JOURNAL OF
Materials
CHEMISTRY

Synthesis and characterization of poly(methyl silsesquioxane)–titania optical thin films†

Wen-Chang Chen,*[a,b] Long-Hua Lee,[a] Bo-Fu Chen[a] and Cheng-Tyng Yen[a]

[a]*Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan 10617. E-mail: chenwc@ms.cc.ntu.edu.tw*
[b]*Institute of Polymer Science and Engineering, National Taiwan University, Taipei, Taiwan 10617*

Received 29th July 2002, Accepted 25th September 2002
First published as an Advance Article on the web 23rd October 2002

Poly(methyl silsesquioxane) (MSQ)–titania optical thin films were synthesized and characterized in this study. An MSQ precursor with a mixed cage and network structure was prepared first, which had end groups of Si–OH and Si–OCH_3. Then, it was reacted with titanium(IV) n-butoxide, followed by spin-coating and multi-step curing to form the optical thin films. The FTIR spectra suggest successful bonding of MSQ and titania. The prepared films were very uniform with an amorphous nanoscale titania segment from the results of FE-SEM, AFM, and XRD. Excellent thermal stability was found for the prepared MSQ–titania materials. The optical properties of the prepared MSQ–titania films could be tuned by the titania content. By increasing the titania content from 10.6 to 41.6 wt.%, the absorption edge and refractive index were increased from 291 to 310 nm, and from 1.394 to 1.561, respectively. These results are attributed to the growing size effect of the titania segment. Optical planar waveguides were fabricated from the synthesized MSQ–titania films on top of a thermal oxide using a silicon wafer as the substrate. The optical loss of the studied planar waveguide decreased from 0.31 to 0.18 dB cm^{-1} with increasing titania content. This resulted from a reduction of the C–H bonding density due to the increasing titania composition.

Introduction

Poly(silsesquioxanes) have attracted extensive research interest because of their excellent thermal, mechanical, electronic, and optical properties.[1–4] They can be hybridized with organic moieties to form molecular composites for various applications.[5–7] Poly(hydrogen silsesquioxane) (HSQ) and poly(methyl silsesquioxane) (MSQ) have been recognized as a being in a class of low relative permittivity materials for deep sub-micron IC processes.[8–16] Poly(phenyl silsesquioxane) was reported to be an optical waveguide material with a very low optical loss of 0.16 dB cm^{-1}.[17]

The primary interest of this study is on the synthesis of poly(silsesquioxane)–titania hybrid materials for optical applications. The hybrid system can solve the problem of poor film thickness of pure inorganic materials for optoelectronic applications. The titania segment should be in the nano-size region for achieving high optical transparence. Synthesis of various polymer–titania hybrid optical films has been studied for applications requiring high refractive index and optical waveguides, the polymers used include poly(methyl methacrylate),[18,19] poly(arylene ether ketone) (PEK),[20] poly(tetramethylene oxide) (PTMO),[21] poly(arylene ether phosphine oxide),[20] poly(vinyl pyrolidone),[22] and polyimide.[23,24] The refractive index was tuned through the titania content and the reported optical loss was in the range of 0.2–1.5 dB cm^{-1}.

Although polymer–titania hybrid films with controllable optical properties have been successfully fabricated from the above studies, two possible drawbacks exist in the above systems. First, the poor thermal stability of the organic moieties results in insufficient curing of the Ti–OH group, which affects the optical properties and long-term stability in comparison with pure inorganic materials. Secondly, it is difficult to make patterns on the above organic–inorganic hybrid films due to the insufficient thermal stability of the organic moieties. Poly(silsesquioxanes) with their inorganic backbones have been recognized as excellent optoeletronic materials because of their optical transparency, thermal, mechanical properties, and processibility for film applications. Hence, it is possible to solve the above problems by replacing the polymer–titania systems with a poly(silsesquioxane)–titania system.

Our laboratories have successfully prepared poly(silsesquioxane) precursors and their corresponding films.[15,16] In this study, the synthesis and characterization of MSQ–titania optical thin films are reported. The titania segment is incorporated into the poly(methyl silsesquioxane) film as shown in Scheme 1. An MSQ precursor solution (MSQT0) with end groups of Si–OCH_3 and Si–OH was prepared according to a previous study[16] and had a mixed cage and network molecular structure. This was then reacted with different ratios of titanium(IV) n-butoxide, followed by spin-coating to provide the thin films. The prepared films were then cured to become the MSQ–titania optical films. The structures and properties of the prepared MSQ–titania thin films were studied by FTIR, FE-SEM, XRD, AFM, UV–Vis–NIR absorption, and refractive index. Optical waveguides were fabricated from the prepared MSQ–titania films using a thermal oxide and a silicon wafer as the cladding layer and substrate, respectively. The optical losses of the prepared optical waveguides were measured using a cut-back method at a wavelength of 1319 nm. The effects of the titania content on the properties of the MSQ–titania optical films and the corresponding waveguides were investigated.

Experimental

Materials

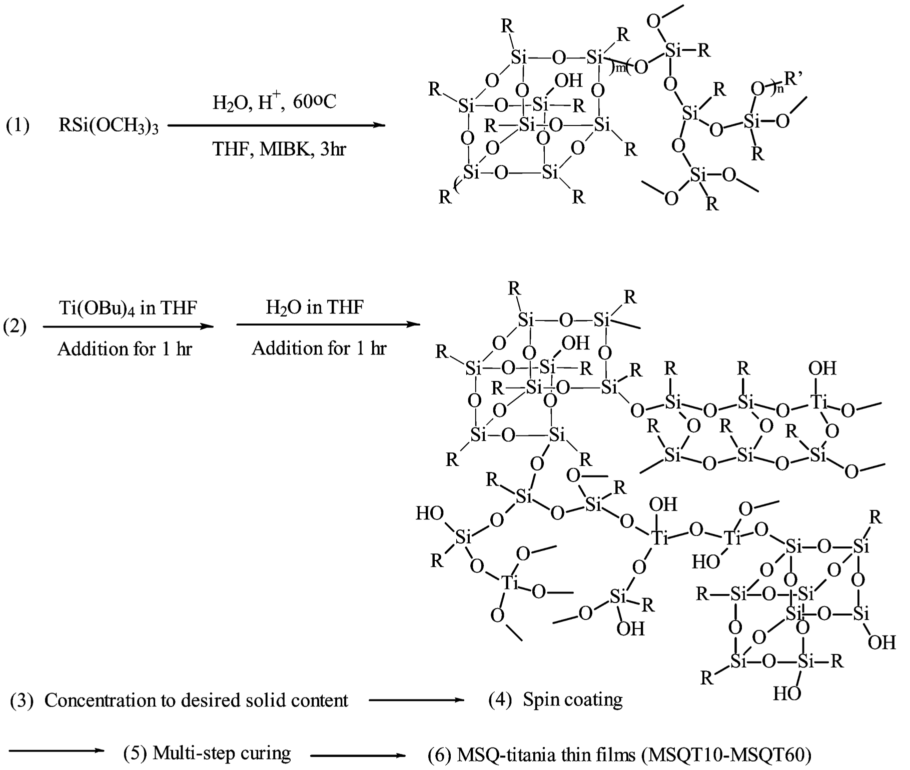
Methyltrimethoxysilane (MTMS, 98%, Aldrich), tetrahydrofuran (THF, 99%, stabilized and anhydrous, Acros), methyl

---

†Electronic supplementary information (ESI) available: FE-SEM diagram of MSQT60. See http://www.rsc.org/suppdata/jm/b2/b207390k/

DOI: 10.1039/b207390k

This journal is © The Royal Society of Chemistry 2002



Scheme 1 Preparation of MSQT0 and MSQ–titania thin films (R = CH_3).

isobutyl ketone (MIBK, semiconductor grade), titanium(IV) n-butoxide ($Ti(OBu)_4$, TCI, >98%), and hydrochloric acid (Yakuri, 35% by assay) and acetone-d_6 (CIL, 99.8 atom% D) were used as received. Poly(methyl silsesquioxane) (Gelest, M_W = 7000–8000, average OH content 5%) was used as the reference in estimating the content of Si–OH of MSQT0.

Synthesis of MSQ precursor solution (MSQT0)

A general reaction scheme for the MSQ precursor solution has been described previously.[16] Here, it was used to prepare MSQT0 by simply modifying the molar ratio of H_2O to MTMS. 4.08 g (0.03 mole) of MTMS and 9.24 g of MIBK were added to a three-necked round bottomed flask and immersed in an ice-bath. 0.88 g of hydrochloric acid/de-ionized water (0.094 wt.%) in 5.13 g of THF was added drop-wise over a period of 30 min with rigorous stirring. The pH value of the reaction mixture could be 2 or 3. The molar ratio of H_2O to MTMS was fixed at 1.5 or 1.625 for the reaction. The equipment was then allowed to warm to room temperature for 5 min and then immersed in silicon oil at 60 °C. The hydrolysis and condensation reaction lasted for 3 h under a nitrogen atmosphere and reflux to obtain MSQT0.

Preparation of MSQ–titania hybrid materials and their optical thin films

Different amounts of $Ti(OBu)_4$ were added into the precursor solution (MSQT0) for the preparation of the different MSQ–titania materials, which was 10–60 mol% in MTMS. The prepared materials are denoted as MSQTX, where X is the ratio of the mol% of $Ti(OBu)_4$ over MTMS. The preparation of MSQT30 is described below as an example. 3.06 g of $Ti(OBu)_4$ diluted in 12.80 g of THF was added drop-wise to MSQT0 at a temperature of 60 °C and maintained for 1 h, this was followed by the addition of 18.0 g of THF into the reaction mixture. An additional amount of 0.081 g of de-ionized water was added to assure a higher degree of condensation of $Ti(OBu)_4$. Upon completion of the addition, the precursor solution was allowed to cool to room temperature and then concentrated to a high solid content. The concentrated solution was then spin-coated onto singly and doubly polished silicon wafer and quartz. The thin films were baked and cured at 80, 150, 250 °C for 30 min, and 400 °C under a nitrogen atmosphere for 1 h. The prepared films were then used for the characterization of the molecular structures and properties.

Characterization

Infrared spectra of the polymer thin films were obtained by spin-coating the precursor solutions on doubly polished silicon wafers, followed by curing, and then recording at room temperature using a Bio-Rad Model FTS-40 spectrophotometer. Samples of MSQT0 before FTIR measurement were baked at 40 °C to eliminate the effect of the solvent. The Si–OH content in MSQT0 was estimated as described previously.[16] Curve fitting of the FTIR spectra for the MSQT0 was performed in the range of 1350–700 cm^{-1} to calculate the quotient of the peak areas at 1275 and 900 cm^{-1}, where the former indicates the CH_3 deformation of the Si–CH_3 group and the latter stands for Si–OH. By comparison with a reference poly(methyl silsesquioxane) sample from Gelest with an OH content of 5%, the approximate content of silanol in the synthesized MSQT0 was estimated. ^1H NMR and ^{29}Si NMR spectra of the MSQT0 were obtained using a Jeol EX-400 spectrometer. Acetone-d_6 was used as the deuterated solvent.

An atomic force microscope (Digital Instrument, Inc., Model DI 5000 AFM) was used to probe the surface morphology of the coated films. The root mean square roughness (R_q) and average roughness (R_a) of the studied films were determined. The microstructure of the prepared hybrid materials was further examined by field emission scanning electron microscopy (FE-SEM, Hitachi, Model-4000). A powder X-ray diffractometer (Material Analysis and Characterization, model number M03XHF) with a Cu Kα radiation source (λ = 1.54056Å) was used to probe the possible presence of a crystalline phase of titania existing in the powder. The detected 2θ range was between 10 and 80°.

Thermal analyses, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), were performed under a nitrogen flow using a Dupont Model 951 thermogravimetric analyzer and a DuPont Model 910S differential scanning calorimeter at heating rates of 20 and 10 °C min^{-1}, respectively. The TGA and DSC samples were prepared as described below. The MSQ–titania sample was added to vials and cured at different temperatures in an oven up to 400 °C under a nitrogen atmosphere. Then, the solid was taken out and ground to a fine powder for measurement.

UV–Vis–NIR spectra of the MSQ–titania thin films were obtained using a Jasco Model UV/VIS/NIR V-570 spectrophotometer at room temperature. The refractive indices at 1319 nm and the thickness of the MSQ–titania thin films were measured using a prism coupler (Metrican Corporation, model number 2010). The optical losses of the prepared optical planar waveguides were measured by a designed optical system (manufactured by the Center of Measurement and National Standards, Industrial Technology Research Institute, Hsinchu, Taiwan) using a cut-back method at 1310 nm. For measuring the NIR absorption spectra of the prepared hybrid materials, a sample with a thickness of a few mm was obtained by evaporating the precursor solution in a 20 ml vial under vacuum. The NIR absorption spectra of the hybrid films were obtained using a UV–Vis–NIR spectrophotometer (Jasco, model V-570, resolution 0.5 nm in the NIR region) in the wavelength range of 1000–1600 nm.

Results and discussion

Characterization of the MSQ precursor solution: MSQT0

The FTIR spectrum of MSQT0 is shown in Fig. 1.The major absorption bands of the Si–O–Si, Si–CH_3, and Si–OH bonds are observed at 1072, 2843–2974, and 900 or 3500 cm^{-1}, respectively. The peak positions are similar to those reported previously.[16] The Si–OH content and the cage/network ratio (*m*/*n* in Scheme 1) in the synthesized MSQT0 were estimated to be 4.89% and 0.54 from the FTIR spectrum,[16] respectively. The ^{1}H NMR spectrum of MSQT0 showed the following peaks: 0.1 ppm (Si–CH_3), 3.48 ppm (Si–OCH_3), and 3.70–4.50 ppm (Si–OH), respectively. The chemical shifts of MSQT0 with one (T^1), two (T^2) , and three (T^3) siloxane bonds (Si–O–Si) determined from ^{29}Si NMR were observed at −54, −57 and −65 ppm, respectively. The ratio of $T^1 : T^2 : T^3$ as determined from their peak areas is 5 : 40 : 55. The ^{1}H NMR and ^{29}Si NMR spectra of MSQT0 showed similar chemical shifts for Si–CH_3, SiOCH_3, Si–OH, and Si–O–Si as those reported in the literature.[16,25–27] The FTIR and NMR results support the chemical structure of MSQT0 shown in step 1 of Scheme 1.

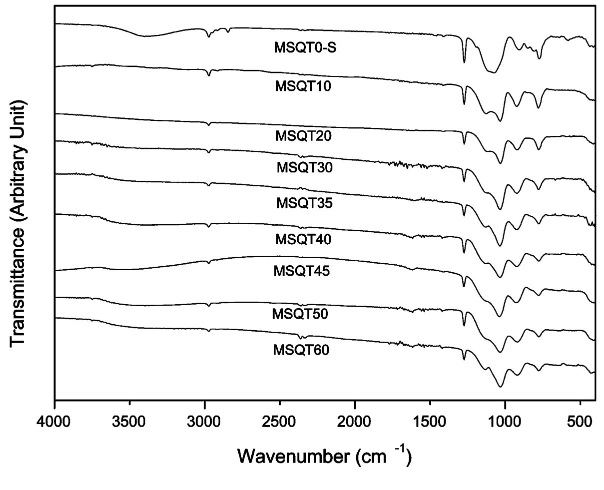


Fig. 1 FTIR spectra of MSQT0 and MSQT10–MSQT60 in the wavenumber range of 400–4000 cm^{-1}.

Characterization of the prepared MSQ–titania materials: MSQT10–MSQT60

The FTIR spectra of the prepared MSQ–titania thin films, MSQT10–MSQT60 are shown in Fig. 1. The characteristic peaks of MSQ are all evident in the spectra of Fig. 1 except the peak at 920 cm^{-1}, which is due to stretching of the Ti–O–Si bond.[28] This confirms the incorporation of MSQT0 and titania. The peaks at 2974 and 1275 cm^{-1} suggest the existence of an Si–CH_3 group after thermal curing. The Si–O–Si band at 1072 cm^{-1} of MSQT0 is split into two bands at 1120 and 1030 cm^{-1}, which are assigned to the cage and network structure of MSQ, respectively. As shown in previous studies,[15,16] the cage structure of MSQ is transformed to the network structure by thermal curing. The stronger absorption band at 1030 cm^{-1} than that at 1120 cm^{-1} suggests a similar cage/network transformation in the studied MSQ–titania materials. Hence, part of the cage structure (*m* in Scheme 1) was transformed to the network structure (*n* in Scheme 1) after thermal curing. The effect of the titania content on the cage/network transformation is not clear because of the difficulty of analyzing the Si–O–Si and Ti–O–Si overlapping absorption bands. The Ti–OH band of MSQT0 at 3500 cm^{-1} is insignificant in the spectra of the MSQ–titania materials. This suggests the successful condensation of Ti–OH by thermal curing.

An FE-SEM diagram for MSQT60 is available as ESI. No detectable phase separation is observed in the diagram. According to the diagram, the size of the titania domains in the MSQ–titania materials are estimated to be probably smaller than 10 nm. Although the actual size cannot be precisely measured, the prepared hybrid materials can be regarded as nano-scale materials from the diagram. The FE-SEM diagrams of other prepared MSQ–titania thin films show an excellent uniformity. No detectable peak intensity is observed in the XRD digrams of the prepared hybrid materials. This indicates that the titania domain in the prepared MSQ–titania is amorphous and thus transparent optical materials can be obtained. Fig. 2 shows the AFM diagram of a MSQT30 thin film, with a film thickness of 1.595 μm. The average roughness and relative roughness shown in Fig. 2 are 3.1 Å and 4.3 Å, respectively. The relative roughness in comparison with the film thickness is smaller than 0.3%. The film thickness, and surface roughness (R_a and R_q) of the MSQ–titania thin films are shown in Table 1. Excellent surface planarity is shown for all prepared MSQ–titania films. For silica–titania thin films prepared by sol–gel reaction, low surface planarity and serious phase separation has been reported in literature.[29] This might be due to the highly acidic reaction environment and the high concentration of reactants required to accelerate the titania growth to a large

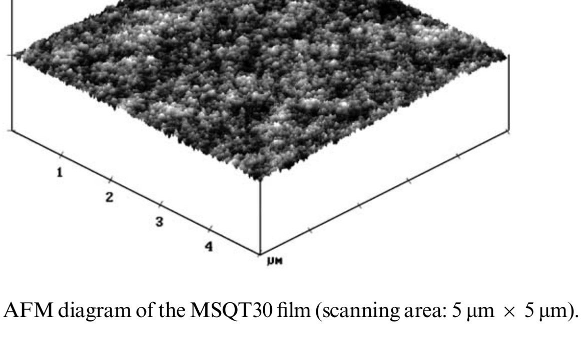


Fig. 2 AFM diagram of the MSQT30 film (scanning area: 5 μm × 5 μm).

Table 1 Properties of the prepared MSQ–titania thin films, MSQT10–MSQT60

Film	n at 1319 nm	Thicknes/nm	R_a/Å	R_q/Å	Band edge[a]/nm	Optical loss TE mode at 1319 nm/dB cm^{-1}
MSQT10	1.394	2656	3.2	4.0	255	—[b]
MSQT20	1.434	1398	2.9	3.7	279	—[b]
MSQT30	1.455	1595	3.1	4.3	291	0.31
MSQT35	1.466	1196	3.3	4.1	294	0.26
MSQT40	1.492	912	2.7	3.4	301	0.21
MSQT45	1.512	1128	2.3	2.9	306	0.20
MSQT50	1.530	938	1.8	2.3	307	0.18
MSQT60	1.562	642	2.0	2.5	310	—[c]

[a] From UV–Vis–NIR absorption spectrum. [b] The refractive index is smaller than the thermal oxide(n = 1.447) and thus cannot fabricate an optical waveguide. [c] The thickness is too thin for optical waveguide measurement.

domain. The efficient coupling between MSQT0 and titania in the studied reaction conditions probably limits the growth of the titania segment and results in a nano-domain.

The thermal stability of the prepared MSQ–titania materials was tested by TGA and DSC. From the results of TGA, the prepared MSQ–titania materials have not started to decompose up to 500 °C and more than 95% of sample residue remains at 900 °C. The DSC curves of the prepared MSQ–titania materials did not show any detectable thermal transition for the studied materials. The results for TGA and DSC suggest the excellent thermal stability of the prepared materials. For the organic–inorganic hybrid materials reported in the literature,[18,19] the thermal stability is generally poor and not suitable for patterning by photolithography or reactive ion etching. Howver, the materials prepared here may have the potential for application in optoelectronic devices.

Fig. 3 shows the UV–Vis–NIR spectra of the MSQ–titania hybrid thin films, MSQT10–MSQT60. Excellent transparency is shown in the studied wavelength range for all the prepared thin films. As discussed previously, the MSQ–titania materials are amorphous and thus excellent transparency is expected. The prepared thin films have absorption maxima in the range between 190 and 210 nm, and band edges between 255 and 310 nm, which result from the titania segment. The absorption maxima and band edges are shifted to longer wavelength with increasing titania content. The charge transfer effect of the Ti–O–Ti segment increases with its size and also there is a reduction of the energy gap with increasing titania size.[30,31] As reported in the literature,[30,31] the shift of the peak maximum becomes significant with a titania particle size of less than 10 nm. As discussed in the FE-SEM diagram of the prepared MSQ–titania film, the sizes of the titania segments of MSQT10–MSQT60 are probably less than 10 nm. Therefore, the red shift of the peak maximum shown in Fig. 3 is due to the growing size effect of the titania segment. Hence, the absorption maximum shows a red shift with increasing titania content. This is consistent with our previous study on the hybrid thin films of acrylic–titania[18,19] and imide–titania hybrid thin films.[24]

Fig. 4 shows the variation of refractive index (at 1319 nm) of MSQT10–MSQT60 thin films with titania content. The refractive index increases linearly from 1.3944 for MSQT10 to 1.5615 for MSQT60, as shown in Table 1. This result suggests that the refractive indices of the prepared hybrid films can be tuned by the titania composition.

One of the potential applications for the prepared MSQ–titania thin films is as optical waveguides for communication. In this study, planar waveguides were constructed with the structures of MSQT30–MSQT60 thin films on top of a thermal oxide (refractive index = 1.447) using silicon wafers as the substrate. MSQT10 and MSQT20 were not suitable for this study since their refractive indices were smaller than that of the thermal oxide. The MSQT60 thin film was also not suitable for the waveguide study as the film was too thin. The optical loss of the TE guiding mode was measured at the wavelength of optical communication at 1319 nm. The optical loss of the studied planar waveguide decreases, from 0.31 dB cm^{-1} for MSQT30 to 0.18 dB cm^{-1} for MSQT50, with increasing titania content, as shown in Fig. 5 and Table 1. The optical loss of the prepared waveguide is lower or comparable to the organic–inorganic hybrid material based waveguides prepared from sol–gel methods.[32–34] The prepared MSQ–titania films have excellent surface planarity and a homogeneous structure. Thus, the scattering loss of the prepared films is not significant. The optical loss probably results from the overtone vibration absorption of the C–H band in the near infrared (NIR) region. Fig. 6 shows the NIR absorption spectrum for the prepared MSQ–titania film, MSQT30. There

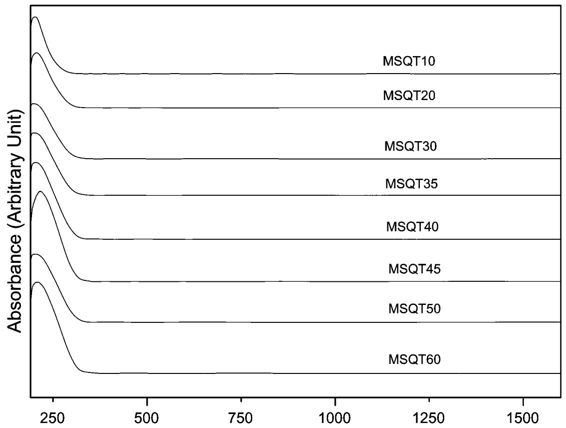


Fig. 3 UV–Vis–NIR spectra of MSQT10–MSQT60 in the wavelength range of 190–1600 nm.

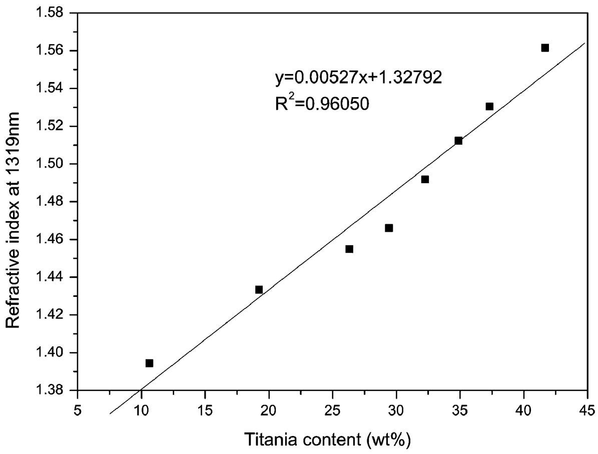


Fig. 4 Variation of the refractive index (at 1319 nm) of MSQT10–MSQT60 thin films with titania content.

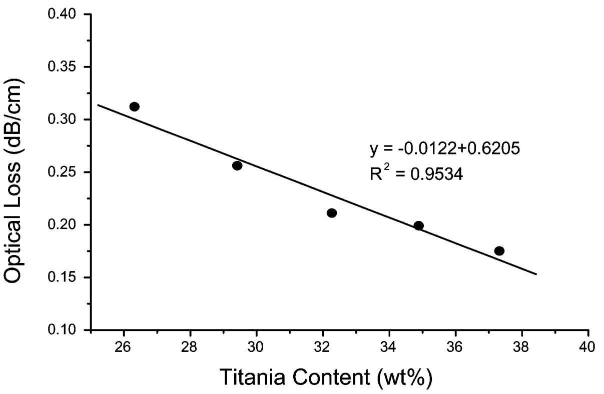


Fig. 5 Variation of the optical loss (TE mode at 1319 nm) of the MSQ–titania optical planar waveguides with titania content.

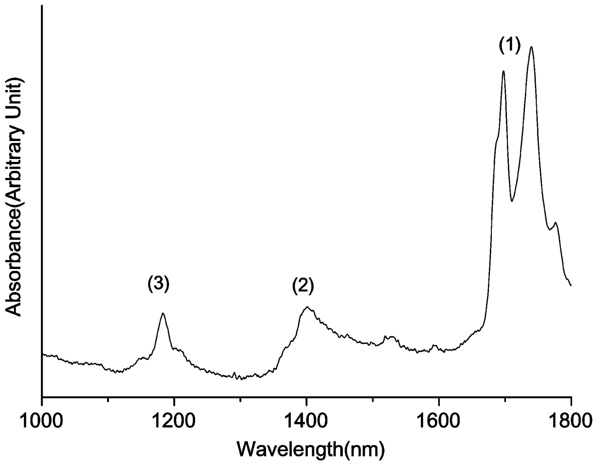


Fig. 6 NIR absorption spectrum of the MSQT30 film in the wavelength range of 1000–1600 nm.

are three major absorption bands shown in Fig. 6. The absorption bands in the range of 1100–1260 and 1600–1800 nm are assigned to be the third (ν_3) and second (ν_2) harmonic stretching vibration absorption bands of the C–H bond. The absorption band in the range of 1320–1500 nm results from a combination of the second harmonic stretching vibration (ν_2), the bending vibration (δ) of the C–H bond and the second harmonic stretching vibration of O–H bond (ν_2). The positions of the overtone absorption bands shown in Fig. 6 are similar to those reported in the literature.[35] The OH absorption might be from the absorbed moisture or the OH residue in the hybrid film. Hence, the intrinsic absorption loss at 1310 nm is mostly from C–H vibration absorption. The C–H bonding density decreases with increasing titania content. Thus, it results in a decrease of optical loss due to a reduction of the C–H bonding density if it is assumed that the OH absorption is the same in the different MSQ–titania films. This explains the results shown in Fig. 6. From the results of Figs. 4–6, it suggests that the optical properties of the MSQ–titania films could be tuned through the titania composition.

Conclusions

Poly(methyl silsesquioxane) (MSQ)–titania optical thin films were successfully synthesized from an MSQ precursor and titanium(IV) n-butoxide. The FTIR spectra showed the successful bonding of MSQ and titania. The prepared films had a homogeneous structure and a very high surface planarity. The optical properties of the prepared MSQ–titania films, including refractive index and optical absorption, could be tuned by using the titania content. This were attributed to the size effect of the titania segment. The optical loss of the studied planar waveguide decreases with increasing titania content, the decrease results from a reduction of the C–H bonding density with increasing titania composition. These results suggest the prepared MSQ–titania materials show tunable optical properties.

Acknowledgement

We thank the National Science Council of Taiwan for the financial support of this work.

References

1 R. H. Banley, M. Itoh, A. Sakakibara and T. Suzuki, *Chem. Rev.*, 1995, **95**, 1409.
2 F. J. Feher, K. Rahimian, A. Budzichowski and J. W. Ziller, *Organometallics*, 1995, **14**, 3920.
3 P. Eisenberg, R. Erra-Balsells, Y. Ishikawa, J. C. Lucas, A. N. Mauri, H. Nonami, C. C. Riccardi and R. J. J. Williams, *Macromolecules*, 2000, **33**, 1940.
4 D. A. Loy, B. M. Baugher, C. R. Baugher, D. A. Schneider and K. Rahimian, *Chem. Mater.*, 2000, **12**, 3624.
5 J. D. Lichtenhan, Y. A. Otonari and M. J. Carr, *Macromolecules*, 1995, **28**, 8435.
6 A. Sellinger and R. M. Laine, *Macromolecules*, 1996, **29**, 2327.
7 R. M. Laine, J. Choi and I. Lee, *Adv. Mater.*, 2001, **13**, 800.
8 C. T. Chua, G. Sarkar and X. Hu, *J. Electrochem. Soc.*, 1998, **145**, 4007.
9 J. K. Lee, K. Char, H. W. Rhee, H. W. Ro, D. Y. Yoo and D. Y. Yoon, *Polymer*, 2001, **42**, 9085.
10 W. C. Chen, S. J. Lin, B. T. Dai and M. S. Tsai, *J. Electrochem. Soc.*, 1999, **146**, 3004.
11 W. C. Chen and C. T. Yen, *J. Vac. Sci. Technol., B*, 2000, **18**, 201.
12 W. C. Chen and C. T. Yen, *J. Polym. Res.*, 1999, **6**, 197.
13 S. Yang, P. Miran, C. S. Pai, O. Nalamasu, E. Reinchmanis, E. K. Lin, H. J. Lee, D. W. Gidley and J. N. Sun, *Chem. Mater.*, 2001, **13**, 2762.
14 H. J. Lee, E. K. Lin, H. Wang, W. L. Wu, W. Chen and E. S. Moyer, *Chem. Mater.*, 2002, **14**, 1845–1852.
15 C. C. Yang and W. C. Chen, *J. Mater. Chem.*, 2002, **12**, 1138.
16 L.-H. Lee, W. C. Chen and W. C. Liu, *J. Polym. Sci., Part A: Polym. Chem.*, 2002, **40**, 1560.
17 K. S. Brown, B. J. Taylor and H. A. Hornak, *IEEE Photo. Technol. Lett.*, 1997, **9**, 791.
18 W. C. Chen, S. J. Lee, L. H. Lee and J. L. Lin, *J. Mater. Chem.*, 1999, **9**, 2999.
19 L. H. Lee and W. C. Chen, *Chem. Mater.*, 2001, **13**, 1137.
20 B. Wang, G. L. Wilkes, J. C. Hedrick, S. C. Liptak and J. E. McGrath, *Macromolecules*, 1991, **24**, 3449.
21 B. Wang and G. L. Wilkes, *J. Polym. Sci., Part A: Polym. Chem.*, 1991, **29**, 905.
22 M. Yoshida, M. Lal, N. D. Kuma and P. N. Prasad, *J. Mater. Sci.*, 1997, **32**, 4047.
23 M. Yoshida and P. N. Prasad, *Chem. Mater.*, 1996, **8**, 235.
24 C. C. Chang and W. C. Chen, *J. Polym. Sci., Part A: Polym. Chem.*, 2001, **39**, 3419.
25 N. Takamura, T. Gunji, H. Hatano and Y. Abe, *J. Polym. Sci., Part A: Polym. Chem.*, 1999, **37**, 1017.
26 R. A. Assink and B. K. Kay, *J. Non-Cryst. Solids*, 1988, **99**, 359.
27 L. Delattre and F. Babonneau, *Mater. Res. Soc. Symp. Proc.*, 1994, **346**, 365.
28 V. A. Zietler and C. A. Brown, *J. Phys. Chem.*, 1957, **61**, 1174.
29 L. Yang, S. S. Saavedra, N. R. Armstrong and J. Hayes, *Ann. Chem.*, 1994, **66**, 1254.
30 M. Anpo, T. Shima, S. Kodama and Y. Kubokawa, *J. Phys. Chem.*, 1987, **91**, 4305.
31 H. Yoneyama, S. Haga and S. Yamanaka, *J. Phys. Chem.*, 1987, **93**, 4833.
32 C. Xu, L. Eldada, C. Wu, R. A. Norwood, L. W. Schacklette and J. T. Tardley, *Chem. Mater.*, 1996, **8**, 2701.
33 N. Yamada, I. Toshinaga and S. Katayama, *J. Appl. Phys.*, 1999, **85**, 2423.
34 S. J. L. Ribeiro, Y. Messaddeq, R. R. Goncalves, M. Ferrari, M. Montagna and M. A. Aegerter, *Appl. Phys. Lett.*, 2000, **77**, 3502.
35 S. Ando, T. Matsuura and S. Sasaki, *J. Am. Chem. Soc.*, 1994, **20**, 304.