



Anhydrous Sol-Gel Synthesis of Titania-Doped Siloxane Polymer for Integrated Optics

XINSHI LUO*, CONGJI ZHA AND BARRY LUTHER-DAVIES

Laser Physics Centre, Research School of Physical Sciences and Engineering, Australian National University, Canberra ACT 0200, Australia

xinshi.luo@anu.edu.au

Abstract. Sol-gel synthesis of organic-inorganic hybrid materials for planar waveguides and devices has received growing interest due to its low-cost processing and good suitability for doping. Titania is an important optical dopant, but homogeneous incorporation of titania in silica is difficult to be achieved by the conventional sol-gel process (aqueous system) because of the significant difference between the hydrolysis rates of the precursors. In this paper, we report an anhydrous sol-gel process for synthesising titania-doped siloxane polymers. The process consists of a hydrolysis of 3-methacryloxypropyltrimethoxysilane (MPS) with boric acid under anhydrous conditions, and a condensation with dimethyldimethoxysilane (DMDMS), diphenyldimethoxysilane (DPhDMS) and titanium ethoxide (TET). Optical characterisations for the produced titania-doped polymer were performed, and results showed that TET doping is useful for reducing the OH concentration of the synthesised polymer and is also effective for improving the optical quality of spin coatings. DMDMS and DPhDMS are favourable in reducing the birefringence and in increasing the thermostability of the material, and the methacryl groups of MPS are UV-polymerizable, which is useful for low cost fabrication of waveguides by photolithographic process. The results of ellipsometry scanning measurements show that titania is homogeneously incorporated in the hybrid matrix, suggesting that the anhydrous sol-gel process is useful for preparation of UV-sensitive titania-doped siloxane polymers for optical applications.

Keywords: anhydrous sol-gel process, waveguides, ormosil materials, optical characterisations

1. Introduction

Silica-on-silicon has become a materials technology for fabrication of planar light circuits because of their low optical losses and high temperature stability [1]. The limitations for this technology however are obvious. Silica must be processed at high temperature, which leads to problems with built-in stress. It has been known that birefringence produced by this thermal stress is a cause of unwanted polarization dependence in any resulting devices. Silica also has a very low thermo-optic coefficient, which is not desired for the devices such as digital thermo-optic switch and thermally tuneable grating.

In seeking solutions for these limitations, polymeric optical waveguides have attracted considerable atten-

tion [2, 3]. Compared with silica-on-silicon technology, planar polymer waveguides for applications as optical components in optical interconnects and optical devices have some distinguished advantages. Polymeric thin films can easily be fabricated at low temperature by various methods such as spin-coating, dipping, thermocuring, and photo-curing. These films are generally flexible and tough, and they can be conveniently patterned to fine structure by photolithography, etching, or stamping. Polymer materials also provide advantages in tuning refractive index and in maintaining low polarization sensitivity. Polymeric materials for planar optical waveguides are considered to be low cost and volume producible.

The major weaknesses of conventional polymer materials for optical applications are their propagation loss and long-term reliability. Substitution of hydrogen in the C–H of polymeric materials with fluorine

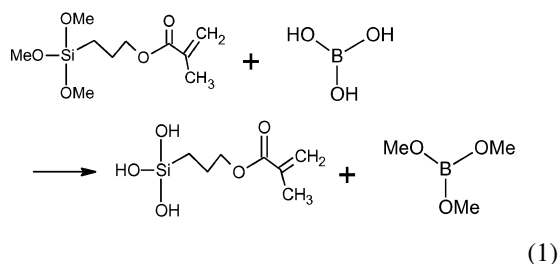
*To whom all correspondence should be addressed.

or deuterium is effective in reducing optical loss [4, 5], but this route is a high-cost technique. Organically modified silicate (ormosil) polymers have received a high attention because they provide the potential for low cost reducing optical loss by diluting the C–H with siloxane (O–Si–O) backbone, and the syntheses of ormosil polymers by sol-gel process and their applications to fabrication of planar optical waveguides have been demonstrated [6, 7]. A main concerned issue for the sol-gel derived ormosil materials for optical applications is their OH absorption because the overtone of OH vibration increases their optical losses particularly at the 1550 nm telecommunications window. This paper reports our recent work on synthesis of low OH titania-doped ormosil polymers via an anhydrous sol-gel process. Optical characterisations for the synthesised polymers and their applications to optical waveguides are also addressed.

2. Synthesis of Materials

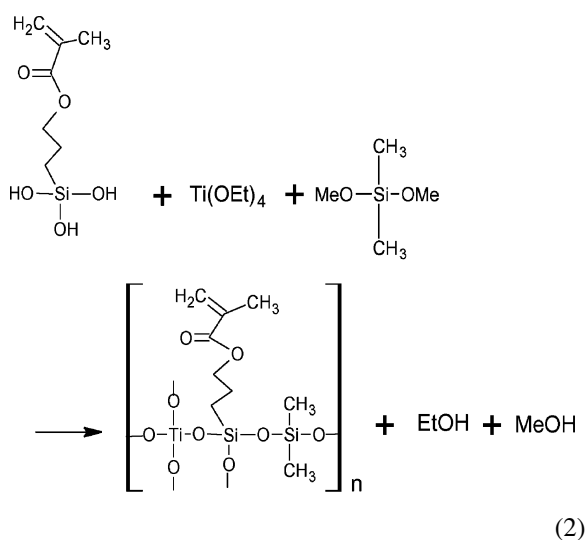
2.1. Synthesis Process

The main objective for development of appropriate materials for integrated devices rests on achieving a balance of desired and required properties, which include low optical absorption in the NIR region (especially at 1310 nm and 1550 nm), low birefringence and PDL (polarisation dependent loss), high thermo-optic coefficient, high thermal stability, and additional UV-patternability. To meet these requirements, we choose 3-methacryloxypropyltrimethoxysilane (MPS), dimethyldimethoxysilane (DMDMS), diphenyldimethoxysilane (DPhDMS) and titanium ethoxide (TET) as precursors. An anhydrous sol-gel process, consisting of a hydrolysis reaction (1) and a condensation reaction (2), was performed for ormosil synthesis. In reaction (1), MPS and boric acid were mixed at a molar ratio of 1:1 with methanol as mutual solvent. The hydrolysis of MPS was achieved by a ligand exchange reaction between the methoxy group (MeO-) of MPS and the hydroxy group (OH) of boric acid.



The hydrolysis reaction was performed under reflux conditions for 2 hours, then the volatile components such as methanol and borate ester (B(OMe)₃) were evaporated under vacuum conditions (400 mbar at 80°C) for 30 minutes, giving a highly viscous resin (assigned as resin A).

In condensation reaction (2), DMDMS and TET were added to resin A, and the mixture was refluxed at 80°C for 1 hour under nitrogen. Catalyst (a base or an acid) was found not necessary for this condensation reaction because titanium alkoxide (TET) is observed showing a self-catalysing effect. DMDMS can be partially or wholly substituted by DPhDMS for tuning the refractive index of the resulting polymer.



The by-products from the condensation such as methanol and ethanol were removed with a rotatory evaporator at 80°C under vacuum conditions (1 mbar), and the resulting organically modified titania/silica hybrid polymer was passed through a 0.2-micron filter before optical characterisations. The refractive index of the produced hybrid polymer is tuneable from 1.4760 to 1.5460 by variation of the composition of DMDMS/DPhDMS/TET/MPS. Generally refractive index rises with the increase of the concentrations of TET and DPhDMS, but decreases with MPS and DMDMS.

2.2. FT-IR Characterisation

In this paper, optical characterisations are based on the resin with a composition (molar ratio) of DMDMS/

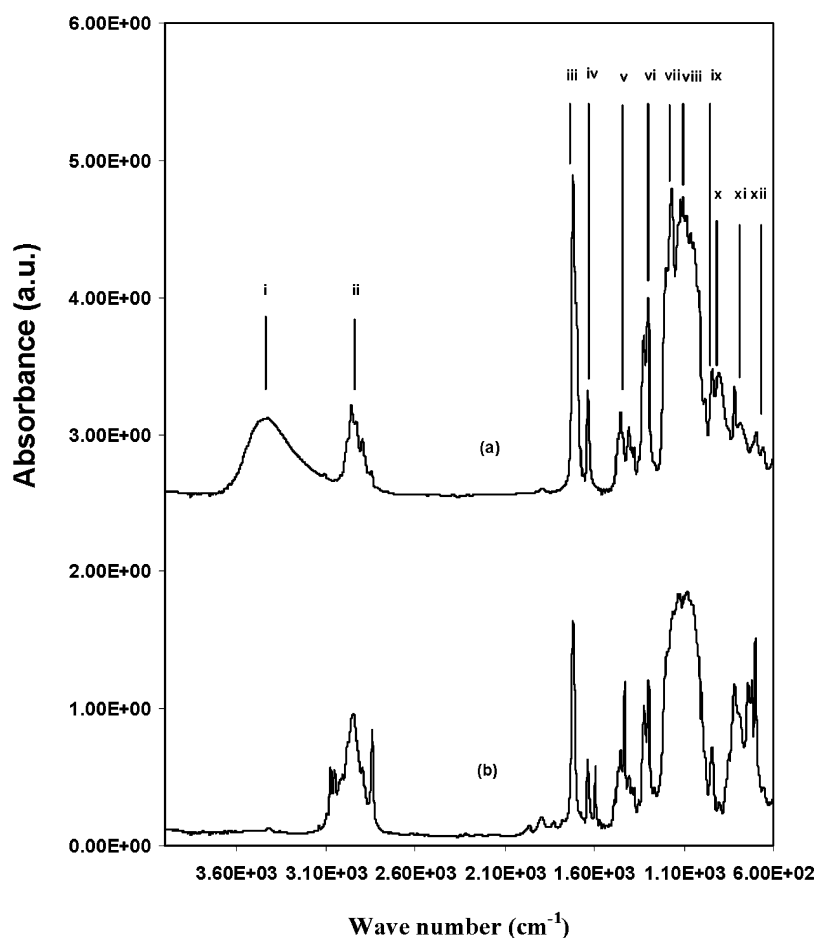


Figure 1. IR spectra of: (a) boric acid hydrolysed MPS (resin A); and (b) TiO_2 -doped ormosil polymer (resin B with DMDMS/DPhDMS/TET/MPS molar ratio of 30/50/20/100).

DPhDMS/TET/MPS 30/50/20/100 (assigned as resin B). The FT-IR spectra of resins A and B are shown in Fig. 1 (curves (a) and (b) respectively). The strong absorption (i) centred at 3400 cm^{-1} in curve (a) is assigned to silanol ($\equiv\text{Si}-\text{OH}$) vibrations because the OH absorption of boric acid is located at 3200 cm^{-1} [8]. The occurrence of silanols in resin A clearly indicates that boric acid has hydrolysed MPS.

The absence of absorption in the range from 3200 to 3700 cm^{-1} in curve (b) indicates that the material has a low OH content. For those resins without TiO_2 doping, their IR spectra always have an OH absorption peak centred at 3400 cm^{-1} , indicating that the incorporation of TiO_2 is useful for reducing OH concentrations of hybrid resins. The mechanism of TET on reducing OH-groups is ascribed to its catalysing effect on the condensation (2) between silanol ($\equiv\text{Si}-\text{OH}$) and alkoxy-

(M-OR) group. Without addition of TET, no reflux was observed within 2 hrs at 80°C ; whereas strong reflux occurred within 30 mins after adding TET, indicating that the addition of TET made the condensation (2) be feasible. Consequently, the produced hybrid polymeric resins showed low OH absorption due to the complete consumption of silanol ($\equiv\text{Si}-\text{OH}$) in the condensation (2).

Assignments of the absorption bands in Fig. 1 are useful for understanding the formation of the hybrid polymer. Absorption (ii) of curve (a) centred at 2900 cm^{-1} is assigned to the aliphatic C-H stretching vibrations, and peaks at higher wavenumber side of this band in curve (b) is due to the aromatic C-H (from DPhDMS) stretching absorption. Absorption (iii) centred at 1720 cm^{-1} is assigned to the C=O stretch, and absorption (iv) at 1640 cm^{-1} is due to

the C=C stretches. Absorptions (v) and (vi) are due to the deforming vibrations of C—H. Absorption (vii) at 1180 cm^{-1} is assigned to the Si—O—C stretches, and the intensity of this absorption is greatly reduced in curve (b), further indicating that the condensation between Si—OH and Si—OCH₃ occurred. Absorption (viii) centred at 1120 cm^{-1} is assigned to the asymmetric stretching vibrations of Si—O—Si. Absorptions (ix) and (x) at 947 and 918 cm^{-1} are assigned to the bending vibrations of Si—O—C and Si—OH respectively, and the intensity decrease in both absorptions (ix) and (x) of curve (b) further suggests the occurrence of condensation (2). Absorption (xi) centred at 810 cm^{-1} is assigned to the symmetric stretching vibrations of Si—O—Si, and the intensity increase of this band in curve (b) indicates a highly polymerised inorganic backbone (Si—O—Si) formed in the resin B. Absorption (xii) located from 670 to 770 cm^{-1} is assigned to the out-of-plane C—H deforming vibrations, and the intensity increase of this band in curve (b) is due to the phenyl groups introduced by DPhDMS.

3. Thin Film Fabrication and Optical Characterisation

The TiO₂-doped polymer resin B was mixed with a photo-initiator (Irgacure 369, CIBA) in the dark, and was coated onto silicon wafer by spin-coating technique after passed through a $0.2\ \mu\text{m}$ filter. The wet film was exposed to UV-light (mercury lamp with 8.0 mW/cm^2 for 30 seconds), followed by baking at 180°C for 3 hours under vacuum conditions. The thickness of coating films depends on spinning conditions such as spinning speed and spinning time. A $9\ \mu\text{m}$ thin film was achieved in one-step coating on silicon by using a 3000 rpm spinning speed for 60 seconds. Optical characterisations (such as thickness, refractive index, and birefringence measurements) for thin films were performed by ellipsometry, and the results show that the hybrid polymer has a low birefringence around 1.2×10^{-4} and good film-forming properties (the refractive index and the film thickness are uniform across the wafer with roughness $<0.1\%$). The low fluctuation of refractive index across film surface suggests that titania is homogeneously incorporated in the hybrid material (at least the inhomogeneity of TiO₂ is smaller than the scale of 632.8 nm , the light wavelength used in the measuring experiments). Compared with the films produced from the resin without TiO₂ doping, the thickness and the refractive index of TiO₂-

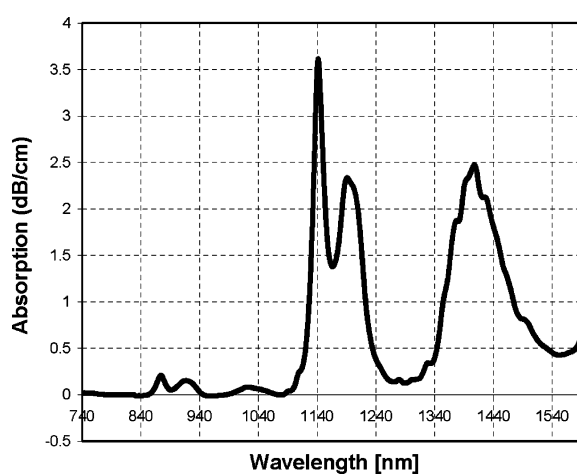


Figure 2. A near-IR spectrum of DMDMS/DPhDMS/TET/MPS (molar ratio) 30/50/20/100.

doped thin films are less fluctuated across the wafer, and this result suggests that TiO₂ incorporation is useful for improving film qualities. The incorporation of DMDMS and DPhDMS is found useful for reducing the birefringence and increasing the thermostability of coating films because, without incorporating these components, the birefringence of the material could reach to as high as the level of 10^{-3} and film cracking is hardly avoidable during baking treatment at 180°C . A near-IR spectrum of the material (resin B) is shown in Fig. 2, which shows that the material's optical losses are around 0.16 dB/cm at 1310 nm and 0.45 dB/cm at 1550 nm .

4. Waveguide Fabrication

Waveguide fabrication was performed by a direct UV-patterning process based on photolithographic technology. A silicon substrate covered with an ormosil layer was exposed to UV-light through a mask, and waveguide channels were defined by washing off the non-polymerised material with a solvent such as isopropanol. Figure 3 shows a SEM image of the developed waveguide structure. The sidewall roughness of waveguide ribs was observed having a dependence on the content of MPS in the material. When MPS concentration is less 30% (by molar ratio) waveguide channels are difficult to be developed as the material is not sufficiently cross-linked and is easily washed off from the silicon substrate by the solvent. A high concentration of MPS is preferred for waveguide structure development.

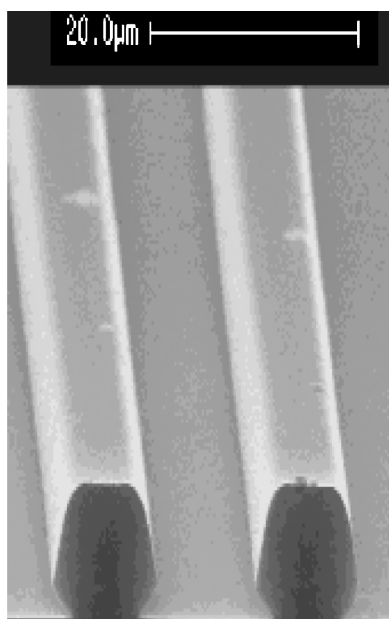


Figure 3. A SEM image of developed waveguide channels.

The effect of TiO_2 on the waveguide structure is similar to MPS, but a high concentration of TiO_2 tends to cause a reduction of the material's thermostability (films are easy crack during thermal baking at 180°C). Further optimisation of the composition of TiO_2 -doped hybrid polymer for waveguide fabrication is in progress.

5. Conclusions

With this work we have demonstrated that anhydrous sol-gel process can be used to synthesise low-OH titania/silica hybrid ormosil polymers for use as optical waveguide materials. The material refractive index is tuneable and can be patterned by UV imprinting technique, which is useful for low-cost fabrication of optical waveguides and devices. The low fluctuation of refractive index across the film surface ($<0.1\%$) indicates that a homogeneous incorporation of TiO_2 in ormosil polymers can be achieved by anhydrous sol-gel process.

References

1. T. Miya, IEEE J. of Sel. Top. in Quantum Electron. **6**, 38 (2000).
2. J.-W. Kang, E. Kim, and J.-J. Kim, Optical Mater. **21**, 543 (2002).
3. W. Shi, Y.J. Ding, C. Fang, Q. Pan, and Q. Gu, Optics and Lasers in Eng. **38**, 361 (2002)
4. J.-W. Kang, J.-P. Kim, W.-Y. Lee, J.-S. Kim, J.-S. Lee, and J.-J. Kim, J. Lightwave Technol. **19**, 872 (2001).
5. Y. Hida and S. Imamura, Jpn. J. Appl. Phys. **34**, 6416 (1995).
6. S.I. Najafi, C.-Y. Li, J. Chisham, M.P. Andrew, P. Coudray, A. Malek-Tabrizi, and N. Peyghambarian, Proc. SPIE **2695**, 38 (1996).
7. P. Coudray, J. Chisham, A. Malek-Tabrizi, C.Y. Li, M. Andrew, and S.I. Najafi, Proc. SPIE **2695**, 92 (1996).
8. B. Stuart, B. George, and P. McIntyre, *Modern Infrared Spectroscopy* (John Wiley & Sons, New York, 1996), p. 110.