Towards better control of sol-gel film processing for optical device applications

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This paper reviews work carried out by the authors in developing nanoporous sol-gel films as hosts for semiconductor crystallites, for applications in nonlinear integrated optics, including aspects of fabrication, characterisation and modelling. Particular attention is given to three novel techniques—optospinography, molecular probe ellipsometry and pore capping, as well as prospects that have been raised from their outcome.

1. Introduction

Glasses doped with nanoparticles of semiconductors or metals have been and are being widely investigated for applications in nonlinear optics. Such materials can be fabricated by a traditional melt route, but the sol-gel technique, in which glasses are formed from organic precursors by low temperature polymerisation reactions, offers attractive advantages in terms of flexibility of composition and structure. Essentially the sol-gel process consists of three steps: first, a colloidal suspension of oxide particles (the ‘sol’) is formed by hydrolysis and condensation of an alkoxide precursor; then the sol is dried such that further condensation creates a semi-rigid ‘gel’; finally, heat treatment of the gel is used to eliminate remaining organic ligands and to complete densification. The method has been widely studied for the fabrication of both bulk glasses and films, the latter being formed typically by dip or spin coating of the sol. In recent years, glass films with thicknesses of several microns or more have been fabricated by the sol-gel route, by using an iterative process of spin coating and high temperature rapid thermal annealing. In this way the high shrinkage stresses which usually limit film thickness are eliminated.

The spin coated sol-gel film is usually porous, and thus can be used as a host matrix for nanoparticulate dopants. This approach is, in principle, more practical than a priori sol doping, in which dopants or their precursors are added to the liquid
sol before film formation. In this latter case, incompatibility among constituents may arise, and alteration of the glass formation chemistry by the dopants means that re-engineering of the fabrication process is required for each host/dopant combination. In the former case, which we call ‘pore doping’, a set of nanoporous passive films can act as universal hosts for a variety of dopants.

While applications exist for bulk nonlinear materials, our interest has been in guided wave devices for applications in optical communication systems. In particular, the silica-on-silicon configuration is promising for guided-wave optical devices.
that are a good match to optical fiber networks. Here the challenge for nonlinear components is to fabricate films of varying refractive index which have sufficiently low stress to allow layer thicknesses suitable for channel waveguides (from 2.5 \( \mu \text{m} \)), while retaining sufficient porosity for dopant insertion. Sol-gel offers high potential for a range of integrated optical components, including passive and amplifying functions as well as nonlinear ones. However, practical exploitation in integrated optics depends on the processes being precise and well controlled, repeatable, and reliable, and much work remains to be done in sol-gel film technology to satisfy these requirements.

Spin coating is widely used in modern optical and microelectronic industries, and has been reported since the beginning of the century.\(^4\) However, understanding of its underlying physics remains limited, a fact attributed to the lack of experimental data for the evolution of various parameters during the process,\(^5\) leading to a need for new evaluation tools. This is particularly true of sol-gel, where there is a higher degree of complexity in the polymerisation chemistry than for the spinning of organic polymer films. Once fabricated, sol-gel films present additional characterisation challenges. Where the intention is to insert dopants into the pore structure, it is vital to measure, and as far as possible to control, total porosity and pore size distribution.\(^6\) However, standard measurement techniques which have been developed for bulk materials are not readily adapted to use with films.

This paper, rather than being an exhaustive review of our work at Imperial College on materials for nonlinear integrated optics, focuses on two novel characterisation techniques that are already contributing to our understanding of sol-gel film formation, namely “optospinography” (OS) for spin coating and “molecular probe ellipsometry” (MPE) for pore characterization. To illustrate the link between these techniques and progress on fabrication of semiconductor doped sol-gel waveguides, we review selected aspects of this latter work, including a “pore capping” technique which enables heat treatment of the film without loss of its desired composite properties. An illustration of the overall processing is shown in Fig. 1.

2. Optospinography

2.1. Overview

Inspired by post-process measurements, as performed by the semiconductor industry for decades, a number of analytical models have been proposed for spin coating for a range of materials. These models variously view the process as flow of a Newtonian liquid of constant viscosity,\(^7\) steady-state flow for Newtonian and non-Newtonian liquids,\(^*\) followed by solvent evaporation at a constant rate,\(^9\) by assuming equilibrium in solvent concentration between film surface and atmosphere,\(^10\) by assuming a linear mass transfer coefficient for solvent transport,\(^11\) and by approximating liquid viscosity as a decreasing function of film thickness.\(^12\)

On the other hand, empirical expressions for final film thicknesses were obtained, such as for electron resists with a variety of solvents on glass substrates,\(^13\) and for
a variety of polymers with different viscosities on silicon substrates, including the contribution of solvent evaporation, but still these originated from post-spinning measurements, while comparison with existing model predictions was qualitative at best.

More recently, a finite-element approach was reported to account for the coupled flow and mass transfer equations for spin coating, seen as a fully transient process, leading to the prediction of a possible “solid skin” formation, which would be responsible for coating defects if convective flow had not previously ceased. This prediction is in direct contradiction with a previous, semi-quantitative model proposed for the spin coating mechanism, where an increasing “crust” is postulated, as concentration exceeds a critical value at increasing depths, to account for the resulting film structure.

In the next two sections, we describe how the OS technique is now showing us essential features of a spinning film in real time, which have contributed to unveiling strengths and weaknesses of the early models, as well as to shedding some light on the conflict between the various models.

2.2. Experimental

Well over a hundred film samples were produced by, and monitored during, spin coating in this investigation, with varying sol compositions, ageing times and speeds of rotation. The standard composition started from the tetraethylorthosilicate (TEOS) precursor diluted in ethanol at 1:1 vol, followed by two 0.1 M HCl hydrolysis steps with 1:1 molar ratio of water to TEOS added at each step (the process is described in more detail in Sec. 3.2). This composition produced consistently uniform films for sol ageing times in the range of one day to several weeks, provided not too small an amount of sol was deposited. The silicon substrates, 25 mm in diameter, were in most cases systematically flooded before spinning, which was carried out at room temperature.

In the experimental setup illustrated in Fig. 2, analysis is made of a laser beam reflected from the sol-gel film on a silicon wafer, which spins at speeds in the range of 700-3000 rpm. The ratio between the sample and the reference signals is computed after processing by an A/D converter, with readings taken every 10 ms. Alignment of the system is critical to insure that the illuminated spot remains at the center of the wafer at all times. Spinning times are typically up to 20 s in open air, depending on process parameters, such as speed of rotation and sol composition (varying degrees of ageing and dilution in ethanol, pH = 1.0-2.2, giving silica and silica/titania coatings).

On the spinner plate, the samples were held mechanically, either by fitting in a rectangular slot surrounded by clamps or in a fixed round-shaped rubber ring. In this way, the center of rotation does reasonably well represent the overall sample for Newtonian flow, as opposed to most commercial spinner configurations, where the vacuum chuck may induce significant thickness variations.”
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An optospinography setup, which allows interferometric monitoring of film optical thickness variations during spin coating, with a HeNe laser source, followed by Att. attenuator, M. mirror, BS. beam splitter, L1-3. condenser lenses, Ch. 1, 2. Reference and sample detection channels (from Refs. 19).

Fig. 2. An optospinography setup, which allows interferometric monitoring of film optical thickness variations during spin coating, with a HeNe laser source, followed by Att. attenuator, M. mirror, BS. beam splitter, L1-3. condenser lenses, Ch. 1, 2. Reference and sample detection channels (from Refs. 19).

The resulting optospinogram is an interferometric representation of the temporal evolution of the spinning film. Typical curves of modulated reflectance can be seen in Fig. 3(a) for a saturated solvent atmosphere, and for open air in Fig. 3(b), with otherwise the same initial conditions, for production of silica films on silicon at 2000 rpm. The process can be divided into four stages: (I) pre-spinning oscillations in the liquid, (II) ultrafast convective mass flow, (III) convection-evaporation, and (IV) limited evaporation from the gel. Detailed discussion of each stage can be found in Ref. 19.

Fig. 3. Typical optospinograms, at 2000 rpm: (a) in a saturated solvent atmosphere; (b) in open air, where reflectance values are as calibrated from that of the bare silicon substrate, for which a refractive index $n = 3.858 + i0.018$ was taken (from Refs. 19).
2.3. Discussion

2.3.1. Early Models

From the successive extremes in the reflectance curve, optical thickness variation in quarterwave units can be plotted, as in Fig. 4, versus $t^{-1/2}$. This is obtained from the optospinogram where evaporation was restricted by the saturated solvent atmosphere, with regard to the EBP model, which predicts a thickness time dependence in the form

$$d = d_0 [1 + (d_0/b)^2 t]^{-1/2}; \quad b^2 = 3\eta/4w^2,$$

where $d_0$ is the initial thickness, $w$ the angular speed, and $\eta$ the kinematic viscosity (i.e., viscosity per unit density).

For times $t \gg (b/d_0)^2$,

$$d \sim bt^{-1/2}.$$

This prediction seems successful in saturated-solvent atmospheric conditions, particularly in the linear region corresponding to a constant $\eta$. The model, however, is not valid where evaporation plays a significant role. More sophisticated
models, without experimental support, have been developed to take evaporation into account.

2.3.2. Latest Models: Sol-To-Gel Transition

The gelation process in drying bulk sols has been closely monitored by a variety of methods,” including measurements of apparent viscosity variations\(^{21}\) and cryogenic transmission electron spectroscopy.\(^{22}\) On the other hand, information is still scarce on the gelation process in films.

As we focus our attention to the latest stages of sol film spin-off,\(^{23,24}\) in the optospinogram for a typical sol composition, passage to the latest stage of limited evaporation is smooth, indicating a continuous, glass-like transition. A slight change in composition (replacement of 0.1 M HCl by equal half-volumes of 0.1 M HCl and 0.1 M Acetic Acid, shifting the measured pH of the catalysed water from 1.0 to 2.2) lead to films that would crack much more readily during spinning, thus exhibiting spots in a variety of colours under fluorescent light illumination. For this sol, optospinography has shown a discontinuous, or very fast inflection, transition to the last stage.\(^{18}\)

Such a change at the onset of the last spinning stage can be explained by the formation of a premature diffusion barrier that nearly prevents solvent evaporation. Therefore, a dilute sol remains below, which, by centrifugally stretching the overlayer, accounts for the higher occurrence of cracked, nonuniform coatings. In this situation, the “solid skin” model\(^{15}\) seems to be more successful than the “growing crust” model.\(^{16}\)

2.4. Prospects

Although the process under study is fabrication of silica spin-on glasses by sol-gel, main aspects of the results described here might well be applicable to a larger class of polymers.

As OS allows direct insight during the spin coating process, it is now possible not only to pinpoint how initial process parameters influence the evolution of film performance, but also to attempt their controlled, systematic modification during the process. Efforts in this direction are now under way in our laboratories.

3. Molecular Probe Ellipsometry

3.1. Overview

Considerable work has been done in porosity characterisation in bulk gels, generally through the gas adsorption BET method,\(^{25}\) using nitrogen or krypton as the adsorbing gas to give the internal surface area. From the variation of adsorbed mass with partial pressure (the isotherm), a pore size distribution can be inferred via Kelvin’s equation.\(^{26}\) However, for integrated optics and other applications where sol-gel film layers are required, the BET method becomes insensitive due to the
limited surface area available for the measurement, and the consequently low mass of adsorbed gas. One method developed to circumvent this difficulty consists of measuring changes in acoustic velocity with vapour pressure on a film that was previously deposited on a surface acoustic wave transducer. Results comparable to those of BET are obtained, but fabrication of a special substrate is required for each film, and still there is no direct information on pore sizes. In addition, pore sizes in acid-catalysed sol-gel films are typically on a nanometre scale, where the validity of Kelvin’s equation is in question.

An IR spectrophotometry alternative has been recently proposed. It is based on the comparison between measured film adsorption, for the main Si-0 adsorption band, and that calculated for a corresponding fully dense material having the same thickness and at the same wavelength. Volume fraction porosity is then determined with simplicity, but internal surface area and pore size distribution cannot be derived in this way.

In a pioneer work, it was shown in this laboratory by Martin and Green that changes in refractive index with relative humidity could be measured by ellipsometry, where the film was deposited on a reflective silicon substrate and water was the adsorbate. As in BET, this method gives some indication of the overall structure from surface area adsorption, as inferred from the isotherm shape. For micropores, however, still only quite crude information about pore sizes is obtained.

For a more direct indication of porosity and pore size distribution, we have extended the above ellipsometric technique by probing the film matrix with near-spherical molecular adsorbates of various sizes. We refer to this method as molecular probe ellipsometry (MPE). From observation of the change in apparent total pore volume with adsorbate species, we can conclude what fraction of the volume consists of pores of a specific size range.

3.2. Experimental

The film fabrication process for silica films is again based upon the hydrolysis and condensation of tetraethylorthosilicate (TEOS), with in this case tetrapropylorthotitanate (TPOT) added to fabricate silica-titania films (all the porosity results below are for silica films unless otherwise specified). A typical sol is made by mixing equal volumes of TEOS and ethanol, then adding water with an acid catalyst to obtain water to TEOS molar ratio of $R = 2$. For some experiments, additional deionised water is added to give solutions with higher $R$ values (while maintaining the molar ratio TEOS:HCl). In other cases, different acid types or concentrations are used. After mixing, the solution is placed in a refluxing bath at 70°C for several hours. The solutions are then aged for 24 hours at room temperature, before being diluted with an equal volume of ethanol and stirred for 10 minutes, to give the solution used for spin coating. To fabricate silica-titania films a TPOT/ethanol (1:1 Vol.) mixture is added after the refluxing stage, with only half of the acid ($R = 1$) being added before the reflux, and half after the TPOT is added. The sols are dispensed
on silicon wafers or glass substrates, through a 0.1 μm filter, and thereafter the substrate is spun at 2000 r.p.m. in air for 15 seconds. The coated substrate is baked in air for 30 minutes.3

The MPE technique is illustrated in Fig. 5. On the sample stage of an ellipsometer, the film is inserted in a sealed work chamber, through which nitrogen is passed, either dry or bubbled through a liquid adsorbate.

![Fig. 5. Schematic diagram of apparatus for molecular probe ellipsometry — MPE (from Ref. 6).](image)

At first, a high flow of dry nitrogen is passed in order to empty the film pores of any condensed adsorbate. The flow rate is then reduced to a typical value of 1000 sccm for 15 minutes, after which an initial measurement of refractive index can be taken.

After this measurement, the sample is exposed to nitrogen that has been bubbled through a liquid adsorbate, typically at 100 sccm for 15 minutes. Comparison between measured film thicknesses for dry and wet atmospheres indicates that no bulk condensed overlayer is formed, while thermocouple data from inside the work chamber ensures that no significant temperature drift is caused by vapor flow.

In each measurement, the refractive index is allowed to stabilize before recording. This can be particularly slow when water is the adsorbate. If the film has been processed at high temperature, internal surface OH groups will have been driven off, but at room temperature the surface will rehydroxylate if the pore structure allows access by atmospheric water. Complete surface hydroxylation is typically obtained after the samples are kept enclosed in stable room conditions for a few days, after which reproducible porosity results are achieved.

In Figs. 6 and 7, the fractional porosity, calculated from the difference in refractive index measured in dry and wet nitrogen as described below, is shown as a function of film heat treatment temperature. In the former case the effect of acid catalyst concentration is seen on this evolution, while the latter indicates the effect of SiO₂/TiO₂ ratio.

Evolution of the porous film structure can be well monitored here. The highest volume fraction porosity in silica films is observed in the 300°C to 500°C region, where water, organic species and hydroxyl groups are expelled from the pores, but the temperature is low enough so that no significant densification occurs. Porosity
Fig. 6. % Porosity vs. annealing temperature for sol-gel silica films made with different acid concentrations (from Ref. 3).

Fig. 7. % Porosity vs. annealing temperature for sol-gel silica/titania films with different titania concentrations. Here "S" and "T" stand for the nominal molar % of SiO$_2$ and TiO$_2$, respectively (from Ref. 3).

is increased for low catalytic concentration, while the main effect of titania addition is reduction of the densification temperature.

Water is the smallest adsorbate molecule used in these studies, and therefore accesses the largest possible porosity; however, we have observed small further increases in refractive index and densification above 800°C, indicating that some porosity remains which is inaccessible to water.
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For a variety of adsorbates, MPE results of fractional apparent pore volume vs. adsorbate size, and their dependence on basic process parameters, are exemplified in Figs. 8 and 9. Here, comparison is made between sols made with different acid concentrations and for films annealed at different temperatures. Six different adsorbates were used: water, methanol, carbon tetrachloride, cyclohexane, 1,5,9-cyclododecatriene and dicyclohexano-24-crown-8, corresponding to a succession of increasing effective diameters, as shown in Table 1.
Table 1. Adsorbate refractive indices and effective probe molecule diameters, as estimated from Van der Waals atomic radii, $^{31}$ and bond length data. $^{32}$ (from Ref. 33).

<table>
<thead>
<tr>
<th>Probe Molecule</th>
<th>Diameter (Å)</th>
<th>Refractive Index (nD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water (H$_2$O)</td>
<td>3.28</td>
<td>1.333</td>
</tr>
<tr>
<td>Methanol (CH$_3$OH)</td>
<td>4.72</td>
<td>1.329</td>
</tr>
<tr>
<td>Carbon Tetrachloride (CCl$_4$)</td>
<td>6.49</td>
<td>1.460</td>
</tr>
<tr>
<td>Cyclohexane (C$<em>6$H$</em>{12}$)</td>
<td>7.36</td>
<td>1.426</td>
</tr>
<tr>
<td>1,5,9-Cyclododecaterene (C$<em>{12}$H$</em>{18}$)</td>
<td>9.30</td>
<td>1.507</td>
</tr>
<tr>
<td>Dicyclohexano-24-Crown-8 (C$<em>{24}$H$</em>{44}$O$_8$)</td>
<td>14.00</td>
<td>1.490</td>
</tr>
</tbody>
</table>

In Fig. 8, we see that the weakly acidic catalyst produces an increased range of pore sizes, whereas for the other cases most pores are inaccessible to adsorbates larger than water. Figure 9 shows the thermal evolution of the pore size distribution, and indicates that the shrinkage does not in this case greatly affect this distribution, apart from a fairly uniform reduction. It is this type of information which is valuable in optimising process parameters which lead to the desired pore structure for doping while being compatible with thick multi-layer deposition.

3.3. Discussion

Experimental results are interpreted under the assumption that all accessible pores are either completely devoid of or completely filled with the adsorbate species in dry or saturated atmospheres, respectively. Pore volume and refractive index of the solid skeleton are determined by an extension of the Lorentz-Lorenz relation $^{34}$:

$$\frac{(n_f^2 - 1)}{(n_f^2 + 2)} = (1 - v_p)^2 \frac{(n_s^2 - 1)}{(n_s^2 + 2)} + v_p \frac{(n_p^2 - 1)}{(n_p^2 + 2)}$$

where $n_f$, $n_s$ and $n_p$ are the refractive indices of the film, solid skeleton and pore material, respectively, while $v_p$ is the volume fraction porosity. Measurement of $n_f$ for both dry and saturated films allows determination of $v_p$ and $n_s$, where for $n_p$ the bulk adsorbate value is taken in the saturated case, and that of air in the dry case.

This is not a rigorous calculation; for example, the Lorentz-Lorenz relation as used, which is based on taking the mean polarisibility of a composite material, does not include effects of shape anisotropy. $^{30}$ There is also the possibility of interior
voids being missed where bottlenecks block access of the adsorbate, although for the purposes of doping, accessibility of pores is the crucial information. Overall, the consistency of results obtained to date indicates that we have a reasonably good approach to distinguish major trends in pore formation.

4. Pore Doping and Crystallite Trapping

4.1. Overview

Prospects for producing semiconductor crystallites with significant third-order optical nonlinearity have been raised in theory, by experimental observation of conventional glasses and, later, in a sol-gel glass environment. Since high purity glasses are obtainable by the sol-gel route, this raises the possibility of avoiding the photodarkening problems found in conventionally fabricated semiconductor doped glasses.

Active channel waveguides could then be produced by introducing these dopants into sol-gel derived silica-on-silicon, with relevance to Kerr effect switches and other nonlinear integrated optical devices. According to the specific application, the semiconductor band gap could be tailored by proper choice of dopants, as well as by control of crystallite sizes. It is thought that these sizes, when comparable to the electron or hole Bohr radii in the semiconductor, induce excitonic quantum confinement and that growth of the semiconductor crystallites can be limited by the pore walls in the glass host.

In what follows, we describe our observations of quantum confinement through the blue-shifted absorption spectra of cadmium sulphide crystallites, as well as an indication that their growth in the sol-gel film matrix can be limited by pore sizes. We achieved this indication with more clarity after devising a technique to keep the CdS crystallites inside the pores when the film is subjected to thermal treatments, also described here.

4.2. Experimental

The sol was prepared as described in Sec. 3.2, and spin coated at 2500 rpm for 30 s. The resulting films were annealed at different temperatures, corresponding to varying amounts of porosity. They were then soaked in an aqueous solution of the cation salt for ten minutes. Before being dried with nitrogen gas, the films were removed from the aqueous solution and rinsed quickly in deionised or distilled water. This last step was found necessary to prevent the formation of large crystals on the bulk surface.

The cation salt used for CdS doping was cadmium fluoride, with molar concentration of 0.05M in deionised water. We have found that the choice of cadmium salt influences strongly the resulting concentration of semiconductor crystallites, but shows no significant effect on their final particle sizes.

Once the sample surfaces were clean, they became ready for the sulphiding process. The experiment, in an oxygen-free atmosphere, was carried out as follows.
At first, the samples were placed in the reaction chamber at 175°C, and left in a sealed condition for 45 minutes to fully remove molecular water from the pore structure. Since previous experiments had showed high process sensitivity to humidity conditions, dry nitrogen was allowed to pass through the chamber at a rate of 2 ml/s for 10 minutes. After the nitrogen valve was closed, dry hydrogen sulphide gas was allowed to flow at a rate of 0.8 ml/s for 10 minutes. The excess of hydrogen sulphide was turned into nitrate before release to the atmosphere, by exposing it twice to a lead nitrate solution, whereupon reaction PbS crystals were precipitated in the containers shown in the figure. After sulphiding, care was also taken to eliminate any traces of hydrogen sulphide that could remain in the chamber, which was opened only after 10 minutes of dry nitrogen flow through the system.

4.3. Results and Discussion

The sulphided films turn visibly yellow, a confirmation of CdS crystallite formation. These doped films then require further thermal treatment to seal the pores, both to prevent oxidation of CdS and to relax inherent film stresses, which cause cracking if additional layers are deposited.

However, a series of experiments has shown the impossibility of annealing the films in air or nitrogen under standard conditions without loss of CdS, which oxidises in air and evaporates in nitrogen. With this reasoning, we developed a procedure to seal the pores before further heat treatment, by adding a high packing density layer over the doped film surface. We refer to this technique as “pore capping” (PC).

In this process, a silica overlayer is deposited by RF sputtering, which produces dense films without excessive heating of the sample. The typical overlayer thickness is 60 nm. A CdS doped silica film was half coated to compare performances with and without CT, under otherwise equal conditions. Heat treatment was carried out in air at a set of temperatures. The sample was heated for 30 minutes at 300°C, absorption spectra were taken from both halves by a UV-VIS spectrophotometer, then similarly at 400°C, and so on. Results are shown in Fig. 10.

The spectral location of the absorption curves in Fig. 10 is well-known for CdS doped glasses. Bulk CdS has an absorption edge at 510 nm, while quantum confinement in small particles increases the semiconductor band gap, as manifested in the blue shift of the absorption spectra. From a simple relationship based on the effective mass approximation, which is good in this case though not always strictly valid, a particle size can be roughly estimated from each absorption cut-off wavelength in Fig. 10. For example, this leads to a crystallite diameter of 4.4 nm for the unbaked film, and 5.8 nm for the PC processed film baked at 500°C. The same range of sizes was shown by TEM pictures of silica-titania films that were pore-doped with the procedure described above.

For the films without PC, absorption drops with increasing baking temperatures, indicating that nearly all the CdS was oxidised after annealing at 400°C, whereas the PC processed films do not appear to lose CdS as they densify. In these, the
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Fig. 10. Absorption spectra of CdS pore doped silica films with and without PC — pore capping, after baking at the temperatures indicated for 30 minutes (from Ref. 40).

absorption edge, blue-shifted with respect to bulk behaviour, shows a significant red shift after annealing at 300°C, which indicates crystallite growth. As annealing proceeds to higher temperatures, a decreasing red shift is observed, accompanied by enhancement of the curve shoulder, which implies a narrowing of the particle size distribution after a size limit is reached. Consistently with previous observations on ZnS particles, this is a clear indication that CdS particle growth is affected by the pore walls of the host glass.

5. Conclusions

Recent progress in the understanding of porous sol-gel film formation, made possible by two novel characterisation techniques, “optospinography” (OS) and “molecular probe ellipsometry” (MPE), was presented and discussed here. It was shown that OS has provided an interferometric representation of the temporal dynamics of the spin coating process, whose results have contributed in testing existing models and may allow controlled real-time modification of process parameters in the future. Subsequent MPE results were shown consistently able to determine major trends in volume porosity and pore size distribution up to pore diameters of 1.4 nm, a size range not suitable for investigation by isotherm analysis.

Now that subnanometer sensitivity of MPE has been demonstrated, we aim at extending the range of the measurement to larger pores, and to further analyse the effect of sol composition, additives and other parameters on porosity and pore size distribution. When there is substantial bottlenecking in the matrix structure, we can assess an effective pore aperture, an important parameter for evaluation of the suitability for pore doping.
We have doped nano-porous films with CdS crystallites. A “pore capping” (PC) technique was devised that prevents significant loss of desired composite properties during heat treatment, and thus allows for the appearance of clear evidence that particle growth is affected by the pore walls of the host glass, since a tightening of the particle size distribution is observed after a size limit is reached.

However, it seems premature to attempt a definite correlation between pore sizes, as measured by MPE, and particle sizes, as estimated from absorption spectra of PC processed films. Much work remains to be done for more accurate determination of both pore and particle sizes, and to characterise the interface between pore walls and crystallites, and the evolution of this interface during processing.

From a practical standpoint, we conclude that both OS and MPE techniques may become increasingly important as sol-gel fabrication, due to its wide flexibility in composition and microstructure, develops further to meet specific applications, including those with smaller band gap materials for operation at standard communication wavelengths, or with multiple dopants for extended device functionality. Also, there is a good perspective in integrated optics for PC processing of a wide range of host glass compositions and dopant species, in addition to those reported here.

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