

SOL-GEL SYNTHESIS OF GLASSES FOR PHOTONICS: A REVIEW OF CURRENT RESEARCH AND FUTURE PROSPECTS

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INTRODUCTION

'Photonics' is the futuristic goal of achieving fast, all-optical signal processing to replace the slower, current electronic methods. High silica glass optical fibres, for the passive transmission of optical signals in the near-infrared spectral region, are the 'workhorse' of the Internet for long distance, 'telecom', communications and local area networks. The recent deployment of the erbium doped silica glass, all-optical fibre amplifier is the best example to date of actively processing light with light. Currently, the commercial development of vapour deposited silica glass in planar, short waveguide format is underway. This type of optically integrated circuitry will execute simple, passive tasks such as wavelength division demultiplexing, that is sorting of digitally encoded optical signals of different signal wavelengths which have been simultaneously transmitted along one silica glass optical fibre. Such planar waveguides are typically monomode, with core sizes in the range 5-8 μm (in one or two dimensions) for butt-coupling to telecom. fibre, and are up to a few cm long with an optical loss $< 1 \text{ dB cm}^{-1}$.

Silica glass for fibre and planar optical waveguides has many advantages over rival materials. The chemical vapour methods of production are now mature technologies, and silica glass has excellent optical transmission in the near-infrared, is resistant to crystallisation and has the best mechanical and chemical durability of any compound inorganic glass. However, silica has a low solubility for rare earth dopants, and its high phonon energy mediates non-radiative relaxation of excited rare earth ions hence lowering the quantum efficiency of rare earth radiative transitions. Thus the continued development of all-optical amplifiers and fibre laser sources based on rare earth dopants other than erbium is impeded. In addition, silica glass has very low optical nonlinearity hence all-optical switching devices based on silica glass would have to be metres long. Finally, using the current methods of production there is no possibility of incorporating potentially useful organic species into the silicate network

It is these disadvantages of silica glass which are driving the development of novel glasses with poten-

tially greater optical versatility than silica. Sol-gel synthesis and processing may provide a route to making such new materials, particularly in a planar waveguide format. Below, the current status of research into passive waveguides from sol-gel is reviewed with attention to linear optical properties together with some speculation regarding future prospects.

This paper will address firstly the recent decline in interest in using sol-gel to make all or part of fibreoptic preforms, for drawing to low loss silica glass optical fibre. Next recent developments in *inorganic oxide* sol-gel processing of high silica and multicomponent silicate glass to make passive planar optical waveguides is discussed. Current progress in making organically modified silicates (ormosils) as passive waveguides based on *organic-inorganic* hybrid glassy materials will be reviewed. Finally, recent investigations into using sol-gel to prepare planar waveguides of *inorganic non-oxide* glasses will be presented. Optical waveguide sensor development is an important aspect of short length communications but is beyond the scope of this review.

SOL-GEL PROCESSING APPLIED TO SILICA GLASS OPTICAL FIBRE PRODUCTION

A review of progress to 1993 of the potential application of sol-gel processing to production of silica glass optical fibre may be found in [1], and is summarised below. Since 1993, there has been little significant further development.

Because the vapour deposition techniques of production of silica fibreoptic preforms, for drawing to fibre, are rapid, cheap and reliable, sol-gel processing would have to present a definite processing or cost advantage in order to be utilised. Potential advantages of sol-gel processing compared to the vapour deposition methods are: lower energy consumption; lower mass

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loss; a cheap precursor in 'fumed silica', and a potentially environmentally friendly, aqueous-based process. A disadvantage of sol-gel is that its aqueous nature leads to residual hydroxide in the consolidated glass even after high temperature reactive atmosphere processing; the lowest optical losses reported for sol-gel derived, silica glass fibreoptic preforms pulled to fibre are around two orders of magnitude (40 dBkm^{-1} at $1.55 \mu\text{m}$ (multimode) [2]) higher than vapour-derived fibre (0.2 dBkm^{-1} at $1.55 \mu\text{m}$) at the current telecom. signal wavelengths.

A less exacting optical specification is required for glass outside the active transmission region, but it must still be of excellent mechanical integrity, containing no cracks, pores or inclusions to lower fibre fracture strength. Current optical fibre systems have a minimum lifetime of around 25 years and are proof-strained during production to around 2 %. MacChesney and DiGiovanni [3] and MacChesney [4] have shown that sol-gel derived, partially gelled, overclad tubes fired onto the outside of a vapour-deposited preform can provide up to 95 % of the total fibreoptic preform mass, thereby potentially lowering costs. The sol-gel derived glass lies outside the active region for optical transmission. However, wet gel bodies around 1m long are fragile; production times are long – around 20 hours even for the one-step Clasen [5] process (involving self-alignment centrifugal casting) and the sol-gel material is prone to cracking because of shrinkage incurred during drying and consolidation. Lastly, the porous gel microstructure means it is difficult to get pore-free material in the finished preform.

SOL-GEL DERIVED INORGANIC HIGH SILICA AND MULTICOMPONENT SILICATE GLASS PLANAR OPTICAL WAVEGUIDES

Inorganic high silica planar waveguides

A major problem of making sol-gel derived inorganic oxide glass films is that films thicker than $0.5 \mu\text{m}$ have usually been difficult to fabricate due to stress cracking during the drying and sintering stages. Submicron films are too small for optical waveguiding. Yeatman's group [6] have achieved high silica films tens of microns thick on a silicon substrate using the new technique of SC RTA (spin coating, rapid thermal annealing), following the lead of Syms *et al.* [7]. The process is iterative and the high temperature heat treatment is very fast, meaning reasonable timescales for making thick films. Here, the term annealing alludes to a fast, high temperature heat treatment which dries and consolidates colloidal thin films into glassy layers, rather than the conventional glass technological term defined as bringing about stress relaxation close to the glass transformation region (T_g).

Further work on adjusting the refractive index with titania addition, and rare earth doping, has been described [8], as well as making semiconductor quan-

tum dot doped films with potential to act as nonlinear optical switching devices. However, titania tends to undergo nanophase separation during RTA thereby increasing light scattering losses in the finished waveguides [9]; quantum dots such as CdS tend to oxidise and/or aggregate during RTA [10] and irreducible hydroxide in the waveguides will reduce the excited state lifetimes of rare earth ion dopants.

Competing technologies to achieve silica-on-silicon are the vapour routes of flame hydrolysis deposition and chemical vapour deposition [6], mentioned above.

Inorganic multicomponent oxide planar waveguides

Recent, elegant work reported by Syms *et al.* [7, and references therein] has demonstrated the excellent progress made in the application of SC-RTA to build multicomponent silicate glass films thick enough for waveguiding in the near-infrared. Colloidal oxides in alcohol or alkoxide derived sols are spin coated onto a silicon substrate in thicknesses of 250 nm to 500 nm and RTA is applied, the sample is cooled ready for the application of the next spin coat. The silicon substrate has a $20 \mu\text{m}$ buffer layer initially applied to cut optical loss through guiding into the substrate.

Core/clad glass waveguides have been fabricated on silicon substrates, and simple structures such as Y-junctions of several levels based on tree structured power splitters. The core may be shaped into a channel by reactive ion etching (CHF₃, Ar and O₂ were used with a chromium mask). To reduce sidewall scattering of the core wall, a reflow step is used and dopants such as P₂O₅ and B₂O₃ ensure that the core reflows easily. After this, the core is buried in a cladding glass layer of lower refractive index, again by repetitive spin coating, heating in the rapid thermal annealer, cooling and recoating again. To avoid crack development in the thin films on silicon, the temperature of thermal "annealing" is selected with care to leave a compressively stressed film.

Channel waveguides have been constructed from multicomponent silicate glasses including germanophospho-silicate, borogermano-silicate, and borogermanophospho-silicate glasses. Excess optical loss in the channel waveguides is due to hydroxide absorption and extrinsic light scattering. Losses have improved during the development and there seems no reason why there should not be further improvement. Losses as low as 0.6 dB cm^{-1} have been reported over the wavelength region 1.1 to $1.7 \mu\text{m}$ for a system composed of GeO₂-B₂O₃-P₂O₅-SiO₂.

A competing method for achieving waveguides in multicomponent oxide glasses is the use of ion exchange [6], for instance Na⁺/Ag⁺ in soda-lime-silica glasses. Good matching of ionic radius of the exchanging ions is required to minimise residual stress which may cause stress birefringence in the finished waveguide.

SOL-GEL DERIVED, ORGANIC-INORGANIC PLANAR WAVEGUIDES

During the 1990s, the introduction of organic functionality to a sol-gel derived siloxane matrix has opened up the richly diverse, new materials field of organic-inorganic hybrid materials with tremendous potential for photonics [11]. These are composite materials on a molecular scale with potentially synergistic macroscopic properties. Here, discussion is limited to materials wholly or partly based on a sol-gel derived siloxane matrix. Other network and modifying inorganic lattices and/or discrete inorganic dopants, such as microcrystallites, may be present. The organic species may be molecular, polymeric, or polymerisable *in situ* during synthesis of the hybrid material. Sol-gel facilitates control over the degree of penetration of the organic and inorganic parts at the molecular level. Uncontrolled phase separation of the organic and inorganic parts does not appear to be a problem in many cases over wide compositional ranges.

Sanchez and Ribot [12] have suggested that such hybrid materials can be conveniently divided into two general classes. Class 1 corresponds to hybrid systems in which organic molecules, oligomers or organic polymers are simply 'embedded' in the inorganic matrix (or *vice versa i.e.* inorganic species embedded in an organic matrix); the organic and inorganic components are attracted by weak interactions only, such as hydrogen bonding, electrostatic attraction or van der Waals forces. Class 2 corresponds to hybrid materials where the organic and inorganic components are chemically bonded to each other through strong covalent, or ionic-covalent, bonds (and hence 'grafted'). Class 2 materials may exhibit weaker organic-inorganic bonding at sites elsewhere in the matrix alongside the strong covalent bonding.

In all, this leads to great flexibility of nanoscale design of new materials,

Synthesis and shaping of Class 1 materials

To make Class 1 materials, water soluble molecular, polymeric or polymerisable organics may be stirred into the initial sol-gel precursor mix of silicon tetraalkoxides. During processing the organics become clathrated in the growing siloxane matrix. Molecular species may also be diffused into the wet gel or xerogel. Undoped xerogels heated at 600-800 °C to form porous glass then cooled to ambient may be back-impregnated with molecular organic species; residual porosity may then be filled with PMMA (polymethylmethacrylate), lowering light scattering and facilitating optical polishing [11].

Undoped xerogels are rather unstable materials, being porous and hygroscopic, and containing many uncondensed silanol groups. Addition of organic molecular and oligomeric organic dopants do not improve these properties substantially. In contrast, incorporation into the sol-gel precursor mix of a vinyl functionalised

monomer which was polymerised *in situ*, has allowed production of large transparent discs 100 mm diameter and 5 mm depth [13].

Synthesis, structure, linear optical properties and shaping of Class 2 materials

The synthesis of class 2 materials (*i.e.* ormosils-organically modified silicate) relies on non-cleavage of the bonding unit [Si-C-organic functionality] during the sol-gel processing so that the organic functionality is network bonded to the silicate matrix in the finished material. A useful synthetic strategy is to use precursor alkoxides $(RO)_xSi(R')_{4-x}$. The persistent organo- group attached directly to silicon, R', may be a saturated/unsaturated, chain/cyclic, aliphatic/aromatic group and may bridge to other silicon centres. Precursor blends may be used. Ideally, the desired macroscopic properties of the hybrid materials may be designed in at the molecular level. Such materials may be synthesised, in general, below 100 °C,

In our laboratory, we have investigated the structure of a range of simple class 2 materials based on $TMOS_nRTAS_{100-n}$ (where TMOS is silicon tetramethoxide; R is the pendant organo group: methyl, propyl, vinyl, phenyl or propyl-methacrylate, and RTAS is organotrialkoxysilane) using solid state NMR (nuclear magnetic resonance spectroscopy) which distinguishes and quantifies Si sites in the final material [11]. Our studies have shown that the total condensation efficiency of the silicate matrix improves with increase in the molar proportion of organotrialkoxysilane up to at least 70 mol%. The greater condensation implies that there are fewer silanol groups left in the matrix, which means fewer sites for hydrogen bonding to water. Infrared spectroscopy of the samples supports these conclusions. Many ormosils prepared by acid catalysed sol-gel reaction exhibit extremely low BET (Brunauer-Emmett-Teller) surface area, which augurs well for material robustness. It remains unclear whether the limited water permeability of the ormosils is along nano-channel porosity or through 'free volume' as organic polymers. Interesting work by the group of Babonneau [14] has demonstrated, by means of solid state NMR, that co-condensation occurs in mixtures between organotrialkoxysilanes, di-organodialkoxysilanes and tetraalkoxysilanes. However, when organotrialkoxysilanes are mixed instead with Zr or Ti tetraalkoxides, for refractive index modification, then although Si-O-Zr and Si-O-Ti oxo bridges initially form, they subsequently cleave [15, 16] during the sol-gel ageing process, resulting in self-condensation reaction and hence decreased homogeneity at the molecular level.

For photonic waveguide applications, low optical attenuation in the desired spectral region and ability to reproduce linear optical properties are prerequisite. Extrinsic absorption such as residual O-H should be minimised, as should extrinsic scattering due to structural inhomogeneities and pores. As discussed in the

preceding paragraph, there is mounting evidence that low extrinsic attenuation materials can be synthesised successfully at temperatures below 100 °C. The intrinsic absorption in the near-infrared spectral region has been studied in our laboratory for simple ormosil systems [17]. Those vibrational functional groups having strong absorption bands in the spectral region ~3-5 μm have the richest near-infrared signature. Hence for ormosils, the O-H, C-H and N-H cause intrinsic absorption in the near-infrared.

The ease of achieving crack-free materials is intimately bound up in the type and amount of organic modification. However even the most simple ormosil, consisting of a methyl modified matrix, shows a marked resilience to cracking compared to inorganic sol-gel derived siloxane matrices. Films of several micron's thickness can be laid down in one step by spinning, dip-coating or doctor-blading, and dried in < 24 h.

Progress in waveguides made from class 2 ormosils based on the organo functionality propyl-methacrylate

Schmidt and coworkers [18] devised the generic sol-gel synthesis using trimethoxysilylpropylmethacrylate in the presence of methacrylic acid, with Zr tetraalkoxide for refractive index modification, to produce photocurable waveguides. This approach for making ormosil photonic devices has so far proved by far the most popular amongst workers in the field. Schmidt's group also first demonstrated patterning of waveguides

In our laboratory, solid state NMR studies [19] of the similar system $\text{TMOS}_{50}\text{TMSPM}_{50}$ (where TMSPM is trimethoxysilylpropylmethacrylate) have shown that carrying out free radical polymerisation of the organic species during the sol-gel processing substantially decreases the overall condensation of the silicate matrix. It may be inferred that this decrease is accompanied by increased residual silanol in the finished material. Micropatterning of Y-junction channel waveguides by embossing during the photocuring has been carried out [19]. Good optical quality, unclad, thin film waveguides of this system prepared without photocuring were deposited on silica substrates [20]. The addition of Zr tetra α -propoxide in the precursor mix gave a refractive index increase of the waveguides at 632.8 nm from 1.4768 to 1.52218 for a rise in atomic fraction $[\text{Zr}/(\text{Zr}+\text{Si})]$ from zero to 0.296. Higher additions of the Zr precursor led to cracking of the films.

Returning to the system proposed by Schmidt's group, which differs from the system discussed in the previous paragraph by not including TMOS and by applying free radical polymerisation, Najafi *et al* [21] have claimed optical loss as low as 0.3 dB cm^{-1} at 1.55 nm yet Mennig *et al.* [22] dispute this claim putting the optical loss at least an order of magnitude higher. Spurred by this dispute in ultimate loss, Mennig and coworkers [22] attempted to eradicate OH and CH spectral absorption from this system by applying a nonhydrolytic route with use of fluoroalkyl-modified

chlorosilane precursors eventually achieving 0.12 and 0.33 dB cm^{-1} at 1.3 and 1.55 nm, respectively.

Andrews and Najafi [21] have monitored the rise in refractive index with UV (ultraviolet irradiation) exposure time of the Schmidt type sol-gel system. They reported a rise of index from 1.518 by 0.013 after 60 minutes exposure followed by a post-cure heat treatment of 140 °C/60 minutes to densify and stabilise the structure. Using mask alignment techniques to make channel waveguides, these authors have shown that the channel profile is sensitive to many processing parameters particularly: sol and photo-initiator type, ageing time of sol, gap between the mask and sol-gel film and UV exposure time [23]. Directional coupler devices and gratings have been made [24, 25].

Etienne *et al.* [26], using a similar sol-gel system have demonstrated multilayer structures of channel waveguides.

SOL-GEL DERIVED, INORGANIC NON-OXIDE PLANAR WAVEGUIDES

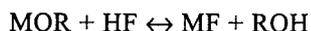
The current telecom. signal wavelengths are 1.55 and 1.3 nm, effectively straddling the irreducible, overtone hydroxide absorption band in silica. The Er^{3+} doped silica fibre amplifier operates around 1.55 nm, yet no optical amplifier is available for 1.3 μm in a silica host glass, effectively limiting the multiplexing capability. The reason is that the phonon energy of silica glass is high relative to the energy level spacing in potential optical amplifier dopant ions. For instance, Pr^{3+} exhibits a fluorescent transition at 1.3 μm from $^1\text{G}_4$ excited state to the terminal level $^3\text{H}_5$, but between these states lies the intermediate level $^3\text{F}_3$. The silica host mediates rapid non-radiative decay from the excited state to the intermediate level, thus preventing a population inversion.

To produce an optical amplifier for 1.3 μm , a host with a much lower phonon energy must be found. Moreover, a host with lower phonon energy than silica would open access to many other potentially useful rare earth transitions further into the infrared for a range of applications like waveguide optical sources and optical sensors. Both halide and chalcogenide glasses, based on heavier atoms, or ions, and weaker network bonding than silica, are lower phonon energy hosts than silica. These glass types are not generally accessible by vapour deposition, except for very simple systems, and glass melting routes are usually used. Development of low temperature sol-gel routes would enable thin films of these glasses to be made for planar waveguide operation. Understanding of the chemical mechanisms required to prepare non-oxide amorphous materials by sol-gel is in its infancy.

Fluoride glasses by sol-gel

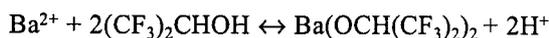
Infrared-transmitting, heavy metal fluoride glasses such as $\text{ZrF}_4\text{-BaF}_2\text{-LaF}_3\text{-AlF}_3\text{-NaF}$ (ZBLAN) were first reported in 1974 and were developed as low loss optical

fibres during the 1980 s [27]. Because the temperature coefficients of vapour pressure of the component fluorides are not well matched, there is no vapour route and bulk glasses are obtained by means of glass melting. Sol-gel processing to obtain amorphous ZBLAN was first described by Melling and Thomson [28] using fluorination of metal alkoxides by means of BF_3 . Later work involved fluorination of metal alkoxide derived gels with either gaseous or aqueous HF at $\leq 200^\circ\text{C}$ [29] but residual carbon and hydroxyl spoilt the optical properties. The suggested sol-gel reaction is:



Subsequent reactive atmosphere processing at 800°C in SF_6 produced good optical quality glass (no optical loss measurements have been reported) but ultimately represents no advantage over conventional glass melting of fluorides, except as a means of engineering thin films.

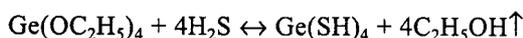
More recently, it has been reported that rare earth and alkaline earth metal fluorides in crystalline form may be synthesised by means of sol-gel processing [30] from the metal fluoroalkoxides *e.g.*:



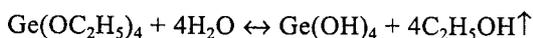
Treatment of $\text{Ba}(\text{OCH}(\text{CF}_3)_2)_2$ with an HClO_4 catalyst in dry $\text{C}_2\text{H}_5\text{OH}$ surprisingly produced BaF_2 from X-ray diffractometry. Thus fluoroalkoxides appear attractive as precursors for sol-gel processing of fluoride glasses.

Sulphide glasses by sol-gel

Sol-gel preparation of GeS_2 by H_2S treatment of germanium ethoxide was first described by Melling [31], but Seddon *et al.* [32] showed that the X-ray diffraction pattern reported by Melling for this product largely corresponded instead to hexagonal GeO_2 . Seddon *et al.* repeated the preparation and were able to make products which were more X-ray amorphous, although granular in appearance, but with good infrared evidence of a large proportion of GeS_2 present. The suggested reaction scheme is thiolysis (analogous to hydrolysis) and condensation:



Oxide contamination is thought to arise from unwanted hydrolysis as follows:



Sanghera and Aggarwal [33] have recently demonstrated that the presence of Er^{3+} catalyses the gelation

and appears to encourage more complete reaction of precursors. By working in very dry conditions they have produced largely GeS_2 as evidenced by measurement of T_g and crystal growth at higher temperatures to monoclinic GeS_2 ; thin films were produced. However, gels were still particulate and exhibit relatively high surface areas. Martins *et al.* [34] investigated methods of synthesis using germanium tetrachloride, or tetraethoxide, with sulphide sources of thiourea ($\text{C}(\text{NH}_2)_2\text{S}$), thioacetamide ($\text{CH}_3\text{C}(\text{NH}_2)\text{S}$) or H_2S . Films on silicon substrates were produced and refractive indices, measured by ellipsometry, gave insight into the relative proportions of germanium oxide and sulphide. Films prepared by H_2S treatment of GeCl_4 had the best optical quality but optical loss has not yet been reported.

CONCLUSIONS AND FUTURE PROSPECTS

- Large bulk high silica tubes made by sol-gel processing for overlapping vapour-deposited fibre-optic preforms appear not viable for future commercial production.
- SC-RTA is proving a successful approach for making silicate based inorganic sol-gel derived waveguides in a reasonable timescale, and with optical properties which compete well with those achieved with other technologies.
- Great scope is available for the future development of organic-inorganic materials for photonics.
- Non-oxide glass films made *via* sol-gel should receive more attention. Use of fluoroalkoxy precursors for fluoride glasses should be investigated. Germanium tetrachloride with H_2S treatment for germanium sulphide sol-gel derived glasses appear promising. The technology should be extended to other chalcogenide glass-forming systems.

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