 Å $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ QWs with 120 Å InGaAsP barriers. Prior to the annealing using a RTP in flowing N_2 ambient for 2 minutes, the sol-gel capped samples were prebaked on a hot plate at 160°C for 5 minutes to evaporate the residual solvent. Bare (uncapped) samples and samples capped by e-beam-evaporated SiO_2 (EBSi) were also annealed for comparison. PL at 77 K was then performed to assess the degree of band-gap shift and linewidth broadening using an Nd:YAG laser (1.064 μm) as an excitation source.

To demonstrate the effect of material composition on QWI, films for $x \leq 0.300$ were spin-coated onto samples of an incomplete InGaAs/InP QWs laser structure, annealed at 630°C. The incomplete structure refers to the laser structure as shown in Figure 5-2 with the highly doped InGaAs contact layers removed. The annealing was performed at 630°C for 2 minutes, at which the annealed bare sample only exhibits the small band-gap blue-shift of ~ 12 nm. Figure 5-3(a) clearly shows that a modification to the PL peak wavelength is affected by the compositions of the germanosilicate cap layer. In any cases, the sol-gel cap enhances the intermixing rate in QWs. At GeO_2 content, $x < 0.1$, the PL peak shifts are similar. For $x \geq 0.1$, there is nearly linear increase in PL shift up to $x = 0.30$.

In addition, an intermixing study was performed on the complete QW laser structure to demonstrate the postgrowth bandgap tuning using a sol-gel cap. Bare (uncapped) samples and samples capped by e-beam-evaporated SiO_2 (EBSi) were also annealed for comparison. In Figure 5-3(b), we obtain four distinguished PL spectra from bare samples and capped samples with the EBSi, and Ge-doped sol-gels ($x = 0.00$ and 0.16). The PL peaks for EBSi, uncapped, $x = 0$ and 0.16 are respectively 1456, 1436, 1408 and 1392 nm. This result highlights the spatial bandgap selectivity using combination of dielectric caps. The control sample and the intermixed sample ($x = 0.16$) exhibits a comparable PL linewidth (~ 40 meV) while the as-grown PL has a linewidth of 44 meV. The absence of linewidth broadening infers the retention of the optical quality after intermixing. The overall blue-shifts in the complete laser structure are enhanced if compared to the incomplete structure. The presence of Ga atoms from InGaAs contact layer underlying the sol-gel cap is responsible for the increase in the degree of intermixing from the complete laser structure.

Figure 5-3 The effect of Ge content (x) of the sol-gel cap on the PL peak shift of the QW partial laser structure. The annealing condition was at 630°C for 2 minutes. (a) The dash line represents the amount of bandgap shift observed from the uncapped sample. The inset shows the atomic force microscope image taken from the intermixed sample after cap-removal. (b) PL spectra at annealing temperature of 630°C from (i) e-beam evaporated SiO_2 -capped, (ii) uncapped, (iii) $x = 0.000$, (iv) $x \sim 0.160$ capped QWs and the dash line represents the as-grown without annealing.

Porosity and thermal expansion of the cap are two important parameters for the dielectric layer in dielectric cap-induced disordering [14]. Apparently, the EBSi in our experiment acts as the intermixing suppressor if compared to the control sample. Such result, while opposing to the results of Helmy *et al.* [39] whose films were claimed to be porous, suggests that our EBSi films are likely to be more dense. A separate measurement of refractive index (RI) was performed on the EBSi films using the ellipsometry to be 1.552 at a wavelength of 632.8 nm. Comparing with the typical thermal oxide (i.e. $n(\text{He-Ne}) = 1.45 - 1.47$), the high index of EBSi confirms the non-stoichiometric SiO_y , $y < 2$, with a dense network; the EBSi is likely to have a higher thermal expansion than SiO_2 [40].

From the curves of (iii) and (iv) of Figure 5-3(b), the sol-gel caps exhibit an enhancement in the degree of intermixing when compared to EBSi film due to its porous nature as observed earlier in our FTIR and ellipsometry results (§3.5.2 and §3.5.7). Figure 5-4 summarizes the relationship of porosity and the GeO_2 content in

the sol-gel films with the annealing treatments. The incorporation of GeO_2 into the films gives rise to the reduction in the porosity of films. This result contradicts the intermixing enhancement results in the $x = 0.16$ caps if the porosity were the dominant effect in the sol-gel cap induced intermixing. From ref. [41], we identify that there is a substantial increase in the thermal expansion with the addition of GeO_2 into the films. Compressive stress is known to favour the transformation of vacancy defects into antisites [14, 31]; hence, degree of intermixing is reduced. Considering the magnitude of change in the cap porosity and the thermal expansion as a result of the increasing GeO_2 content, an estimate can be obtained from Figure 5-4 $((4.4\% - 6.8\%)/6.8\% \times 100) \sim -35.3\%$ for porosity and $((2.4 - 0.5)/0.5 \times 100) \sim 380\%$ (from ref. [41]) for thermal expansion. Although the relative effect of the above two parameters for the current material system is unclear at present, the change in the thermal expansion is likely to be the dominating factor which enables the control the QWI via vacancy diffusion by the addition of GeO_2 .

Figure 5-4 A porosity-Ge map demonstrating both the effect of annealing temperature and Ge content on film porosity; dash lines represent a fit-by-eye guide for the data points at each annealing temperature [1].

A study was also preformed with QW samples of $\text{AlGaAs}/\text{GaAs}$ using the above caps and annealing temperature of 650°C . A similar behaviour was found [42]. The blue shift increases with GeO_2 content in the cap layer. From the aforementioned

observation that the out-diffusion of group III constituents is responsible for the increased efficiency of the QWI for both InGaAs/InGaAsP and AlGaAs/GaAs systems, this result further validates the role of efficient creation of beneficial vacancies via stress relaxation in the $\text{GeO}_2\text{:SiO}_2$ sol-gel leading to the pronounced degree of intermixing.

The activation energy and diffusion coefficient corresponds to the energy associated with the motion and formation of defects during dielectric cap annealing process. The annealing temperature-dependent band-gap shift can be used to deduce the diffusion coefficients (which is assumed to be independent of defect concentration), D_{QW} and the activation energy, E_A [43]. These quantities represent the interdiffusion process that takes place between mobile atomic species in the QWs. Ref. [43] describes the concepts of the numerical codes used in determining D_{QW} in great depth. Briefly, the change in the compositional profile (characterized by D_{QW} and diffusion time) across the MQW causes a change in the strain distribution, bulk bandgap value, effective mass for each carrier (i.e. the electron, heavy hole and light hole). As a result, the potential energy profile for each charge carrier changes. By solving for the bound states in all the sub-bands, the change in the electron—heavy hole transition energy corresponds to the peak shift observed in PL.

Figure 5-5(a) summarizes the relationship of annealing temperature and bandgap shift for caps of $x = 0.00$ and 0.16 from the InGaAs-InP QWs using Ge-dopant. For completion, we also include the experimental data of sol-gel cap induced intermixing on GaAs substrate by Lee *et al.* [44]. As shown in Figure 5-5(b), the experimental data is linearly fitted over $1000/T$ to the Arrhenius equation $D_{QW} \sim \exp(-E_A/k_B T)$, where k_B , T and E_A refer to the Boltzmann's constant, annealing temperature in Kelvin and the activation energy, respectively. Thus, $E_A = 1.7 \pm 0.5$ eV for both cases, which is significantly lower than the common InP-based and GaAs-based QWI processes [45, 46]. Nearly identical E_A intuitively implies that the discrepancy in interdiffusion behavior between $x = 0.00$ and $x \sim 0.16$ is only attributed to the difference in the number of beneficial vacancies that involve in the QWI. A good agreement with the experimental data of GaAs/AlGaAs QW intermixing as described above. This result further corroborates postulation that the compressive stress reduces the effective vacancy responsible for intermixing enhancement in the cap film. Therefore, the enhancement of QWI by the increased doping of GeO_2

content can be ascribed to the large magnitude of change in thermal expansion leading to the retention of vacancies that drives QWI.

Figure 5-5 (a) The PL peak shift versus annealing temperature from InGaAs/InGaAsP QW laser structure. (b) The diffusion coefficient of QW (D_{QW}) deduced from the experimental data as a function of the inversed annealing temperature for doped and undoped sol-gel caps in this work (InP substrate) and Lee *et al.* (GaAs substrate) in ref. [44]. A representative best linear fit is shown for both data sets. The slope of the linear fits corresponds to the activation energy.

The above understanding of the effects of $\text{GeO}_2\text{:SiO}_2$ caps on QWI may provide practical implications for implementing the sol-gel caps for QWI. Because stress (rather than porosity) has more influence on QWI, processes that involve repetitive lithography—etching—and deposition of layers of different compositions as demonstrated before may not be commercially viable [28]. In the author's view, the findings provided here necessitate new opportunities for the use of the many available solution deposition processes where multilayer caps can be avoided. More discussion of this subject is presented in Chapter 6.

5.3. Design of arrayed waveguide gratings (AWGs)

The key photonic application explored in this work is planar waveguide devices making use of the arrayed waveguide gratings. In high-capacity optical communication, involving multiple-frequency carriers (i.e. the DWDM scheme), critical functions such as filtering, multiplexing/demultiplexing and routing must be

performed. AWG devices were conceptualized as a technological replacement of traditional micro-optic dispersive elements [47]. A number of comprehensive reports has been published on the design strategy for AWG devices [48-50]. Since the AWG in this work is used as a demonstration of the sol-gel fabrication, only a brief description of the construction of AWGs, the relevant critical structure parameters and their relations to the performance of the devices are summarized below. The implications that the optimized values of the structural parameters (adopted from ref. [51]) have on the fabrication process are discussed. No attempt was made by the author on performance optimization of the AWG design.

Like many dispersive devices (i.e. prisms and gratings⁴), an AWG contains a dispersive element that is composed of an array of waveguides (AWs). In the case of AWGs, the optical path difference is introduced by a constant increment of waveguide length (ΔL) between each successive AW (i.e. a *phased* array or 'PHASAR'). Besides the ease-of-manufacture attribute, the PHASAR can be designed such that the dispersion angle is approximately linear with change in frequencies [47].

A schematic drawing of the shape⁵ of the $N \times N$ AWG (according to the one first proposed by Dragone *et al.* [58]) adopted in this work is shown in Figure 5-6. Basically, the AWG structure is made up of one pair of $N \times M$ star couplers that are joined by an AW. The device is physically symmetric and thus the input and output parts of the device are mirror images of each other. Optical signals containing up to N number of frequencies enter the device via one of the input waveguides (IWs). The slab waveguide that is part of the input star coupler provides a free propagation region (FPR) so that the input lightwave can be broadened by diffraction and coupled (almost equally) to all of the array waveguides. The IWs and the AWs are positioned according to the Rowland-circle configuration [50, 59], whereby the AWs forms an aperture plane which is a focal distance, f_L , from the centre of the input plane. On the other hand, the IWs and output waveguides (OWs) are aligned on an object plane that

⁴ They are traditionally associated with free-space optics, however, analogues have been used in integrated optics [47, 52-54].

⁵ Other AWG shapes have been proposed to reduce the device size [11, 55, 56] and enhance performance attribute such as crosstalk level [57].

has a focus⁶ at $f_L/2$ as in Ref. [50]. As the dispersion is afforded by the PHASAR, waves enter the second star coupler, with the different frequencies focused via constructive interference (also diffraction) onto the various positions on the image plane where equally spaced OWs are located. In a sense, the first star coupler serves as a lens element to redistribute the input lightwave before the dispersion element. The PHASAR functions very much like a miniature diffraction grating that induces a dispersion which after passing through the second FPR spatially disperses the individual frequency components to the different output ports (i.e. OWs).

Similar to diffraction gratings, the dispersion behaviour can be derived for AWGs via a grating equation with an optical path difference of $n_{\text{eff}} \Delta L$ between each AW [50],

$$d_a \sin \theta = \frac{2\pi}{\lambda_c} \left(\frac{n_{\text{eff}} \Delta L - m \lambda_c}{n_{\text{FPR}}} \right) \quad (5.1)$$

where d_a is the lateral spacing between each AW at the output aperture, θ is the angle between and fan out from the centre of the array's output aperture, λ_c is the designed central wavelength of the device, n_{eff} is the effective index of a specific optical mode of interest and n_{FPR} is the effective index of the media into which the optical signals exit after the AW. By taking the linear approximation for θ , the dispersion of the array is characterized by [50],

$$D_G = \frac{dX}{d\nu} = f_L \cdot \frac{d\theta}{d\nu} = \frac{f_L \cdot n_{\text{eff}} \cdot \Delta L}{\nu_c \cdot n_{\text{FPR}} \cdot d_a} \quad (5.2)$$

where X refers to the distance along the output plane opposing the output aperture of the AW and $\nu_c = c/\lambda_c$. Most of the properties of the AWG are determined by this equation.

In order to meet some typical performance specifications of AWG (i.e. for telecommunications), structural parameters have to be devised accordingly. These parameters are shown in Figure 5-6. The AWG specifications and the optimized structural parameters are shown in Table 5-1. The design has been adopted from the earlier work of Zhou *et al.* [51] which follows the general guidelines provided by Smit *et al.* [50].

⁶ The focal distance of the object plane may vary from $Ra/2$ to Ra (i.e. confocal arrangement) [49, 58]. By adjusting the focal distances of the aperture or I/O planes, phase errors incurred in the FPR can be minimized.

Figure 5-6. Schematic of a symmetric $N \times N$ arrayed-waveguide grating (AWG). Several structural parameters are indicated. A block diagram showing the functionality of each major section of the AWG is shown at the top.

The waveguide is designed to be a single mode for $1.55\text{ }\mu\text{m}$, symmetric buried type with a cross-section of $4 \times 4\text{ }\mu\text{m}^2$. An index contrast of $\sim 1\%$ between the core and the cladding RIs yields a mode width of $\sim 3.11\text{ }\mu\text{m}$. This attribute was ideal for fibre-device coupling via a microlens array. In order to keep crosstalk level to $< -30\text{ dB}$, all the waveguide spacings (i.e. for AWs at the two apertures (d_a) and IWs (d_i) and OWs (d_r)) were set at $14\text{ }\mu\text{m}$. For $d_a = d_r = d_i = d = 14\text{ }\mu\text{m}$, an estimated crosstalk of the nearest-neighbours coupling is calculated to be -35 dB by the overlap integral method [49]. Certainly, d_a can be reduced with an appropriate increase in M to suppress insertion loss without much penalty on crosstalk. Considering the in-house photomask-resolution is conservatively at $0.3\text{ }\mu\text{m}$ [60] and test patterns revealed that accurate pattern transfer can be achieved for a feature period of as low as $2.5\text{ }\mu\text{m}$, a pitch (d) of $14\text{ }\mu\text{m}$ can be readily achievable. For the obvious reasons, any inaccurate

pattern transfer will lead to scattering and phase errors which will increase both insertion loss and crosstalk.

Once the AW spacing is fixed, M is the sole parameter⁷ to minimize the loss due to diffraction (i.e. energy coupled to undesired diffraction modes) on the aperture plane. However, as will be discussed later, higher M will incur higher magnitude of phase errors and non-uniformity due to bend loss which deteriorates the crosstalk performance and channel non-uniformity of the AWG, respectively. As determined in ref. [51], the necessary M (i.e. $M = 129$) that will capture intensity within the $1/e^2$ points of the divergent Gaussian intensity profile at the input aperture of the 1st FPR. $M = 87$ was selected based on the intensity profile at half maximum intensity points in an effort to relax fabrication constraints. However, the discussion below will demonstrate that additional considerations are required to accommodate for AWGs fabricated using films synthesized in this work (cf. Chapter 4).

Besides optical loss incurred at the coupler, the bend loss of the waveguides (i.e. AWs, IWs and OWs), especially for low- Δn devices, is significant. The orientation of the coupler axes, θ_C , and the separation of the two couplers were primarily identified as the factor that determine the pure bend loss of the entire device. With the separation of the couplers fixed at 2 cm, an optimized orientation angle was found to be $\theta_C = 58.6^\circ$ [64]. Adapting the formulation of ref. [65-67], the calculated bend loss is ~ 0.067 dB for the device considered in this work. Such AWG design is shown in Figure 5-7. Additional physical parameters of the structure can be found in ref. [64]. The corresponding optical simulation for the AWG considered above is performed by a commercial beam propagation method package from Optiwave BPM 6.0. The transmittance characteristics are shown in Figure 5-8. The insertion loss is better than -3 dB, channel uniformity or the difference in transmission peak between the central and the fringe output channel, $L_u = T(N = 7) - T(N = 1)$ is < 1.75 dB and crosstalk is < -30 dB.

⁷ In fact, the loss incurred in the FPRs has been shown to be further reduced by implementing adiabatic transition regions in waveguide array before FPR junction [61-63].

Table 5-1. A summary of AWG specifications and determined structural parameters.

Parameter	Description	Optimized values
Specifications		
λ_c	Central frequency in vacuum	1.55413 μm
$\Delta\lambda$	Channel width	0.8 nm
Crosstalk	Designed crosstalk	< -30 dB
L_u	Channel non-uniformity (relative loss between central and peripheral channels)	< 2 dB
Bandwidth	Designed 1-dB bandwidth	> 0.2 nm
N	Number of input and output channels (ports)	16 $\times$ 16
Mode	Modal design of each waveguide element	Single-mode
$Loss_{total}$	Insertion loss at central waveguide	< 5 dB
Structural parameters		
$a \times b$	Waveguide cross-section	4 $\times$ 4 μm^2
n_1	RI of core	1.472
n_2	RI of cladding	1.457
f_L	Focal length	3200 μm
d	Waveguide spacing at coupler junctions	14 μm
ΔL	Constant length increments between AWs	126.05 μm
m	Diffraction order	114
M	Number of arrayed-waveguides	87
θ_c	Slab waveguide orientation angle	58.6°

Figure 5-7. The final design of AWG. The same pattern is used in fabricating the appropriate photomask.

Figure 5-8. Transmission spectrum (TM mode) of AWG simulated by the beam-propagation-method analysis.

The design above was provided by Dr. Jun Zhou from Nanyang Technological University for the preliminary fabrication trials discussed below undertaken by the author.

5.4. Fabrication of AWG

The conventional processes of optical lithography and reactive ion etching (RIE) were used for patterning of the AWGs. After the sol-gel deposition, a film of Cr, 300-nm in thickness, was deposited by e-beam evaporation and used as a hard mask for reactive ion etching (RIE). The device features were patterned on the Cr mask using photolithography techniques (i-line aligner and a photoresist of AZ5412) and followed by RIE to create the pattern. The RIE was performed by a generic, in-house equipment. To achieve a 4- μm etch depth, a CF_4/O_2 (20/2 sccm) chemistry was used to achieve an etch rate of ~ 50 nm/min. A schematic of the process flow is shown in Figure 5-9. After the removal of the Cr mask, the etched pattern can be seen in Figure 5-10. However, the poor etch quality and particle-inclusions in the earlier films shown in §4.3 led to optically inferior structures. Patterned AWGs (without uppercladding) were found to be not operational with no transmission detected. To form the buried waveguide device, a number of process and materials are readily available at the laboratory for the realization of the uppercladding such as CVD of silicate films or spin coating of optical polymers.

Using the improved film as depicted from the end of Chapter 4, the performance of the devices is expected to be elevated to practical level with a better etching process which is quite readily achievable with the current commercial tools [57, 68-70]. Further fabrication attempts are not documented in this work. In an effort to provide some quantified indication of the performance of the films, as presented in Chapter 4, in the fabrication of AWGs, some figure-of-merits that describes the quality of the deposited film (i.e. uniformity of thickness and refractive index) are used to estimate the performance of an hypothetical AWG from the designed parameters shown in Table 5-1. This analysis is presented in the next section.

Figure 5-9. After thick sol-gel waveguiding slab has been deposited (a), a Cr hard mask is deposited by e-beam evaporation followed by photolithographic patterning using photoresist, then Cr wet etch and RIE is performed (b) and lastly, upper cladding is applied by spin coating (c).

Figure 5-10. Viewgraphs of the patterned AWG structure after RIE.

5.5. Estimation of the effects of fabrication constraints and imperfections on the AWG performance

For the purpose of the foregoing discussion, some fine tuning of the design was implemented to model the $\text{GeO}_2\text{:SiO}_2$ ($x \sim 0.16$) films as obtained from the Chapter 4. The set of new parameters are summarized in Table 5-2. The above design can be seen to yield a theoretical performance of an insertion loss < 7 dB and channel non-uniformity of < 1.20 dB. The simulated transmission characteristics are presented in Figure 5-11.

As the crosstalk performance of real devices is typically limited by constraints imposed by the current fabrication technologies, an estimation of the effect is valuable. Fabrication imperfections (i.e. roughness and verticality of side-wall of waveguides and tolerances on feature dimensions) lead to phase errors and scattering that ultimately degrade crosstalk and insertion loss. Since the spatial frequency side-wall roughness is $\gg 1/\lambda_c$, the effect of scattering can be considered small and weakly wavelength-dependent.

Table 5-2. AWG parameters adjusted for the planar waveguides demonstrated in Chapter 4.

Structural parameters		
$a \times b$	Waveguide cross-section	$4 \times 4 \text{ }\mu\text{m}^2$
n_1	RI of core	1.4616
n_2	RI of cladding	1.4449
f_L	Focal length	$2950 \text{ }\mu\text{m}$
d	Waveguide spacing at coupler junctions	$14 \text{ }\mu\text{m}$
ΔL	Constant length increments between AWs	$126 \text{ }\mu\text{m}$
M	Number of arrayed-waveguides	79
m	Diffraction order	118

Figure 5-11 Transmission spectrum (TE polarization) of 16×16 AWG for the TM mode simulated by the BPM method of analysis. The transmission output from each of the 16 output ports are labelled 1 to 16.

The fabrication imperfections can be envisaged as follows:

- width of waveguides/side-wall roughness, δw ,
- height of waveguides, δh ,
- straightness of wall,
- finite fluctuation of the refractive index of the waveguiding materials, δn , and
- the error due to the finite photomask resolution, δL_{ph} .

All of the above imperfections contribute to a deviation in the effective index, $\delta n_{\text{eff}}(\delta\omega, \delta h, \delta n)$ which introduces an error in n_{eff} and ultimately in the phase, $\phi(i)$,

$$\phi(i) = k_c n_{\text{eff}} L(i) = k_c (n_{\text{eff}})(L_0 + i\Delta L), \quad (5.3)$$

where $L(i)$ denotes the physical length of each path through the i^{th} array waveguide, n_{eff} is the effective index of the fundamental mode of the single-mode device in this work and $k_c = 2\pi/\lambda_c$. Eq. (5.3) should be treated separately for both TE and TM polarizations if the waveguides are birefringent.

Figure 5-12. Normalized power distributions in the arrayed waveguides for the case of (a) $M = 87$ and (b) $M = 129$. The coordinate, X , refers to the planar dimension perpendicular to the direction of light propagation in the slab waveguide. (c) The random phase error generated with a mean of -0.2 rad and a standard deviation of 0.2 rad.

To understand the effect of such phase error on the AWG performance, the radiation pattern of a phased array is considered. Due to the construction of the two couplers (i.e. in this case, the Rowland-circle), the only substantial optical path difference of any given paths through the device lies in the ΔL . After the first star-coupler, the input optical signal is distributed across the PHASAR (according to Figure 5-12(a) and (b)). Since the dispersion function depends solely on the relative phase relation between each array member, any deviation from the designed phase difference, ΔL affects the wavelength-dependent focusing property. Consider the

function of the 2nd FPR (§5.3), it can be modeled by a transfer function of the electric field, $H(k_c)$ [49, 71-75],

$$H(k_c) = \sum_{i=0}^{M-1} C(i) e^{j\phi_0(i)} e^{jk_c n_{eff} i \Delta L} \quad (5.4)$$

where $C(i)$ is the magnitude of the electric field across the AW—2nd FPR interface and $\phi_0(i) = k_c \cdot n_{eff} \cdot L_0$. $C(i)$ can be calculated by the square root of the Gaussian power distribution as shown in ref. [51]. Then, the transmission spectrum of the central channel (i.e. $\lambda_c = 1.55413 \mu\text{m}$) at the output aperture can be represented by, $T(k_c) = |H(k_c)|^2$ where the factor of $e^{jk_0 L_0} \cdot e^{-jk_0 L_0} = 1$ in $T(k_c)$, thus omitted in Eqn. (5.4). Taking the normalized field distribution shown in Figure 5-12(a) and (b) and the randomized phase error (i.e. normal distribution with a mean at -0.2 rad and a standard deviation at 0.2 rad) as presented in Figure 5-12(c), the resultant transmission spectra can be approximated and shown in Figure 5-13. The phase error used in Figure 5-13(a) and (b) is similar to the one measured on an AWG with channel spacing of 100 GHz [71]. The shaded region represents the spectral width of the central channel considered in this work (i.e. 0.8 nm). For illustration purpose of the affect of M and phase error on the transmission spectra, the calculated spectra in Figure 5-13 do not account for the insertion loss caused by bend loss, the splitting loss in the first coupler (i.e. truncation of the far-field radiation at the plane of the input aperture) and phase error [74]. In addition, $C(i)$ has been spatially discretized using only the peak intensity of the peak modal profile of each AW. This discretization is manifested through spectral features that are much narrower than that of the full simulations (e.g. the width of the transmission peak).

Comparing T1 to T3 in Figure 5-13(c) where $\delta\phi(i) = 0$, the phase error clearly causes an increase in the average crosstalk across the FPR. For the sake of completion, an increase in M , where the input aperture embodies the $1/e^2$ -far-field intensity (i.e. $M = 129$), may further reduce the crosstalk (viz. comparison of T3 and T4 in Figure 5-13(c) and (d). The same phase error distribution was added to T4 resulting in T2. The dominant effect of the phase error is clearly seen through the fact that crosstalk across the band increases to level very close to that of T1.

Figure 5-13. Dependence of the transmission at the central channel for four designs: (a) $M = 87$ with non-zero phase error from Figure 5-12 (b) $M = 129$, $\delta\phi \neq 0$, (c) $M = 87$, $\delta\phi = 0$ and (d) $M = 129$, $\delta\phi = 0$. The shaded region denote the spectral width of the central channel. The shaded region represents the spectral width of the central channel considered in this work (i.e. 0.8 nm).

The fabrication tolerances (i.e. uniformity in thickness and RI in Chapter 4) of the sol-gel synthesis presented in this work can be used to provide a good estimate on the real performance of the AWGs. The approach of Kamalakis *et al.* [74] is adopted for the foregoing analysis. The deviation in the field distribution, $C(i)$, has been determined to be $< 5\%$ [76]. In the case where the photomask resolution is better than 25 nm, there is only negligible contribution to crosstalk [76].

If the deviation of any of the parameters, $\wp$, that are subjected to fabrication errors result in a corresponding linear shift⁸ in n_{eff} , the variance, $\sigma_{n_{\text{eff}}}^2$,

$$\sigma_{n_{\text{eff}}}^2 = \sum_{\wp} \left(\frac{\partial n_{\text{eff}}}{\partial \wp} \right)^2 \sigma_{\wp}^2 \quad (5.5)$$

where $\sigma_{\wp}^2$ refers to the variance on any of the fabrication parameters. The above assumption of the linearity is justified for the waveguide design used in this work in Figure 5-14. All the values of $\partial n_{\text{eff}} / \partial \wp$ are subsequently derived from a linear regression analysis of data sets in Figure 5-14. Instead of using the effective refractive index method in [74], BPM was used to determine the $n_{\text{eff}}(\wp)$ relationships. The bending radii of silica-based AWGs are large so that Eqn. (5.5) holds. From Eqn. (5.3), the variance or the standard deviation on the phase, $\phi(i)$, is,

$$\sigma_{\phi(i)} = \left(\left(\frac{\partial \phi(i)}{\partial n_{\text{eff}}} \sigma_{n_{\text{eff}}} \right)^2 + \left(\frac{\partial \phi(i)}{\partial L_{\text{ph}}} \sigma_{L_{\text{ph}}} \right)^2 \right)^{1/2} = k_c \left(\sigma_{n_{\text{eff}}}^2 L(i)^2 + n_{\text{eff}}^2 \sigma_{\text{ph}}^2 \right)^{1/2} \quad (5.6)$$

where $\sigma_{L_{\text{ph}}}$ denotes the phase error introduced by imperfect photomask resolution,

$$\sigma_0 = k_c \left(\sigma_{n_{\text{eff}}}^2 L_0^2 + n_{\text{eff}}^2 \sigma_{\text{ph}}^2 \right)^{1/2} \text{ and } \Delta\sigma = \sigma_{\phi(M-1)} - \sigma_{\phi(0)}.$$

⁸ The nature of the fabrication errors is assumed to be random with a normal distribution. If the linearity holds within appropriate error limits, the variance of the resultant linear combination (i.e. n_{eff}) is simply a summation of quadratures.

Table 5-3. Quantitative analysis for strategies to improve crosstalk performance of the pre-designed AWG.

Cases	Ref. [74]	Ref. [76]	Ref. [76]	A	B	C	D	E	F	G
$\partial n_{\text{eff}}/\partial H, \mu\text{m}^{-1}$	1.97×10^{-4}	4.50×10^{-4}	4.50×10^{-4}	0.0015569	0.0015569	0.0015569	0.0015569	0.0007784	0.0015569	0.0015569
$\Delta H, \mu\text{m}$	0.002	0.002	0.002	0.078	0.010	0.005	0.002	0.002	0.002	0.001
$(\partial n_{\text{eff}}/\partial H)/\Delta H$	1.97×10^{-7}	9.00×10^{-7}	9.00×10^{-7}	0.000121	1.49×10^{-5}	7.46×10^{-6}	3.73×10^{-6}	1.87×10^{-6}	3.73×10^{-6}	1.87×10^{-6}
$\partial n_{\text{eff}}/\partial w, \mu\text{m}^{-1}$	1.97×10^{-4}	4.50×10^{-4}	4.50×10^{-4}	0.001628	0.001628	0.001628	0.001628	0.000814	0.001628	0.001628
$\Delta w, \mu\text{m}$	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.002
$(\partial n_{\text{eff}}/\partial w)/\Delta w$	1.97×10^{-7}	9.00×10^{-7}	9.00×10^{-7}	3.26×10^{-6}	3.26×10^{-6}	3.26×10^{-6}	3.26×10^{-6}	1.63×10^{-6}	3.26×10^{-6}	3.26×10^{-6}
$\partial n_{\text{eff}}/\partial n_{\text{core}}$	1.05	0.3	0.3	0.7834956	0.7834956	0.7834956	0.7834956	0.7834956	0.7834956	0.7834956
Δn_{core}	1.90×10^{-6}	2.70×10^{-5}	2.70×10^{-5}	3.93×10^{-6}	3.93×10^{-6}	1.96×10^{-6}	1.96×10^{-6}	1.96×10^{-6}	9.82×10^{-7}	9.82×10^{-7}
$(\partial n_{\text{eff}}/\partial n_{\text{core}})/\Delta n_{\text{core}}$	2.45×10^{-6}	8.10×10^{-6}	8.10×10^{-6}	3.08×10^{-6}	3.08×10^{-6}	1.54×10^{-7}	1.54×10^{-7}	1.54×10^{-7}	7.70×10^{-7}	7.70×10^{-7}
$\partial n_{\text{eff}}/\partial n_{\text{clad}}$	0.2	0.1	0.1	0.1601455	0.1601455	0.1601455	0.1601455	0.1601455	0.1601455	0.1601455
Δn_{clad}	1.90×10^{-6}	2.70×10^{-5}	2.70×10^{-5}	3.93×10^{-6}	3.93×10^{-6}	1.96×10^{-6}	1.96×10^{-6}	1.96×10^{-6}	9.82×10^{-7}	9.82×10^{-7}
$(\partial n_{\text{eff}}/\partial n_{\text{clad}})/\Delta n_{\text{clad}}$	3.80×10^{-7}	2.70×10^{-6}	2.70×10^{-6}	6.29×10^{-7}	6.29×10^{-7}	3.15×10^{-7}	3.15×10^{-7}	3.15×10^{-7}	1.57×10^{-7}	1.57×10^{-7}
$\partial n_{\text{eff}}/\partial n_{\text{buff}}$	0.2	0.1	0.1	0.06067	0.06067	0.06067	0.06067	0.06067	0.06067	0.06067
Δn_{buff}	1.90×10^{-6}	2.70×10^{-5}	2.70×10^{-5}	3.86×10^{-8}	3.86×10^{-8}	1.93×10^{-8}	1.93×10^{-8}	1.93×10^{-8}	9.64×10^{-9}	9.64×10^{-9}
$(\partial n_{\text{eff}}/\partial n_{\text{buff}})/\Delta n_{\text{buff}}$	3.80×10^{-7}	2.70×10^{-6}	2.70×10^{-6}	2.34×10^{-9}	2.34×10^{-9}	1.17×10^{-9}	1.17×10^{-9}	1.17×10^{-9}	5.85×10^{-10}	5.85×10^{-10}
$\sigma_{n_{\text{eff}}}$	2.15×10^{-6}	9.05×10^{-6}	9.05×10^{-6}	1.21×10^{-4}	1.56×10^{-5}	8.29×10^{-6}	5.20×10^{-6}	2.93×10^{-6}	5.01×10^{-6}	3.83×10^{-6}
$L_0, \mu\text{m}$	10000	1000	1000	16000	16000	8000	8000	8000	4000	4000
$\Delta L, \mu\text{m}$	125	42	42	126	126	126	126	126	126	126
M	65	131	131	87	87	87	87	87	87	87
$\sigma_{n_{\text{eff}}} \times L_0, \mu\text{m}$	0.02148	0.00904	0.00904	1.93776	0.24947	0.06632	0.04156	0.02346	0.02005	0.01533
$\sigma_{n_{\text{eff}}} \times L(M-1), \mu\text{m}$	0.03866	0.05843	0.05843	3.25011	0.41843	0.15616	0.09785	0.05523	0.07438	0.05688
n_{eff}	1.5	1.45070015	1.45070015	1.45344678	1.45344678	1.45344678	1.45344678	1.45344678	1.45344678	1.45344678
$\sigma_{\text{ph}}, \mu\text{m}$	0.025	0.025	0.05	0.3	0.3	0.025	0.025	0.025	0.025	0.025
$n_{\text{eff}} \times \sigma_{\text{ph}}$	0.0375	0.0363	0.0725	0.4360	0.4360	0.0363	0.0363	0.0363	0.0363	0.0363
σ_0	0.175	0.150	0.294	8.030	2.031	0.306	0.223	0.175	0.168	0.159
$\Delta \sigma$	0.0431	0.1263	0.0806	5.228	0.412	0.342	0.199	0.092	0.167	0.113
n	0.55	1.60	1.03	66.6	5.25	4.36	2.53	1.18	2.12	1.44
μ, dB	-22.0	-29.0	-23.0	> -6	> -6	-17.3	-23.0	-27.0	-25.2	-27.2
SI, dB	-27.0	-33.5	-28.0	> -9	> -9	-23.3	-27.4	-32.0	-29.7	-32.0

Figure 5-14. The variation of the n_{eff} of a $4 \times 4 \mu\text{m}$ $\text{GeO}_2:\text{SiO}_2$ channel waveguide with a number relevant parameters: height (h), width (w), refractive index of the core (n_{core}), RI of the cladding (n_{clad}) and RI of the buffer or undercladding (n_{buff}). All n_{eff} values were calculated by BPM simulations at a wavelength of $1.55413 \mu\text{m}$.

Kamalakis *et al.* [74] have developed useful empirical relationships from a statistical study of numerical results for the mean value of maximum sidelobe level, μ_T and the standard deviation, s_T as functions of σ_0 , $\Delta\sigma$ and M . The AWG studied in the work is very similar to the design used in this work, namely, a 16×16 AWG with channel spacing of 100 GHz, an Δn of 0.75% and waveguide dimensions of $6 \times 6 \mu\text{m}$ (more details are shown in the first column of Table 5-3). The estimation of μ_T and s_T of AWG crosstalk is expressed in decibels as,

$$\mu_T(M, \sigma_0, \Delta\sigma) \cong \mu_0(M) + \mu_1(\sigma_0, \Delta\sigma) \quad (5.7)$$

and

$$s_T(M, \sigma_0, \Delta\sigma) \cong s_0(M) + s_1(\sigma_0, \Delta\sigma) \quad (5.8)$$

Following these relationships, Eqs. (5.5) and (5.6), the performance of the above AWG design fabricated using films with attributes from Section 4.3.6 can be quantitatively estimated. The working table is shown in Table 5-3. The first three columns show the cases taken from refs. [74, 76]. The results agree with those from the references, albeit a number of assumptions for some values (viz. italic values in Table 5-3). The rest are cases pertaining to this work and can be identified in Table 5-4. A remark about the sensitivity of μ_T and s_T to M is insightful. While an

increase in M lowers the values of μ_0 , but an subsequent increase in $\Delta\sigma$ is more dominant in effecting an increase in μ_T (see graphical illustrations in ref. [74]). Thus, as mentioned above, to serve practical considerations, using the maximum M that would minimize coupling loss at the FPR is undesirable.

Table 5-4. Summary of details for test cases in Table 5-3.

Test Cases	μ_T , (dB)	Details
A	> -6	Worse case in Δh ; photomask resolution is appropriate to one that is used in this work (i.e. $\sigma_{ph} = 0.3 \mu m$).
B	> -6	Best case in Δh ; $\sigma_{ph} = 0.3 \mu m$; other wise same as A.
C	-17.3	Reduced device size by half (i.e. L_0 is half of that in Case B); $\sigma_{ph} = 25 \text{ nm}$; otherwise same as B
D	-23.0	Assuming that Δh can be reduced by half by reducing the necessary iterative deposition cycles by half; otherwise same as C.
E	-27.0	Assuming that by reducing the RI contrast, Δn , between the core and cladding, $\partial n_{eff}/\partial H$ is reduced by half.
F	-25.2	Same as D; L_0 is half of that in Case D.
G	-27.2	Same as E; L_0 is half of that in Case E.

From Table 5-4, the thickness uniformity across the PHASAR (ΔH) is increased by almost 8 folds in Test Case B, but the crosstalk remains below any useable range. This increase in DH is practically done by choosing area on the wafer that is most uniform (see Figure 4-37 and 4-40). In both Case A and B, the large device size ($L_0 \approx 16,000 \mu m$) and the very restrictive photomask resolution of $0.3 \mu m$ limits the proper operation of the AWG, or possibly energy has been spilled across the spectrum in a way that intensity at any frequency could be difficult to detect (c.f. §5.4). By reducing the critical size (area occupied by the PHASAR) by half and using advanced photomask with resolution of 25 nm , the average crosstalk seems marginal (Case C). In the considerations for Case D and subsequent cases, a linear scaling with the L_0 has been assumed for Δh , Δn_{core} , Δn_{clad} and Δn_{buff} . The crosstalk performance

can be further improved to ~ -27.0 dB (Case D) if Δn is reduced from 1.37% to less than 0.80%. As a result of a lowered Δn , the $\partial n_{\text{eff}}/\partial n_{\text{core}}$ would be reduced if the lateral dimensions of the waveguide do not increase by much. However, this effect is not accounted in the above calculations. Further reduction in the size of the PHASAR (i.e. L_0) can only provide little improvement in the crosstalk characteristics (cf. Case E and F) while the device may begin to suffer from significantly increased bend loss in the AWs. Alternatively, if further reduction of L_0 is desired, a reflective type AWG can be considered [57].

Certainly, if the cost allows, a state-of-the-art photomask at a resolution < 15 nm can be used to reduce crosstalk by about -3 dB for the Case E but the effect almost diminishes for Case C (data not shown).

5.6. Chapter summary

By a simple step of spin-coating thin-films of sol-gel derived $\text{GeO}_2\text{:SiO}_2$ synthesized on III-V quantum well laser structures, the bandgap energy of quantum-well structures has been shown, in this work, to be tuned by simply varying the composition of the encapsulant films through the QWL. The porosity of the encapsulant film was found to have only minimal effect on the shift of the bandgap. However, the bandgap shift that was found to be positively changing with GeO_2 content was attributed dominantly to the effect of increasing thermal expansion of $\text{GeO}_2\text{:SiO}_2$ films of higher GeO_2 content. This finding enables a selection of possible fabrication processes that can implement spatially-selective quantum-well intermixing on a single wafer. The use of sol-gel encapsulant layer potentially leads to a low-cost alternative for quantum-well intermixing of III-IV photonics that is amenable to low-temperature processing.

A simple AWG design was used to evaluate the capability of the sol-gel synthesis process developed in Chapter 3 and 4 for applications in integrated optics. The structural parameters were established based on some simple but general criteria aimed to demonstrate the quality of optical films shown in Chapter 4. The operation of preliminary devices was likely inhibited by a combination of factors: particle-inclusions of early sol-gel-synthesized $\text{GeO}_2\text{:SiO}_2$ films, poor etch results and fabrication intolerances of the initial design and process. Using a theory-based

inclusions of early sol-gel-synthesized $\text{GeO}_2\text{:SiO}_2$ films, poor etch results and fabrication intolerances of the initial design and process. Using a theory-based estimation, AWGs fabricated with the mSC-RTA deposition process, lithography tool and AWG design, AWGs are expected to be non-usable due to an inhibitive crosstalk level of > -6 dB. However, with a quantitative analysis provided in this chapter, a number of feasible recommendations are suggested to elevate an AWG to a versatile level of crosstalk of < -23 dB: reduction in AWG size (i.e. L_0), advanced photomask (resolution < 25 nm), improvement of current best thickness uniformity by half of its current level. A crosstalk of < -27 dB can be expected if, in addition, a reduction in the refractive index contrast (Δn) of the waveguide can be implemented. Accounting for propagation loss of < 0.6 dB/cm, an insertion loss of the AWG can be expected to be < 8 dB.

5.7. References

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Chapter 6 Conclusions and future work

In order to meet the economical requirements of the continual proliferation of photonic technologies, the exploration of low-cost fabrication techniques is paramount. This work has addressed the scientific and engineering aspects using the sol-gel—spin coating process for producing components used in photonic applications. Work undertaken in this project has resulted in the noteworthy demonstration of inorganic $\text{GeO}_2\text{:SiO}_2$ amorphous planar waveguides on 4"-silicon wafers by the alkoxide-route sol-gel—spin coating deposition process. These waveguides exhibit the following attributes that are rarely reported in the literature:

- ☐ low optical propagation loss—less than 0.6 dB/cm at 1550 nm (estimated by prism-coupler),
- ☐ low particle-inclusion— < 0.3 scattering centre/cm (inspected by eye and by prism-coupler),
- ☐ narrow edge exclusion—5 mm, and can be improved with automated tools,
- ☐ undetectable surface striations—less than 1 nm (measured by profilometry on 4- μm -thick film across 4" wafer),
- ☐ high uniformity—better than 3% across the entire 4" wafer; single layer on 6" wafer exhibit uniformity better than 1%,
- ☐ good uniformity in refractive index—the standard deviation of as much as six points measured across the wafer by prism-coupler is better than the full swing sensitivity of the prism-coupler measurements of 0.0008, translating to a uniformity of 0.060%, and
- ☐ thickness of $\sim 4 \mu\text{m}$ is achievable with only 10 repetitions of SC-RTA.

The fabrication process developed in this work has been shown to be repeatable and preliminary experiments showed the process can be scalable up to 6" wafers. The films, both single-layer and multi-layer, are free of cracks as seen under optical microscopes and are free of chuck marks and any skin rupture by visual inspection. With further improvements and studies as proposed in this chapter, the sol-gel—spin coating deposition is expected to have an impact in the fabrication of low-cost photonic components and in large-area optical integration. In addition, the shift of the bandgap energy of quantum-well structures via quantum-well intermixing has been shown to be adjustable by tailoring the composition of the porous $\text{GeO}_2\text{:SiO}_2$ sol-gel-derived films. The increase in thermal expansion of the film with higher GeO_2

content is likely the dominant factor that affords higher degree of quantum-well intermixing.

This work first evaluated the material properties of the films made from the sol-gel—spin coating process in a routine fashion for a single-layered film (see Chapter 3). After the necessary conditions were established for synthesizing a film of optical quality, the issues of the defects of the spin coated films were examined and improvements upon the generic process [1-6] were eventually found to yield high quality, purely inorganic $\text{GeO}_2\text{:SiO}_2$ films on 4" Si wafers. These results were presented in Chapter 4. The fabrication capability (i.e. uniformity of film thickness and RI) was then used to evaluate the performance of a simple AWG design (Chapter 5).

6.1. Summary of contributions

In Chapter 3, a comprehensive investigation was performed to probe the material properties of the thin films of sol-gel derived $(x)\text{GeO}_2\text{:}(1-x)\text{SiO}_2$ ($x \leq 0.400$) under the different thermal treatment conditions. Characterization equipment including infrared spectroscopy, ellipsometry, Raman spectroscopy and X-ray diffractometry revealed that the thermal treatment of temperature 800°C or above (with decreasing value of x) yielded films with desirable optical properties for passive optical waveguide applications. Besides useful data of film properties was obtained for a range of temperature, composition and wavelength, the limitations of the various characterization equipment used in this study were established experimentally.

A summary of the contributions presented in Chapter 3 is outlined as follows:

- A suitable sol preparation procedure has been devised to obtain stable sols at $x \sim 0.400$. The procedure developed here makes use of TPOG as a Ge alkoxide precursor and employed optimization of existing two-step sequential mixing methodology. Comparing the intensity of the infrared absorption peaks with bond distribution as simulated by Monte Carlo, the solution process used in this work yielded random mixture of $\text{GeO}_2\text{:SiO}_2$. This study will be included in a manuscript,
- Useful spectral characteristics and optical constants from a broad spectral range of 9 eV down to 0.5 eV have been deduced, to the best of the knowledge of the author, for the first time, with the range of compositions studied with rigorous experimental justifications. By linear interpolation on the Sellmeier-based dispersion relations, the RI of the spin coated $\text{GeO}_2\text{:SiO}_2$ films at any given wavelength (210 – 1700 nm) and GeO_2

content ($0 \leq x \leq 0.4$) can be predicted. Other material dispersion parameters were derived and shown in ref. [7],

- The resolution of OH concentration in dielectric films as detected by the Fourier transform IR technique, in transmission under normal incidence, was estimated at $\sim 1 \times 10^{21} \text{ cm}^{-3}$, and
- UV-Raman spectroscopy, being the more sensitive alternative to detect the nanophase crystalline GeO_2 compared to XRD and visible Raman, showed that the resolvable crystal size limit is $< 25.1 \text{ nm}$ (c.f. Appendix E). This study will be submitted for publication.

Chapter 4 presented studies related to the fabrication of thick films (i.e. $4 \mu\text{m}$ or greater) that are required as the core layers of planar optical devices. Leveraging on the low-cost aspects of the sol-gel technique, the mSC-RTA process was adopted, as previously demonstrated by Syms *et al* [1]. Using the equipment available in the laboratory, many of the common defects related to spin coating were observed, namely, cracks, particle inclusions, chuck mark, striations, thickness non-uniformity and skin rupture. Despite of the plentiful existing literature on these topics, the understanding of each of the defect generation mechanism is far from complete, especially for the synthesis of sol-gel-derived films. An effort to advance the understanding has been provided here by a critical analysis of a comprehensive collection of the available experimental and theoretical treatments and subsequently using them to develop the enhanced sol-gel—spin coating process in this work.

The fabricated films were deposited on a 10-micron SiO_2 buffered Si wafer in a planar waveguide structure. Both optical and physical characterization was extensively performed on the films. The uniformity of the refractive indices, birefringence and manufacturability issues were discussed (§4.3). The major achievements presented in Chapter 4 are outlined below:

- A unified thermo-stress evolution is described. Organically modified silane was used to increase the compliance of the gel structure, leading to an increase in critical crack thickness. After rapid thermal annealing, a single-layer thickness of $\leq 0.45 \mu\text{m}$ was achieved without cracks. An alternative method is proposed to identify the zero-stress point by correlation with available data of the glass transition point of bulk glasses from the literature. This information was to successfully fabricate crack-free thick-film ($\sim 4 \mu\text{m}$) by multiple-deposition spin coating on 4" Si substrates. A manuscript will be submitted for publication based on this study;

- Particle-inclusions has been reduced significantly by a simple solvent technique; edge-beading is concurrently eliminated;
- A striation suppression process has been developed without compromising the single-layer thickness of the film. This process employs butanol as a replacement co-solvent. By modification of the Birnie's plot, a more robust co-solvent selection strategy has been developed. A manuscript is in preparation for this study [8];
- Radially thickness non-uniformity observed using the in-house spin coater was eliminated. An hypothesis was proposed to explain the efficacy of lidless spinning. This result will be submitted for publication; and
- By using a simple optimization scheme, with the necessary construction and modification of the spin coating equipment and the necessary improvements to the mSC-RTA process, thick films of 4-microns were synthesized in only 10 repetitions. The improved mSC-RTA process described in this chapter is capable of synthesizing purely inorganic films from the alkoxide sol-gel route with much less iterative cycles, improved film uniformity and better optical film quality (i.e. reduction of inclusions) than reported in the literature. A manuscript is in preparation to disseminate this work.

In Chapter 5, the sol-gel derived $\text{GeO}_2\text{:SiO}_2$ films were put to use in two applications in communications, namely, wavelength tuning of quantum-well laser structures and filtering by using arrayed-waveguide gratings. The major contributions made by the author are listed as follows:

- demonstration of the ability to control the porosity of the $\text{GeO}_2\text{:SiO}_2$ sol-gel films developed in this work by a simple porosity—composition—annealing temperature relationship [9],
- demonstration of the bandgap engineering of quantum-well structures by varying the composition of the sol-gel dielectric encapsulant layer. The results on InP quantum-well (QW) structures were published in ref [10] while results on GaAs structures has been submitted [11], and
- evaluation of the fabrication capability of the sol-gel synthesized films in terms the performance of a 16×16 -channel arrayed waveguide grating (AWG) device based on buried sol-gel derived waveguide channels. With some adjustments in design parameters and process tool, a crosstalk performance of < -23 dB can be expected. These adjustments include a reduction in AWG size (i.e. L_0), advanced photomask (resolution < 25 nm), improvement of current best thickness uniformity by half of its current level. The crosstalk can be expected to improve to < -27 dB, if in addition, a reduction in the refractive index contrast (Δn) of the waveguide can be implemented. Accounting for propagation loss of < 0.6 dB/cm, an insertion loss of the AWG can be expected to be < 8 dB.

6.2. Recommendations and future works

A comprehensive and from-ground-up approach has been taken for the development of the sol-gel spin-coating process of $\text{GeO}_2\text{:SiO}_2$ films for photonics applications in this work. Hence, the recommendations covering a number of scientific and engineering disciplines are proposed as follows in the three categories: characterization and instrumentation, experimental investigations and theoretical analysis, and device fabrication.

Throughout Chapter 3, commercial characterization equipment was used to qualify the sol-gel derived thin films. However, in many instances, the careful analysis of the measurement data revealed some practical limitations of the equipment. In the section of characterization and instrumentation, techniques that provide improvements in resolution of thin-film measurements are suggested for the benefits of future works related to the scope of this project.

Modifications to fabrication equipment are proposed for further improvement in the quality of film deposited by spin-coating. In the section of experimental investigations, additional experiments are suggested for the continual advancement in the understanding of spin-coating defects. Additional studies are suggested to elucidate the interplay between capping film properties (such as porosity and expansion coefficient) and the efficacy of quantum-well intermixing. The recommended fabrication requirements for arrayed waveguide gratings are again summarized.

Lastly, in theoretical analysis, a two-dimensional sellmeier parameterization of the material dispersion curves can be very useful in optical film design, proposed studies in instability criteria in the hydrodynamical behaviour of spin-coating deposition and cracking behaviour of evolving porous films are outlined.

6.2.1. Characterization and instrumentation

6.2.1.1. Thin-film characterization

The absorption loss in a waveguide due to OH groups is often measured after the fabrication of the waveguide by using an optical spectrum analyzer. One advantage

of the waveguide configuration is that the interaction length (i.e. the length over which the absorption of light in the material take place) can be in the range of centimetres to metres. However, if the sensitivity of thin film characterization techniques is adequately high, then feedback to the fabrication process of the film, to a certain extend, can be performed simply with the film before the waveguide fabrication. Fourier-transform IR spectroscopy (FTIR) is often used to obtain information about the quality of dielectric films. Specifically, in some cases, FTIR is commonly used in studies of dielectric films for applications in optics or microelectronics [12-14]. However, for the characterization of thin films (i.e. thickness $< 1\ \mu\text{m}$), care should be taken in the resolution limit of the concentration of the certain molecular constituents (e.g. OH) whose absorptivity is not high. As shown in Chapter 3 (§3.5.2, §3.5.3 and §3.5.7), the IR absorption spectra at normal incidence has been shown to be less effective than spectroscopic ellipsometry in the UV—visible—near infrared wavelengths when probing the concentration of OH in thin films. The absorbance of IR active species is dependent both on the concentration of the molecular species and the interaction length of the film (see Eqn 3.7). Hence, for a given resolution limit in absorbance, the limit in concentration can be improved by increasing the interaction length. The obvious solution is to increase the thickness of the film, which is limited by the critical cracking thickness (cf. Chapter 4). Alternatively, a multiple deposition process similar to the one described by Figure 4-1 (cf. §4.1) can be performed to increase the thickness of the sol-gel-derived film. In such case, to avoid grading in any properties throughout the depth of the multi-layer, sol-gel chemistry, spin-coating conditions and thermal treatment have to be well controlled in a consistent manner for layers deposited by each cycle. Such requirements are difficult to realize in a typical laboratory setting.

In addition, the substrates that are most commonly used are lightly doped semiconductors. They typically exhibit high values of refractive index. Therefore, thin-film interference occurs, casting an overlapping undulation in the spectra that renders semi-quantitative analysis difficult and inaccurate. An example of a SiO_2 film with the various thickness values on a Si substrate is simulated as shown in Figure 6-1. The complex refractive index of SiO_2 was obtained from ref. [15] and the simulation (spectra iii and iv) was performed by the WVASE32 software. The measured spectra of a thermal SiO_2 and 5 mol% GeO_2 annealed at 500°C , spectra i and ii, respectively,

are provided for comparison. The band produced by some interference can sometimes be of comparable width with the composite OH bands. Hence, resolving the concentration of OH species in the film can be very restricted.

Figure 6-1. a) FTIR spectra of SiO_2 films of various thickness values; b) an enlarged section of the spectra around the OH composite absorption band (2600 – 3800 cm^{-1}).

Alternatively, for thin films, increasing the interaction length by an oblique incidence can be readily performed. In some cases, LO modes of certain IR active species appear to be more well-defined [13, 14]. To further increase sensitivity, ellipsometry¹ performed with an IR source can be used to replace the typical photospectrometry. IR ellipsometry has been experimentally shown to be more sensitive than FTIR in the determination of OH content in dielectric films [16]. By a rough calculation, the above can be understood. As mentioned in Appendix G, the typical resolution of ellipsometers in the extinction coefficient (κ) is ~ 0.001 [17] which translates to an absorptivity of $\sim 43.98 \text{ cm}^{-1}$ at a wavenumber of 3500 cm^{-1} . The detection limit of the FTIR in normal incidence for thin films as estimated in §3.5.2, is $\sim 1 \times 10^{21} \text{ OH molecule/cm}^{-3}$. This value is translated to absorptivity by

¹ Advantages of ellipsometry over photospectrometry have been briefly summarized in §3.5.7.

using Eqns. (3-7) and (3-9) and $\epsilon_l = 64 \text{ L}_{\text{glass}}/\text{mol}\cdot\text{cm}$ [18] to be $\sim 1 \times 10^2 \text{ cm}^{-1}$. The FTIR characterization technique used in this work is clearly inferior to the capability of an ellipsometer as stated above. Another technique is known as attenuated total reflectance (ATR) which makes use of evanescence wave at an extended prism-film interface. In this case, the interaction length (i.e. the length of the prism) can be increased to centimeters.

6.2.1.2. Spin-coating equipment

As concluded from Chapter 4, the quality of films deposited by spin coating depends critically on the spin coating equipment. Repeatability, reproducibility and thickness control require a tight control in spin mechanics and internal environment. The process of spin coating is not novel and has been practiced in the microelectronics industry for decades. However, the deployment of spin coating has only been restricted to secondary functions in processes such as lithography patterning. Although spin-on glasses or polymers are available as alternatives to interlayer dielectrics realized by conventional dry deposition methods, there has been no wide adoption of the spin-on products in the industries. As dimensions of electronic or photonic devices (e.g. photonic crystal and plasmonic devices) continue to shrink, there will be more stringent requirements even for lithographic functions (e.g. ref. [19, 20]). Hence, further research and development to enhance the spin coating process will benefit this low-cost fabrication technology and promote wider deployment across the different industries. The spin coating technique will also benefit applications where the performance of photonic components made by hybrid sol-gel are sufficient.

Most commercial spin-coating equipment attempt² to provide more flexibility by incorporating exhaust control, solvent-saturated enclosure and other automation functions. However, future developments will require advances in the knowledge of the spin-coating process.

Only a window of exhaust flow rate may prevent any re-circulation of air current which ultimately leads to particle-inclusions [22, 23]. Deviation from a laminar airflow atop of the film boundary layer leads to radially-dependent thickness. One good example is the turbulent flow at the wafer edge results in increased flow

² For list of manufacturers of spin coaters, see ref. [21].

and subsequently the common film defect of the edge bead. As powerful computers are readily available, the exhaust rate and bow design can be optimized to ensure laminar-flow and turbulent-free current during spinning. Knowledge of how the rate of evaporation will excite hydrodynamic instability during spinning may contribute to flexibility of the equipment.

The encouraging results from Chapter 4 show that, with further understanding of the spin-coating process, simple solutions can be devised to improve the film quality that is paramount to advanced photonic applications. Certainly, more work is required for the process to be competitive. Some suggestions are given in the following section.

6.2.2. Experimental investigations and theoretical analysis

The discussion on defects of films formed by spin coating according to the scheme described in Chapters 3 and 4 also benefits other alternative chemical solution techniques (such as organic-inorganic hybrid films and colloidal solutions as mentioned in Chapter 4). For any film forming techniques that require multiple spinning cycles as in this case. Therefore, further understanding of film defects from spin coating is worthy of consideration.

Cracking, typically occurs as a result of the tensile stress cumulated on the film during the thermal treatment, yielded in dense films. In this work, cracking was found to occur during the low temperature regime when evaporation of solvents took place. By adding ORMOSIL to the inorganic sol recipe, as presented in §4.3.1.4, the xerogel structure becomes more compliant; hence, the critical thickness was improved to 0.45 μm per layer. In fact, a further improvement to $\sim 0.8 \mu\text{m}$ has been shown possible after annealing treatment of 800°C [24, 25] Although not an order-of-magnitude improvement, such capability, when achieved or exceeded, is expected to yield a substantial increase in performance due to reduction in deposition iteration. In Chapter 4, only optical loss pertaining to a composition of 60 mol% MtES and 40 mol% of alkoxides was measured. Based on the experience of the author, for a film made with EtES instead of MtES, a remarkable increase in scattering was noted in a loss scan on the prism-coupler. Therefore, further study of the effect of ORMOSIL to the optical performance of films after densification will be beneficial.

In general, the volume shrinkage is inevitably unavoidable; yet, a number of methods can be explored to reduce the amount of shrinkage. First, some knowledge of which thermo-stress stage cracking ensues (the approximate temperature regime where cracking occurs for a given thickness evolution, c.f. §4.3.1.2) is helpful in devising or selecting a solution. For instance, cracking at low temperatures tend to be caused by the capillary pressure during the evaporation of solvent(s). The capillary pressure depends on the parameters shown in Eqn. 4.10,

$$P_{cap}^{max} = \frac{2\gamma_{LV} \cos(\varphi)}{r_p}, \quad (6.1)$$

which can be reduced by performing the following:

- solvent(s) of low surface tension (thus low γ_{LV}) can be selected (e.g. [26]),
- sols can be tailored to yield gel with larger pore size (r_p), for example, adjusting the pH [27] and using ORMOSIL doping [28],
- xerogel network can be strengthened by an immersion in a basic medium or just water [29-31] and
- postponing or reducing evaporation of solvents [32, 33].

At the intermediate temperature regime, organic constituents are decomposed; condensation and structural relaxation become effective, tensile stress increases dramatically while thickness experiences a large shrinkage causing a substantial reduction in the release rate of the critical elastic strain, films become more susceptible to cracking. At even higher temperatures, viscous flow takes place while the accumulating stress is relieved. The viscous sintering is described as [34],

$$\frac{\gamma_{SV} n^{1/3} t}{\eta} = f(\rho) - f(\rho_0) \sim \Delta H, \quad (6.2)$$

where γ_{SV} and η refer to surface energy of the glass composition and viscosity at the annealing temperature, $f(\rho)$ is a function of the relative density of the xerogel film to its skeletal density, t is annealing time, $n^{1/3} \propto 1/d_{pore}$ and d_{pore} is the dimension of a cavity. The change of density can be related to the shrinkage of film after heat treatment (i.e. ΔH). The following can be considered to reduce the chances of film failure:

- colloidal solutions can be used to reduce shrinkage [35],

- proper tailoring of the porosity (see Eqn. (6.2)) to control the amount of shrinkage [34] while stress relief is afforded by viscous flow and
- the glass composition can be modified to obtain a lower glass transition so that stress relaxation occurs at a lower temperature (i.e. lower viscosity, η , at lower temperature) [1, 9].

However, if the theoretical performance can be compromised for manufacturability and practical performance³ then hybrid sol-gel composites (such as the HYBRIMER and others [36, 37]) is an attractive alternative where the processing temperature is kept low.

To facilitate the implementation of the above techniques, theoretical models and simulations such as those reported in ref. [38] can be used for optimization. Improved models can be validated by performing improved stress analysis (i.e. using thin substrates and carrying out corrections to the Stoney's equation [39-41]). Once accurate models are developed, parameters that characterize the above methods can be used to optimize the process temperature and the critical thickness of the film. Therefore, further work in improving the mechanical dynamic models would prove to be useful in process design and optimization. Paving the way forward, if a combination of large-scale molecular and fluid dynamic simulations can be used to derive mechanical properties of as-deposited gel film and improved mechanical dynamic models during densification treatment, critical crack thickness can be predicted for various precursors, sol compositions and sol-gel routes.

Another defect, as studied in the current work, is the surface striations. This phenomenon not only plagues the conventional sol-gel solutions, but also conceivably affects other type of sol-gel coatings such as the hybrid sol-gel solutions (as experienced by the author), polymers and colloidal solutions [42] which are useful in reducing film shrinkage. By extending experimental observations⁴ of the author, the occurrence of the so-called 'orange peel' defect [43-45] may have similar origin as the surface striations observed in this work, but for the special case where the viscosity is high. The universality of the problem is evident. Yet, the understanding of the effect from the published literature is rather incomplete. What is known at the

³ The distinction between theoretical and practical performance refer to the intrinsic material loss and the combination of material loss and loss due to fabrication defects and tolerance respectively.

⁴ In cases where there was a significant ORMOSIL content in the sol, an Benard cell pattern extends across almost the entire dimension of the sample with striations barely visible on a small area at the peripheral. Such a pattern is very similar to patterns that are known as 'orange peel' in the literature.

moment is that surface striation is a result of hydrodynamic instability. A theoretical treatment of all known hydrodynamic forces (as discussed in section 4.3.3.1) can be used to gain information about the critical conditions beyond which striations ensue.

In Section 4.3.3.3, a modification to Birnie's plot has been proposed. Although Birnie had originally suggested that co-solvents that are higher in surface tension and lower in volatility are undesirable, results of the current work and those of Kozuka [46] suggested that surface tension is indeed a stabilizing force. Also, viscosity is a stabilizing force as observed by Kozuka [46] and Rehg [47]. As indicated before, the boundaries of the regions of stability as shown on the modified Birnie's plot (Fig. 4.25) are only schematic and approximate in nature. Further experiments can be designed to validate the dependence of surface tension and viscosity by selecting solvents that vary in only one of the above properties. In order to establish more definite critical boundaries for co-solvent or principal solvent selection, a full hydrodynamic analysis is necessary by incorporating, but may not be limited to: Marangoni forces, differential evaporation, surface tension (capillary force) and viscosity.

In this work, the thickness non-uniformity observed was due to the non-uniform evaporation rate. As an alternative to the experimental approach taken in this work, this problem may be understood and mitigated by computational fluid dynamic simulations (e.g., see ref. [22, 48]). Thickness non-uniformity is also known to be caused by non-Newtonian fluid properties (i.e. non-linear shear dependence of the viscosity) of the sols when they are approaching the gel time. Most models show a some degree of discrepancy with the experimental thickness profile [49, 50]. This discrepancy is likely due to the assumptions made such as laminar flow and uniform rate of evaporation. Although an empirical criterion has been established (i.e. $t < 0.5 \times T_{gel}$) by using the change in viscosity characteristics as a reference point [49], an improved model (i.e. accounting for the non-ideal air-flow pattern atop of the substrate) will advance the understanding of how ageing affects the uniformity so as to establish more optimized criterion.

Viscous flow, as mentioned above, is one way to relieve stress at high temperature. Experimental studies can be performed to characterize the way in which glass composition and porosity affect viscous flow in xerogel films. Quantities such

as pore size and compositional-dependent activation energy are useful for materials selection.

6.2.3. Device fabrication

The work involving sol-gel dielectric cap on quantum-well laser structures for the quantum well intermixing has revealed implications on the possible fabrication strategies of multiple-well integration. Understanding that stress, rather than porosity, has a dominant affect in the quantum-well intermixing (QWI) in the scheme explored in Section 5.2, some inferences can be made about the selection of a suitable process that takes advantage of the QWI control using the $\text{GeO}_2\text{:SiO}_2$ sol-gel caps in implementing spatially-selective QWI on semiconductor platforms. One possible way to achieve spatially-selective QWI is to deposit layers of sol-gel films, varying in compositions, and a subsequent patterning using lithography after each layer. However, in this case, there will be areas that require QWI covered by multiple layers of sol-gel of varying compositions. This accumulation of layers leads to difficulties in controlling the QWI. Pepin *et al.* [51] and Deenapanray *et al.* [52] have shown that by depositing a Si_3N_4 layer atop of the patterned or non-patterned encapsulant SiO_2 layer, QWI was univocally suppressed while a single layer SiO_2 typically enhances QWI. This unexpected observation was attributed to the fact that the near-surface stress distribution in the semiconductor was drastically modified (i.e. reversed). Therefore, the QWI performance of spatially-selected areas, below any multiple-layer of varying the composition of $\text{GeO}_2\text{:SiO}_2$ sol-gel films, is likely to deviate from results found in the present work. On the contrary, if the cap porosity was the more dominant factor in the QWI process, then the above stress-induced QWI deviation is unlikely to occur. As a foresight, there are a number of low-cost processes that are well-suited to implement the above QWI scheme. Such process as printing, involving the simultaneous deposition of multiple solutions, may open up new opportunities for low-cost photonic integration.

Alternatively, porosity-dominated QWI could make spatially-selective QWI possible with the above generic scheme of performing spin coating and lithography. Porosity of the $\text{GeO}_2\text{:SiO}_2$ sol-gel-derived films can be explored by adjusting pH [27] for one $\text{GeO}_2\text{:SiO}_2$ composition or multiple compositions.

The performance of AWG will undoubtedly benefit from the continual improvement of the quality of the glass film. For the current process, the resolution of the mask is a dominant factor in causing performance deterioration in a real device (i.e. crosstalk and insertion loss). In order to fabricate a practical device, the following enhancements are recommended:

- increase thickness of each crack-free layer and use reflow to reduce the thickness non-uniformity [53, 54],
- advanced photomask having resolution of < 15 nm, and
- The total phase error can be further reduced if the refractive index contrast (Δn) of the waveguides is lowered leading to a reduction in the variation of the modal effective index of the waveguide with the height, width and refractive index of the core, respectively, $\partial n_{eff}/\partial h$, $\partial n_{eff}/\partial w$ and $\partial n_{eff}/\partial n_{core}$ (see §5.6).

6.3. References

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APPENDICES

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Appendix B Chemicals and materials

A list of all chemicals used in the sol-gel process is tabulated in this appendix. For the fabrication of planar waveguides and AWGs, the core layers were synthesized using chemical of the highest purity as shown in the following table. Note that water content may vary from supplier to supplier. Solvents of anhydrous quality are most preferred to enhance controllability and repeatability in experiments. The deionized water used in the sol-gel reaction and cleaning was provided by a Millipore Milli-Q Element system (resistivity at 18 MΩ·cm).

Table B-1. List of essential chemicals used in this work.

Chemical (Purity)*	Supplier	Water content	Particulars
Tetraethoxysilane, Si(OC ₂ H ₅) ₄ (≥ 98%)	Aldrich	--	Sol-gel precursor
Tetraethoxysilane, Si(OC ₂ H ₅) ₄ (≥ 99.999%)	Aldrich	--	Sol-gel precursor
333 Trifluoropropyl trimethoxysilane, SiCF ₃ C ₂ H ₄ (OCH ₃) ₃ (98.6%)	FlouroChem	--	Sol-gel precursor
Germanium isopropoxide, Ge(OC ₃ H ₇) ₄ (≥ 97%)	Aldrich	--	Sol-gel precursor
Germanium isopropoxide, Ge(OC ₃ H ₇) ₄ (≥ 99.99%)	Chemat Technology Inc.	--	Sol-gel precursor
Hydrochloric acid, HCl (37%)	Ashland Chemicals	63 %	Sol-gel catalyst
Acetyl acetone, CH ₃ COCH ₂ COCH ₃ (≥ 99%)	Merck	< 0.1 %	Chelating agent
Methoxyethanol, CH ₃ OC ₂ H ₄ OH (≥ 99.8%)	Aldrich	< 0.005 %	Solvent/co-solvent
Acetone, C ₃ H ₆ O (≥ 99.999%),	BestChem	< 0.1 %	Solvent/co-solvent
Ethanol, C ₂ H ₅ OH (≥ 95%)	BestChem	< 0.1 %	Solvent
Ethanol, C ₂ H ₅ OH (≥ 99.9%)	BestChem	< 0.1 %	Solvent
Isopropanol, C ₃ H ₇ OH (≥ 99.5%)	BestChem	< 0.2 %	Solvent/co-solvent

Chemical (Purity)*	Supplier	Water content	Particulars
Isopropanol, C ₃ H ₇ OH (≥ 99.5%), anhydrous	Aldrich	< 0.003 %	Solvent/co-solvent
Isobutanol, C ₄ H ₉ OH (≥ 99%)	Allied Signal	< 0.1 %	Solvent/co-solvent
1-butanol, C ₄ H ₉ OH (≥ 99%)	Aldrich	< 0.1 %	Solvent/co-solvent
1,3 propanediol, HOC ₃ H ₆ OH (≥ 98%)	Alfa Aesar	< 0.1 %	Solvent/co-solvent
Dibutyl ether, C ₄ H ₉ OC ₄ H ₉ (≥ 99.9%), anhydrous	Aldrich	< 0.003 %	Solvent/co-solvent
n-butyl acrylate, CH ₂ =CHCOOC ₄ H ₉ , (≥ 99.3%)	Fluka	< 0.1 %	Solvent/co-solvent
Chromium, Cr (≥ 99.999%)	Pure Tech	--	Metal film hard mask (random pieces: 0.1 - 5").
CR-9S1OP, (13%(NH ₄) ₂ Ce(NO ₃) ₆ +6%HClO ₄ +surfactant)	Cyantek	81%	Cr etch solution
PEH-1 (HCl + H ₂ O + surfactant)	Cyantek	--	Pre-etch
AZ5214	Clariant	--	Photoresist
AZ300-MIF	Clariant	--	Photoresist developer

*Purity refers to metallic content only.

Appendix C Table of equipment

A large number of equipment was used for both fabrication and characterization was used in this work. A complete listing is provided in this appendix for ease of referencing. To enable SE in the range of 6 to 9 eV, measurements were carried out in vacuum to avoid absorption of atmospheric molecules.

Table C-1. Listing of the essential fabrication equipment used. Maximum is abbreviated to 'Max.' in the table.

Equipment	Manufacturer/model	Remarks
Spin coater	Laurell/WS-400-6NPP-LITE	Full-body polypropylene; closed coating chamber.
Electric furnace	Thermodyne/F47900	Max. temperature 1200°C.
Rapid thermal processor	JIPLEC/JetFirst	Max. temperature 1300°C; thermocouple sensing from room temperature to ~ 850°C; pyrometer sensing from 400 – 1300°C; Max. wafer size: 4"; heating elements: 12 halogen lamps N ₂ and O ₂ gas feeds.
Mask aligner	Quintel Q2001/IR	i-line (365 nm) source; max. wafer size: 4".
Reactive ion etcher	Custom-built generic unit	Max. RF power: 120W; max. etch duration: 15 mins; max. wafer size: 4"; O ₂ /H ₂ /CF ₄ gas feeds.
Electron beam deposition system	Denton DV502	Average substrate temperature during deposition: 60°C; rotating substrate holder.

Table C-2. Listing of characterization equipment used.

Measurement	Manufacturer /model	Light source	Particulars
FTIR spectroscopy	Perkin-Elmer/ Spectrum 2000 spectrometer	Wire coil at 1350 K.	Range: 370 – 7800 cm ⁻¹ (using DTGS detector and optimized KBr beamsplitter); beam size: ~ 4×6 mm ² .
UV-Vis spectroscopy	Hewlet-Packard/HP 8453 spectrophotometer	W Halogen and D ₂ O Arc Lamp.	Transmission mode (190 – 1000 nm); beam size: ~ 1.5 cm.

Measurement	Manufacturer /model	Light source	Particulars
Micro-Raman scattering	Renishaw/Ramascope	Argon ion laser (514.5 nm line, average output 15 mW).	Fitted with microscope by Olympus for operation in a backscatter geometry; for a 40x objective lens, exposure dosage: < 3 mW over < 2 μ m diameter.
Micro-Raman scattering	Renishaw/Ramascope	Frequency doubled Argon ion laser (244 nm line, average output 7 mW).	Fitted with microscope by Olympus; for a 40x objective lens, exposure dosage: < 1 mW over ~2 μ m diameter.
Spectroscopic ellipsometer	J. A. Woollam Co./VASE	Xenon Arc Lamp	9 to 0.72 eV fitted with a rotating analyzer element; beam size ~ 3 x 7 mm ² at 75° incidence.
Reflectometer	Filmetrics F20	Tungsten Halogen	600 – 1100 nm; 20 nm – 50 μ m film thickness; beam size: ~ 5 mm diameter.
Prism-coupler	METRICON 2010	He-Ne 632.8 nm Laser diode 1550 nm.	Scattered light shield used; Half-step scan precision: 0.00009; spot size: 0.5 mm (632.8 nm) and 1 mm (1550 nm)
X-ray diffractometer	Siemens/D5005	CuK α source.	Slit used for glancing angle scan (1-2°): 1 mm; generator power setting: 40 kV/40 mA.
Rutherford backscattering	National University of Singapore/Custom built	--	2 MeV He ²⁺ (errors on thickness $\leq$ 5%; composition $\leq$ 2%).
Atomic force microscope	Digital Instruments/Dimension 3000	--	Nanoscope IIIa control module (noise: ~ 0.5 Å).
Profilometer	Tencor P10	--	Tip dimension: 2 μ m; scan rate: 500 points/sec to 2000 points/sec; z resolution: 0.008 Å.

Measurement	Manufacturer / model	Light source	Particulars
Surface Profiler	Veeco Dektak 3	--	Tip dimension: 12.5 μm ; scan rate: 500 points/sec to 2000 points/sec; z resolution: 10 $\text{\AA}$.
Optical Microscope	Olympus	Halogen lamp	Obj. lens: 100X (requires immersion oil) 50X, 10X; eyepiece: 10X.
Transmission electron microscope	Philps-FEI/CM200 FEG	--	Highest resolution ~ 10 nm.

Appendix D Rutherford backscattering measurement on $x\text{GeO}_2:(1-x)\text{SiO}_2$ thin films

The Rutherford Backscattering (RBS) measurement was carried out at the Ion Beam Centre at the National University of Singapore. The incident ion beam used was $^4\text{He}^{2+}$ accelerated at 2 MeV. In general, the errors¹ on the thickness values of the films are $\leq 5\%$ and on composition are $\leq 2\%$. There were 10 samples designed for multi-sample ellipsometric measurements (c.f. §3.5.7); two samples, fabricated for each composition $0.05 \leq x \leq 0.40$, are of different thickness. The measurement geometry is shown in Figure D-1(a). The sampling area is approximately 1.0 mm in diameter. In order to increase the sampling length for the thinner films, the detector was adjusted to a scattering angle of $\theta_s = 112.5^\circ$ (i.e. the 'A' samples, see Table D-1). The scattering angle was 160.0° for the thicker films (i.e. the 'B' samples, see Table D-1).

Figure D-1. (a) Schematic of RBS measurement geometry. (b) Representative RBS spectra with fitting curves generated by the RUMP software.

The raw scans were analyzed by the RUMP software [1]. The fitting results by RUMP for two representative samples are shown in Figure D-1(b). The parameter values derived from the RUMP software are tabulated in Table D-1 and

¹ These uncertainties were provided by staff at the Ion Beam Centre in the year 2004.

Table D-2. The results on the composition are shown in Table D-1 in percentage of each atom with the respective nominal compositions denoted by x for comparison. The uncertainty on the parameter, x , is calculated from the measurement error on the relative concentration of each element. The discrepancy between the measured x and nominal x is ≤ 0.008 (with the exclusion of sample 40a1²). This discrepancy is comparable to the estimated error incurred in the chemical mixing procedure (i.e. adopting Process IV from §4.3.6.4) of $x < 0.0054$ which translates to a tolerance in refractive index of < 0.0009 . Thus, a large part of the discrepancy between nominal x and measured x is due to the chemical mixing procedure. This discrepancy can be reduced further by an appropriate optimization in the chemicals mixing procedures as shown in §4.3.6.4.

From the results shown in Table D-1, the stoichiometry of the oxide films (i.e. in terms of the form $\text{Ge}_x\text{Si}_{1-x}\text{O}_y$) was derived and shown in Figure D-2. While all samples are close to the stoichiometric state, where $y = \text{O}/(\text{Ge} + \text{Si}) = 2$, in general, there is over abundance of oxygen. Therefore, in the context of this work, the films have been assume to be stoichiometric with $y \approx 2$, and notation $x\text{GeO}_2:(1-x)\text{SiO}_2$ have been used throughout this thesis to represent the composition of the films.

² From the substantial deviation of the sample, 40a1, from the nominal composition, there is a likelihood of an error in the arrangement of samples.

Table D-1. Summary of the results of RBS measurements on the compositions of the test samples.

Sample ID	Nonimal x	Composition				Error on x
		Ge (f _{Ge}), %	Si (f _{Si}), %	O (f _O), %	x	
Series A						
5a1	0.050	1.742	28.378	69.880	0.058	0.002
10a1	0.100	3.393	28.414	68.193	0.107	0.003
20a1	0.200	6.742	25.843	67.415	0.207	0.005
40a1	0.400	10.272	20.706	69.022	0.332	0.006
40a2	0.400	12.853	18.786	68.361	0.406	0.004
Series B						
5b1	0.050	1.899	31.646	66.455	0.057	0.001
10b1	0.100	3.356	29.53	67.114	0.102	0.002
20b1	0.200	6.800	26.609	66.591	0.204	0.002
40b1	0.400	13.043	20.067	66.890	0.394	0.003
40b2	0.400	13.613	20.942	65.445	0.394	0.003

Figure D-2. The calculated stoichiometry of the binary oxide films.

The areal density was derived from the RUMP simulation for the layer of $\text{GeO}_2:\text{SiO}_2$ film. Taking the thickness determined by the ellipsometric measurements,

the atomic density of the film was calculated, the areal density divided by the thickness. The atomic density (ρ_{at}) was converted to mass density (ρ_{ma}) by the following equation, the results of which are shown in Figure 3.19,

$$\rho_{\text{ma}} = \rho_{\text{at}} \left(\frac{f_{\text{Ge}} M_{\text{Ge}}^{\text{m}} + f_{\text{Si}} M_{\text{Si}}^{\text{m}} + f_{\text{O}} M_{\text{O}}^{\text{m}}}{N_{\text{A}}} \right), \quad (\text{D-1})$$

where f_{Ge} , f_{Si} and f_{O} are taken from Table D-1, M_i^{m} is the molar mass for the respective atom $i \in [\text{Ge}, \text{Si}, \text{O}]$. Likewise, the thickness of the SiO_2 layer can be determined by areal density/atomic density. A 5% error is assumed for the areal density and indicated next to each thickness value derived from the RBS results. The results of the densities and thickness determined by RBS and SE are summarized in Table D-2. A desirable agreement within the boundaries of uncertainty is observed between the thickness values of the SiO_2 -layer measured by RBS and SE.

Table D-2. Summary of results of RBS measurements on the thickness of the test samples. The thickness as determined by spectroscopic ellipsometer (SE) is provided for comparison.

Layer 2 ($\text{GeO}_2\text{:SiO}_2$)						Layer 1 (SiO_2)			
SE Thickness			RBS Areal density	Calculated atomic density		RBS Thickness	SE Thickness		
ID	[nm]	Error, [nm]	$[10^{17} \text{ ats/cm}^2]$	$[10^{22} \text{ ats/cm}^3]$	Error, $[10^{22} \text{ ats/cm}^3]$	[nm]	Error, [nm]	[nm]	Error, [nm]
Series A									
5a1	62.1	0.2	4.25	6.844	0.207	49.0	2.5	--	--
10a1	103.2	1.0	6.72	6.512	0.205	25.0	1.3	25.3	0.2
20a1	95.2	0.3	6.03	6.334	0.191	25.0	1.3	26.1	0.1
40a1	68.2	0.9	4.44	6.511	0.213	38.0	1.9	--	--
40a2	157.1	1.0	9.75	6.206	0.190	29.0	1.5	28.4	0.1
Series B									
5b1	341.1	0.3	22.30	6.538	0.196	28.0	1.4	--	--
10b1	290.1	1.0	18.80	6.481	0.196	23.0	1.2	23.0	0.2
20b1	346.6	0.3	20.90	6.030	0.181	20.0	1.0	20.8	0.1
40b1	250.2	2.0	15.50	6.195	0.192	35.0	1.8	31.5	0.1
40b2	420.6	2.0	25.60	6.087	0.185	20.0	1.0	--	--

References

[1] M. O. Thompson, "GENPLOT and RUMP Documentation," Computer Graphic Service, Ltd, <http://genplot.com/doc/index.htm>, 2006.

Appendix E Sensitivity of Raman spectroscopic and X-ray diffraction measurements to nano-sized heterogeneous phases

The motivation of the study stems from the fact that when even annealed GeO_2 -doped films were exposed to electron beams in electron microscopy, an observable material change occurs. This change was experienced by the author and a similar behaviour has been reported by others [1]. Under this circumstance, the detection of any precipitation of crystalline phases will have to rely on other characterization techniques, for example, Raman spectroscopy and X-ray diffractometry.

The x-sectional TEM micrographs of the samples were taken at the Institute of Microelectronics, Singapore¹. The samples were prepared by grinding one of the lateral dimensions down to a few microns followed by ion milling (Ar^+) at a glancing angle to thin the cross-section further to $\sim 0.2 \mu\text{m}$ on a copper ring. The equipment used to perform the TEM observation was Philips/FEI CM200 FEG with a CCD camera. The micrographs shown in Figure E-1 were taken at intermediate magnification, after high magnification observation (i.e. $\times 1,000,000$). Unambiguously, segregation (i.e. GeO_2 -rich phase) has taken place in regions exposed to the probing electron beam giving rise to the compositional contrast for both 20Ge^2 and 40Ge samples shown in Figure E-1(a) and (b) respectively after 15 minutes of annealing at 900°C . In fact, similar phenomenon was noted for samples of all composition down to 5 mol% GeO_2 . The thermal SiO_2 (lightest region within the cross-section sample) that was grown underneath the $\text{GeO}_2:\text{SiO}_2$ during annealing was shown to be unaffected by the electron beam. After the thermal annealing, the sol-gel derived films were believed to be dense and free of organic impurities as presented in Chapter 3. Also, similar effect has been reported in other studies with $\text{GeO}_2:\text{SiO}_2$ materials made by other techniques [2, 3]. Therefore, this effect can be understood to

¹ Both the sample preparation and TEM observation was performed by staff at the Institute of Microelectronics.

² Reminder: the notation $(100-x)\text{Ge}$ is a shorthand for denoting a composition of $x\text{GeO}_2:(1-x)\text{SiO}_2$.

be common for all $\text{GeO}_2\text{:SiO}_2$ binary oxides. Resolving nano-sized phase in $\text{GeO}_2\text{:SiO}_2$ by a TEM can be difficult.

Figure E-1. Cross-section TEM micrographs of $x\text{GeO}_2\text{:}(1-x)\text{SiO}_2$ thin films on Si with an interlayer SiO_2 ; (a) $x = 0.2$ —the main figure shows that at high magnification operation, the e-beam alters the microstructure of the film and induces phase separation after zooming out from a view shown in the inset; (b) $x = 0.4$ —a time sequence of the TEM view is shown at high magnification (inset) and then zooming out at the same position after 30 seconds of high magnification viewing (main figure). The region outside of the e-beam beamwidth seems to be homogeneous, unaffected by the otherwise high dose of electron energy.

Alternatively, nano-sized crystalline particles can be resolved by X-ray diffraction and Raman spectroscopy [4, 5]. As a reference, 100Ge samples were made by spin coating (1000 rpm; $\sim 30\%$ RH) the solution of IPA-diluted TPOG (after 12 hrs of mixing) on Si substrates. The as-deposited thickness of the samples was around 200 nm. The samples were subjected to annealing in the electric furnace for 15 mins at 400°C or 1000°C. Scans of XRD, visible (excitation wavelength: 514.5 nm) and UV (excitation wavelength: 244.0 nm) Raman spectroscopy were all performed and the results are shown in Figure E-2. The XRD measurements were done at a glancing angle geometry at $\sim 1^\circ$; the scan step of θ was 0.1° and the scan time was 2 s/step. Full input power was used and each scan was a sum of 10 scans with a detector time of 30 s. The scan resolution was $\sim 1 \text{ cm}^{-1}$ for the visible Raman and $\sim 4 \text{ cm}^{-1}$ for the UV Raman. The crystalline characteristics of the hexagonal phase are clearly seen when compared to the sample of 40Ge. The peaks of 300 and 520 cm^{-1} , observable from the visible Raman spectra, are ones of Si [6].

While in the visible Raman spectra the band located at $\sim 450 \text{ cm}^{-1}$ is the only one that is discernible, many more phonon bands are observable in the UV Raman spectra. Such observation is likely traceable to the resonance Raman and the wavelength dependent (i.e. $1/\lambda^4$) effects [7-10]. Since the excitation wavelength of the laser (244 nm $\equiv 5.081 \text{ eV}$) is rather close to the bandgap of GeO_2 of $\sim 5.61 \text{ eV}$ [11], the enhancement due to the resonance Raman effect can be appreciable. The peaks shown on both the visible and UV Raman spectra are compared to peaks identified by prior reports as summarized in Table E-1. All peaks are accountable when the spectra of the GeO_2 films are compared to the Raman peaks of the hexagonal GeO_2 (h- GeO_2) powders except for the bands at $605 - 612 \text{ cm}^{-1}$, $770 - 773 \text{ cm}^{-1}$ and 1056 cm^{-1} . The peak at $605 - 612 \text{ cm}^{-1}$, though is not one that belongs to the spectrum of the h- GeO_2 powders, it is however found in the GeO_2 gel (at 590 cm^{-1}) and 70Ge xerogel dried at 70°C and heated up to 720°C [12, 13]. This peak likely corresponds to the peak of 595 cm^{-1} as reported in the work of Scott [14]. Since the spectra of the GeO_2 gel and the 70Ge samples were demonstrated to be predominantly consisted of precipitated crystalline phase of h- GeO_2 , the peak at $605 - 612 \text{ cm}^{-1}$ is likely related to h- GeO_2 phase derived from the sol-gel process. The peak around $770 - 773 \text{ cm}^{-1}$ has been attributed to the stretching mode of GeOH [12, 13]. This OH

content is likely due to H₂O absorption during handling of the samples in air even though that they were stored in a dry box. The assignment of the peak around 1056 cm⁻¹ is unclear but it is found also in the spectrum of the GeO₂ gel [12, 13].

Figure E-2. Investigation of sensitivity of XRD (a), UV Raman (b) and visible Raman (c) to GeO₂ crystalline phase. All vertical axes represent intensity in arbitrary units. The intensity scale for the plot in (a) has been translated to a log scale to facilitate the visualization of the peak characteristics for all peaks. Crystallinity of hexagonal GeO₂ is verified by XRD with JCPDS card #36-1463.

Table E-1. A comparison of the location of Raman peaks (in cm^{-1}) as found from this work (h- GeO_2 film) with results reported in the literature. The abbreviations in the brackets indicate the relative intensity of the peak: vs – very strong; s – strong; m – medium; w – weak; vw – very weak; sh – shoulder; br – broad. Reference spectra were taken with excitation wavelength of 488 nm [12].

UV		visible			
h- GeO_2 film	h- GeO_2 film	70Ge xerogel ^a	GeO_2 gel ^b	h- GeO_2^c	t- GeO_2^d
		128 (m)		112 (s)	
				116 (s)	
		166 (m)			166 (s)
		210 (w)		212 (w)	
			221 (vw)	246 (w)	
		262(w)		262 (w,sh)	
				286 (vw)	
		330 (vw)		326 (w)	
				360 (vw)	
451 (vs)	441-448 (s)	442 (s)	444 (s)	442 (vs)	
525-535 (w)		514 (w)	510 (w)	516 (w)	
			576 (w)		
605-612 (w)		605 (w)	590 (w)		
			738 (sh)	698 (vw)	700 (vs)
770-773 (s)		770 (w, br)	772 (w)		
		856 (sh)	860 (sh)	858 (vw)	874 (m)
888 (w)		880(w)	880 (w)	880 (w)	
			962 (vw)	960 (vw, sh)	
972 (w)		968(vw)		970 (w)	
1056 (b)			1044 (vw)		

^a see Ref. [12]; the sample was an gel treated at 70°C.
^b see Ref. [12]; the sample was a dried gel.
^c see Ref. [12]; the sample was consisted of crystalline powders. Similar bands can be found in Ref. [14].
^d see Refs. [12] and [14]; the sample was likely consisted of crystalline powders or small pieces of crystalline materials.

In order to test the resolution limit of UV Raman and XRD for nano-sized GeO_2 embedded in films of $\text{GeO}_2\text{:SiO}_2$, samples containing 60 mol% Ge were made. Two sets of samples were made with one from a solution made from a Sol-G (Figure 3.1) that involved acetylacetone (AcAcH) as a chelating agent and the other with methoxyethanol (MoE) to replace the IPA. The process was otherwise the same as described in §3.2 and §3.3. The control of the crystal size of the precipitated GeO_2 is

performed by annealing the samples in an electric furnace from 700 to 1000°C for different duration. Samples were stored in a dry box.

While all samples with MoE were without detectable trace of crystalline phase, peaks were found for the samples with AcAcH as seen in Figure E-3. The UV Raman spectra shown in Figure E-3(a) reveal distinct peaks that were identified in Figure E-2(b) for samples annealed at 900°C for 20 mins and greater in thermal energy. These peaks are located at: i) 440 – 448 cm⁻¹, ii) 510 – 519 cm⁻¹ and iii) ~ 770 cm⁻¹. Peaks i and ii are traceable to the h-GeO₂ origin, whereas peak iii is due to GeOH. On the other hand, the XRD scans presented in Figure E-3(b), which were taken at a scan rate of 10 s/step, crystalline GeO₂ phase was detected (with the two peaks of [100] at 2θ of 20° and [101] at 2θ of 26°) when the sample was annealed at 1000°C for 5 mins. By invoking the Scherrer's equation, the size³ of the nano-crystalline phase of h-GeO₂ can be estimated as follows [4]:

$$\langle D \rangle_{vol} = \frac{4}{3} \frac{K \lambda_X}{B \cos \theta}, \quad (E-1)$$

where B is the FWHM of the peak which can be calculated from $\sqrt{B_{obs}^2 + B_{ins}^2}$, λ_X is the X-ray emission used in the scan (i.e. Cu K_α at 0.1542 nm), constant K is assume to be 0.9 and θ refers to half of the angle subtended by the incident ray and the line between the sample and the detector. The prefactor of 4/3 is a conversion from column length as predicted by the Scherrer's equation to an assumed geometry of a spherical particle [4]. From the analysis of Krill *et al.* [4], the volume-weighted average size is practically an upper limit of a typical log-normal size distribution.

³ The size estimated using the Scherrer's equation is a volume weighted average.

Figure E-3. Comparison of the resolution limit between UV Raman (a) and XRD (b) with 60Ge samples chelated by AcAcH. All vertical axes represent intensity in arbitrary units. Phases of GeO_2 can be detected for samples annealed below 1000°C by UV Raman but not by XRD.

At the moment, the instrumentation broadening has not been determined experimentally; however, a quantitative estimation can be established from some observations as discussed below. First, using Eq. (E-1), an estimate of the volume-averaged size of nano- GeO_2 crystallites is obtained for the various values of instrumentation broadening, B_{ins} . The results derived from two of the strongest peaks (from $[100]$ and $[101]$ planes) are shown in Figure E-4. Secondly, the FWHM of the $[101]$ peak in the spectrum of the 100Ge 1000°C sample (c.f. Figure E-3(b)) is found to be 0.43802° by performing a Gaussian fit; thus, the instrumentation broadening cannot exceed this amount. From Figure E-4(b), if one were to assume a B_{ins} of 0.4 , an estimate of the crystallite size is < 44 nm. In terms of the contribution of nano-crystallite to scattering loss, the numeric average [4] is likely a better indication. Since the derivation of the numeric average requires a more demanding analysis [4], for the present purpose, some estimates will be inferred to advance the arguments. For a

numeric average of < 20 nm, the estimate of contribution to scattering loss (α_p) according to Figure 3.13 (16Ge) is < 0.06 dB/cm.

Figure E-4. (a) Gaussian fitting of the two diffraction peaks of the 60Ge annealed at 1000°C shown in Figure E-3(b). The vertical axis represents arbitrary intensity. (b) Estimation of the size of nano-crystalites (for a spherical geometry) for the various values of instrumentation broadening factor.

Therefore, for practical purposes, typical commercial XRD and UV Raman systems have enough resolution to estimate the scattering loss in waveguide materials due to nano-sized phase separations (from amorphous to crystalline). And from the experimental findings above, acetylacetone is more likely to cause phase precipitation of GeO₂ than methoxyethanol.

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Appendix F Estimation of optical loss due to scattering of sub- wavelength particles of a heterogeneous phase

This section provides the details for all the values required to calculate the attenuation coefficient due to scattering loss as shown in Eq. 3.10 and is reproduced again for convenience,

$$\alpha_p \text{ [dB / cm]} = \frac{40\pi^4 n_m^4}{\ln 10} \cdot \left(\frac{q^2 - 1}{q^2 + 2} \right)^2 \frac{d^3 f_p}{\lambda^4} \quad (\text{F-1})$$

where q is the relative refractive indices of the particles and the amorphous matrix (n_p/n_m), d is the particle diameter, f_p is the volume fraction of particles, $\frac{4}{3}\pi r^3 N$ with $r = d/2 \ll \lambda$ and N is the number of particles per unit volume of the matrix.

Since the composition dependence of density and refractive index (RI) of the films is linear (c.f. §3.5.7), the effective properties are assumed to be linear combinations of the constituents. During the progress of phase precipitation, the monophasic mixture of amorphous GeO_2 (a- GeO_2) and SiO_2 , having an RI of n_m and density of ρ_m , begins to give rise to a new phase of crystalline hexagonal GeO_2 (h- GeO_2) in terms of dispersed particles with a diameter, d , RI of n_p and density of ρ_p . The molar fraction of precipitation (i.e. h- GeO_2 /a- GeO_2) is defined to be f_x^M . Such a parameter assignment is shown in the following schematic diagram, Figure F-1. An analogous analysis was performed for the $\text{TiO}_2\text{:SiO}_2$ material where the precipitated crystalline phase is assumed to be tetragonal TiO_2 (anatase) [1].

Figure F-1. Schematic diagram showing the crystallite precipitation process and parameter definition.

Table F-1. Values used in Eq. (F-1).

Parameters	Abbrev.	GeO ₂ :SiO ₂	TiO ₂ :SiO ₂
RI of amorphous matrix (1550 nm)	n_m	$1.4425 + 0.1434x(1 - f_x^M)^*$	$1.4430 + 0.4795x(1 - f_x^M)$ [2]
RI of crystallite particles (1550 nm)	n_p	~ 1.586	2.379 [1, 3]
Density of α -SiO ₂ [g/cm ³]	ρ_s	2.20 [4]	2.20
Density of α -GeO ₂ or α -TiO ₂ [g/cm ³]	ρ_g or ρ_t	3.604 [4]	3.56 [5]
Density of h -GeO ₂ or t -TiO ₂ [g/cm ³]	ρ_{Gx} or ρ_{Tx}	4.228 [6]	3.8 [3]

*developed in this work, see Figure 3.18b.

The values used for each variable in Eq. (F-1) are summarized in Table F-1. Lastly, the volume fraction of particles, for $f_x^M = 1$, can be expressed as follows, in terms of molar masses and density for α -SiO₂, α -GeO₂ and h -GeO₂, namely, M_s , M_g , M_{Gx} , ρ_s , ρ_g and ρ_{Gx} ,

$$\begin{aligned}
 f_p &= \frac{V_{Gx}}{V_s + V_g + V_{Gx}} \\
 &= \frac{M_{Gx} / \rho_{Gx}}{M_s / \rho_s + M_g / \rho_g + M_{Gx} / \rho_{Gx}}, \quad (F-2) \\
 &= \left(\frac{M_s \rho_{Gx}}{\rho_s M_{Gx}} + \frac{M_g \rho_{Gx}}{\rho_g M_{Gx}} + 1 \right)^{-1}
 \end{aligned}$$

where V_s , V_g and V_{Gx} are the volumes of a-SiO₂, a-GeO₂ and h-GeO₂, respectively, for a unit volume of film.

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Appendix G Practical considerations of thin film characterization by spectroscopic ellipsometry

Practical limits for resolving layers of similar refractive indices do exist but are seldom studied. In general, the determination of the precision of the derived optical constants (i.e. real and imaginary refractive indices) from spectroscopic ellipsometry data is not straightforward [1]. Hence, the uncertainties related to the derived optical constants are not commonly quoted with published data [2-6]. This appendix illustrates some of the limits of resolution for the different physical parameters of the film structure of the samples under study. An indication of the uncertainty for the derived optical constants was inferred from the 90%-confidence-level of the fitting algorithm. Improvement in the uncertainties of refractive index is achieved ($\sigma_n < 0.001$) by the use of a spectroscopic ellipsometer (SE) system with a new rotational analyzer element (RAE), performing multi-sample and multi-angle analyses. The detection limit of the extinction coefficient (κ) is shown to be close to 0.001. This work demonstrates a semi-quantitative method to explore and evaluate the limitations of thin film measurements by SE. These resolution limits ultimately dictate the suitability of SE measurements in the different optical and photonic applications. This work has been published in a conference proceedings [7].

Fundamentally, the number of independently measured values of Ψ and Δ is $2W$ for a W number of measured wavelengths, then the number of optical parameters, P , should be uniquely solved if $P \leq 2W$ [1, 8]. However, the measured pairs of Ψ and Δ are likely to yield relationships that are interdependent, hence, inter-parametric correlation [1, 8, 9] are not uncommon in spectroscopic ellipsometry. Pertaining to the situation encountered in this work, correlations were observed if the thickness of the thermal oxide (t-oxide) layer (c.f. §3.5.7) is allowed to be fitted, especially when the refractive index contrast between the layers is not high. Such correlation causes degenerate sets of optimized solutions between a number of correlated-pairs of

parameters (in this case, the thickness of the t-oxide, ε_0 and S_1 of the Sellmeier dispersion of the $\text{GeO}_2\text{:SiO}_2$, see Eq. 3.14). Uniqueness tests were performed to lift the interparameter correlations. Since no significant correlation was observed when the value of thickness or ε_0 was fixed, the uniqueness-fit test proceeds by first fixing the ε_0 at values within a range, in which a local minimum exists for the mean-square-error (MSE, see §3.5.7) values (see Figure G-1). The MSE is a measure of the discrepancy between the values of the model and of the measurements. For the uniqueness-fit test of ε_0 , the initial values of t-oxide for the B1 samples and the A1 samples were fixed at the estimates deduced from the Rutherford backscattering measurements (Appendix D). Once an optimal value of ε_0 was chosen for each set of multi-sample fit (i.e. for each set of samples of a specific composition), the thickness of t-oxide for the B1 samples, then for the A1 samples were determined sequentially by a similar uniqueness-fit test. An indication of the accuracy of the uniqueness-fit test can be inferred from the agreement (within uncertainties) between the thickness of the t- SiO_2 determined by the uniqueness-fit test and the values obtained from RBS measurements (Table H-2).

From the experience of the author, the MSE minima were no longer observable in a reasonable range of t-oxide thickness for $x \leq 0.100$ if the fitting range was between 270 and 1700 nm and using the data for only one angle of incidence at 75° . This limitation is likely caused by indiscernible differences between the measured SE spectra of $\text{GeO}_2\text{:SiO}_2$ layer and the t-oxide layer. Extending the fitting range on the short-wavelength side from 270 to 210 nm and using data at two angles of incidence ($\phi_0 = 60^\circ$ and 75°) yielded a better resolution limit to $x \sim 0.050$. Hence, determination of the film structure for samples with $x \leq 0.050$ relied on alternate methods, namely, Rutherford backscattering. The data used for the above analysis was measured by the SE with a new rotation analyzer element. Such distinction is discussed below.

Figure G-1. Uniqueness-fit test to determine the thickness of the thermal oxide for a sample with $x \sim 0.200$ in order of process sequence, first, ϵ_0 (a), then t-oxide thickness of B1 (b) and lastly was the t-oxide thickness of A1 (c). Measurements were done by VASE at JAW.

Figure G-2 shows the measurement data and analysis results of $x \sim 0.200$ samples as measured by two SE systems; one fitted with an earlier version of the rotational analyzer element (RAE) and the other fitted with a new generation RAE. The measurement done with the old RAE system involved a scan from 270 to 1700 nm at one angle of incidence of 75°; the data range used, as measured by the new system, is from 210 to 1700 nm at two angles of incidence at 60° and 75°. The left and right columns in Figure G-2 pertain to results of the old RAE and the new RAE respectively. One noted improvement is in the ability to measure $\Delta(\omega)$ adequately at extrema. This improvement is clearly shown by comparing Figure G-2(b) and (h).

Figure G-2(c-f) and Figure G-2(i-l) plots the dispersion relationships of the Sellmeier model and NK-wavelength-by-wavelength (NK) fitting (with film thickness fixed at the value determined by using the Sellmeier model) for the old and new RAE systems, respectively. Due to the inadequacy of the old RAE, spurious inflections are observed in Figure G-2(c) at each Δ extrema as illustrated in Figure G-2(b). At these inflection points, peaks of error (i.e. 90% confidence values, σ_n) in the refractive index, n , are noted in Figure G-2(d) along with corresponding spurious absorption peaks as shown in Figure G-2(e). These inflection points and their artefacts are clearly absent in the new RAE scans (see the right column in Figure G-2). Consequently, these artefacts affect the ability for the fitting algorithm to deduce parameters with a high degree of certainty, albeit the use of a biased fitting algorithm used in the WVASE software [1].

When data for multiple samples of different thickness (A1, 95.2 nm; B1, 346.6 nm) and multiple angles of incidence are incorporated in the analysis of the results obtained from the new RAE system, σ_n can be reduced effectively (see Figure G-2 (d) and (j)). Note that the Sellmeier dispersion and the NK-fit of 'A1&B1' in Figure G-2 (j) are derived from a simultaneous fit of both the A1 and B1 results.

Lastly, from the derived κ values and their error values (Figure G-2 (e,f,k,l)), the minimum detection limit of κ is shown to be approximately 0.001, and for all intensive purposes, κ (for silicate glasses, $\kappa \sim 10^{-6}$) can be assumed to be zero which validates the use of Sellmeier dispersion relationship.

Figure G-2. The analysis results of SE data of samples with 20 mol% Ge by WVASE32. Measured and fitted SE parameters of old RAE SE system at NTU (a, b) and new RAE system at JAW for the A1 sample only (g, h) for two angles of incidence. The derived optical properties (n and κ) of the films ($\text{GeO}_2\text{:SiO}_2$) layers and their corresponding estimation of uncertainties for the old RAE scan (c – f) and the new RAE scans for A1 and B1 samples (i – l).

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Appendix H Application of Croll's equation for drying stress on sol-gel film

At the spin-off-evaporation transition (SET) while spin-coating (c.f. §2.4.7), the radial mass flow is halted as viscosity of the coating sol increases [1] and thickness of the sol has been significantly reduced (typically $< 10 \mu\text{m}$ [2-4]), a gel film begins to form with a discernible elastic modulus as evaporation drives further thinning. Further volume shrinkage is restricted to thickness reduction; hence, an in-plane tensile stress is developed as strain along the substrate is hindered. Brinker [5] proposes the use of the expression by Croll to account for this drying stress,

$$\sigma_f = \left(\frac{E}{1-\nu} \right) \left(\frac{V_1^s - V_1^x}{3} \right) \cong \left(\frac{E}{1-\nu} \right) \frac{(1-s)}{3} \left(1 - \frac{H_x}{H_s} \right) \quad (\text{H-1})$$

where V_1^s and V_1^x represent the volume fraction of solvent at the point of solidification and in the xerogel respectively. Assuming negligible in-plane strain, the original Croll's expression (used for amorphous and elastic polymers) can be simplified to the expression on the right-hand side of the Eqn. (H-1), where H_s and H_x are the thicknesses of the film at the onset of solidification and of the xerogel film; s is the shrinkage fraction between H_x and the thickness of film after high temperature densification. Taking some typical values of $Z = 0.1$, $s = 0.31$ [6-8], $H_x = 1 \mu\text{m}$, $H_s = 4 \mu\text{m}$ [4], $\nu = 0.2$ [9, 10], $H = 0.6 \mu\text{m}$ and $E = 22.5 \text{ GPa}$ (TEOS-derived xerogel film) [11], using Eqs. (4.7) and (H-1), G_f can be estimated at 1000 J/m^2 which is about 5 orders larger than the surface energy of a TEOS-derived xerogel film (TXGF) of 0.04 J/m^2 [12-15]. Even if the E is assumed to be 0.5 GPa as reported for a bulk gel [10], G_f is $\sim 20 \text{ J/m}^2$. With such high elastic energy stored in the film, a mechanical failure is guaranteed for thickness $> 3 \text{ nm}$. From experience in the laboratory, cracks are noted for films with $H_x > 0.6 \mu\text{m}$ once exposed to ambient environment. The thicker is the film, the faster cracks grow in a denser fashion. Christodoulou *et al.* [16] suggested that Croll's expression may fail to describe gel films due to large deformation (i.e. from $H_x/H_s \ll 0.1$) where elasticity may deviate from linearity and that rheological and transport properties during the sol-to-gel transition may vary by orders of magnitudes over the course of drying. Clearly, the use of Croll's expression

for the drying of sol-gel-derived films deserves a more thorough study. The preferential evaporation of the more volatile alcoholic solvents leaves behind an increased concentration of water which will increase polycondensation and ultimately changes E . In ref. [6], Parrill showed that RI increases monotonically with R for spin-coated films which is in contrast with the existence of a maximum in RI at a certain moderate R for dip-coated film. The dominance of capillary force in the case of spin-coating is postulated. The increase in viscosity of the sol in a relatively short time scale may hinder molecular diffusion that effect polymerization. The 'skin' layer (i.e. the surface layer of the film which is likely more deprived of solvents, hence, gels faster) [2, 16, 17] further complicates the description of the potential drying stress developed in a spin-coated xerogel film. Another difficulty lies in the lack of appropriate real-time characterization tools.

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Appendix I Determination of effective fluidic properties of sols

Since that in the analysis of §4.3.3.2, solutions of solvents were found in the sols. This section is dedicated to provide the mixing rules and relevant details used to estimate the effective liquid properties of the sols. The calculated values of these properties are shown in Table 4.10 (§4.3.3) for the solvent—co-solvent mixtures found in the various sols (STR3-STR6). Again, all the basic properties used are shown in Table 4.9. No visually discernible phase separation was observed for any of the solvent—co-solvent mixtures found in STR3-STR6; hence, all are assumed to be monophasic solutions in the analysis presented in §4.3.3.2. All properties are expressed in SI units. The molar fraction of each solvent component, i , is denoted by f_i^m . The mass diffusion coefficient is taken to be in the order of 10^{-11} m²/s [1-3].

Table I-1. A summary of the mixing rules for the respective fluid properties use in the analysis as presented in §4.3.3.

Property	Mixing rule	Remarks
Peak temperature difference between the surface and bottom of the liquid film	$\Delta T_{mixture} = \sum_i f_i^m \Delta T_i$	$\Delta T_i = T(z = L) - T(z = 0)$ and values were approximated from interpolation of volatility and ΔT data from ref. [4].
Heat conductivity	$k_{mixture} = \sum_i f_i^m k_i$	Assumed linear dependence.
Density	$\rho_{mixture} = \sum_i f_i^m \rho_i$	Ref. [5]
Viscosity	$\eta_{mixture} = \prod_i \eta_i^{f_i^m}$	Ref. [5]
Heat capacity	$c_{p,mixture} = \sum_i f_i^m c_{p,i}$	Assumed linear dependence.
Enthalpy of vaporization	$\Delta H_{vap,mixture} = \sum_i f_i^m \Delta H_{vap,i}$	Ref. [6]
rate of evaporation	$\dot{e}_{mixture} = \sum_i f_i^m \dot{e}_i$	The rate of evaporation seems to be linear with composition [7].

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Appendix J Derivation of error in the glass composition and refractive index from uncertainties of the chemical procedures

In this appendix, the error propagation of measurement uncertainties of the chemical mixing procedures as reflected in the glass composition of the films is worked out. The ultimate effect of the batch volume and tool precision on the yield composition (viz. refractive index) has been shown in Figure 4-39 (c.f. §4.3.6.4).

Consider again the mixing procedure in the following schematic diagram Figure J-1 (adopted from Figure 3.1). All chemicals were measured by volume using glass pipettes with markings of various precisions. These pipettes are group into two types for the present discussion: Type A with a capacity of 10 mL and a potential error in the entire extraction process of 0.10 mL and Type B with capacity of either 2 mL or 1 mL and an associated error of 0.02 mL. As far as the yield composition is concerned, only measurements (critical steps) that will affect the number of moles of Si and Ge (i.e. M_S and M_G) are considered in the foregoing analysis. The error incurred in the critical steps, 1 – 4, are indicated in Figure J-1 as σ_{pi} , where $i = 1, 2, 3, 4$. The only solvent of concern in this analysis is the one used in Sol-G. This quantitative analysis considers properties in the temperature range of 20 to 25°C.

Figure J-1. Flow diagram of the sol preparation procedures with the measurement error indicated (σ_{pi}).

The error in M_G , σ_{M_G} , is accounted by considering the volume of TPOG (V_G) extracted in step 4 (V_{DT}),

$$V_G = V_{DT} \left(\frac{V_{TG} - \delta V}{V_{sol} + V_{TG}} \right) \approx V_{DT} \left(\frac{V_{TG}}{V_{sol} + V_{TG}} \right), \quad (\text{J-1})$$

where V_{TG} and V_{sol} are volumes of TPOG and solvent used in Sol-G (see Figure J-1). δV represents the change in volume due to the transesterification or the chelation process as discussed in Section 2.4.6. If the solvent used in Sol-G is IPA, δV can be assumed to be zero. However, in the case where a chelating agent (e.g. methoxyethanol) is used instead of the IPA, the δV is non-zero but, nonetheless, can be shown¹ to be < 2% of either V_{TG} or V_{sol} . Therefore, δV can be neglected as shown in Eq. (J-1). The corresponding error in V_G is,

¹ For a typical chemical mixing condition: room temperature and enclosed container whose volumetric capacity is comparable to the volume of the liquid solutions inside.

Appendix J:

J-3

Derivation of error in the glass composition and refractive index from uncertainties of the chemical procedures

$$\begin{aligned}\sigma_{V_G} &= \sqrt{\sigma_{V_{sol}}^2 \left(\frac{\partial V_G}{\partial V_{sol}} \right)^2 + \sigma_{V_{TG}}^2 \left(\frac{\partial V_G}{\partial V_{TG}} \right)^2 + \sigma_{V_{DT}}^2 \left(\frac{\partial V_G}{\partial V_{DT}} \right)^2} \\ &= \sqrt{\sigma_{V_{sol}}^2 \left(\frac{-V_{DT}(V_{TG})}{(V_{sol} + V_{TG})^2} \right)^2 + \sigma_{V_{TG}}^2 \left(\frac{V_{DT}(V_{sol})}{(V_{sol} + V_{TG})^2} \right)^2 + \sigma_{V_{DT}}^2 \left(\frac{V_{TG}}{V_{sol} + V_{TG}} \right)^2}\end{aligned}\quad (J-2)$$

Note that in this case, V_{sol} is related to V_{TG} by $M_{sol}/M_{TG} = R_{S-G} = 4$ (c.f. §3.2), where M_{sol} is the number of moles of the solvent in Sol-G. And the error in M_G is,

$$\sigma_{M_G} = \sqrt{\sigma_{V_G}^2 \left(\frac{\partial M_G}{\partial V_G} \right)^2} = \sigma_{V_G} \left(\frac{M_G}{V_G} \right). \quad (J-3)$$

Likewise for the Sol-S, error for M_S is given by,

$$\sigma_{M_S} = \sqrt{\sigma_{V_{TS}}^2 \left(\frac{\partial M_S}{\partial V_{TS}} \right)^2} = \sigma_{V_{TS}} \left(\frac{M_S}{V_{TS}} \right), \quad (J-4)$$

where V_{TS} is the volume of TEOS used in Sol-S. The composition of the sol is designated by the molar fraction of Ge in the sol (i.e. x). Explicitly, x is expressed as,

$$x = \frac{M_G}{M_G + M_S}, \quad (J-5)$$

and its error is estimated as follows,

$$\begin{aligned}\sigma_x &= \sqrt{\sigma_{M_G}^2 \left(\frac{\partial x}{\partial M_G} \right)^2 + \sigma_{M_S}^2 \left(\frac{\partial x}{\partial M_S} \right)^2} \\ &= \sqrt{\sigma_{M_G}^2 \left(\frac{M_S}{(M_G + M_S)^2} \right)^2 + \sigma_{M_S}^2 \left(\frac{-M_G}{(M_G + M_S)^2} \right)^2} \\ &= \frac{M_G(1-x)}{M_G + M_S} \sqrt{\left(\frac{\sigma_{V_G}}{V_G} \right)^2 + \left(\frac{-\sigma_{V_{TS}}}{V_{TS}} \right)^2}\end{aligned}\quad (J-6)$$

Making use of the fact that (c.f. Eqn. (J-5)),

$$M_{TG} = \frac{x}{1-x} M_{TS} = \frac{x}{1-x} \frac{V_{TS} \rho_{TS}}{M_{TS}^m}, \quad (J-7)$$

V_G is related to V_{TS} in the following fashion,

$$\begin{aligned}
 V_G &= V'_{TG} + V'_{sol} \\
 &= M'_{TG} \left(\frac{M_{TG}^m}{\rho_{TG}} + R_{S-G} \frac{M_{sol}^m}{\rho_{sol}} \right) \quad , \quad (J-8) \\
 &= \frac{x}{1-x} \frac{V_{TS} \rho_{TS}}{M_{TS}^m} \left(\frac{M_{TG}^m}{\rho_{TG}} + R_{S-G} \frac{M_{sol}^m}{\rho_{sol}} \right)
 \end{aligned}$$

Where M_i^m and ρ_i denote the molar masses and densities of the respective components of $i \in [TS, TG, sol]$. The direct dependence of V_G on V_{TS} is clearly illustrated in Eq. (J-8).

Finally, the binary glass film, synthesized from the Sol-SG with a composition determined by x (i.e. $x\text{GeO}_2:(1-x)\text{SiO}_2$), has a refractive index for a particular wavelength which can be expressed as,

$$n_{GS} = x \cdot n_G + (1-x) \cdot n_S \quad (J-9)$$

where n_G and n_S are refractive indices for pure GeO_2 and pure SiO_2 films, respectively, for a specific wavelength of interest. Eq. (J-9) can be derived from the linear equations shown in Figure 3-19(b). The error on the refractive index is, while taking into account on error for n_S and n_G in terms of σ_{n_S} and σ_{n_G} respectively,

$$\begin{aligned}
 \sigma_{n_{GS}} &= \sqrt{\sigma_x^2 \left(\frac{\partial n_{GS}}{\partial x} \right)^2 + \sigma_{n_S}^2 \left(\frac{\partial n_{GS}}{\partial n_S} \right)^2 + \sigma_{n_G}^2 \left(\frac{\partial n_{GS}}{\partial n_G} \right)^2} \quad (J-10) \\
 &= \sqrt{\sigma_x^2 (n_G - n_S)^2 + \sigma_{n_S}^2 (1-x)^2 + \sigma_{n_G}^2 x^2}
 \end{aligned}$$

One notes that a number of parameters dictate the resultant error in n_{GS} ($\sigma_{n_{GS}}$) from Eqs.(J-6), (J-8) and (J-10): n_G , n_S , σ_{n_S} , σ_{n_G} , x , $\sigma_{V_{TG}}$, $\sigma_{V_{sol}}$, $\sigma_{V_{TS}}$, σ_{V_G} and V_{TG} and V_{TS} . The results of varying the *process-related* parameters have been presented in Figure 4-39 with x , n_G , n_S , σ_{n_G} and σ_{n_S} are 0.16, 1.590, 1.4450, 0.001 and 0.0005 respectively. The Table J-1 below shows the variables of the Process I-IV used in Figure 4-39(b) to illustrate the effect of tool precision at different critical steps on the $\sigma_{n_{GS}}$. The ceiling operation (Table J-1) represents a rounding up mathematical operation to the nearest integer.

Table J-1. Summary of processes (c.f. Process I-IV in Figure 4-39(b)) using laboratory tools of different precision at different critical steps.

Critical step	Error	Process			
		I	II	III	IV
1	$\sigma_{V_{TG}} = \text{ceiling}\left(V_{TG}/V_1^{\text{cap}}\right)\sigma_{p1}$	Type A	Type B	Type B	Type A
2	$\sigma_{V_{sol}} = \text{ceiling}\left(V_{sol}/V_2^{\text{cap}}\right)\sigma_{p2}$	Type A	Type B	Type B	Type A
3	$\sigma_{V_{TS}} = \text{ceiling}\left(V_{TS}/V_3^{\text{cap}}\right)\sigma_{p3}$	Type A	Type A	Type B	Type A
4	$\sigma_{V_G} = \text{ceiling}\left(V_G/V_4^{\text{cap}}\right)\sigma_{p4}$	Type A	Type A	Type A	Type B