

Tunable Near-Infrared Optical Properties Based on Poly(methyl Methacrylate)–Oxide Waveguide Materials

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ABSTRACT: In this study, two classes of low-loss optical planar waveguides were prepared from trialkoxysilane-capped poly(methyl methacrylate) (PMMA)–silica and PMMA–titania hybrid materials, respectively. The prepared hybrid films had very uniform structure and surface planarity. The incorporation of the silica or titania segments into the acrylic polymer matrix reduced the intermolecular interaction and thus induced an increase in anharmonicity of the C–H bond in the acrylic segment. Therefore, the third harmonic stretching vibration absorption of the C–H bond was red-shifted and resulted in a tuning of near-infrared (NIR) optical absorption. The optical loss of the studied

waveguides was reduced from 0.65 dB/cm of the PMMA waveguide to 0.26 and 0.28 dB/cm with increasing the silica and titania content in the hybrid materials, respectively. The reduction of the C–H number density and shifting of the NIR absorption spectra accounted for the relationship between the optical loss and the inorganic oxide content. The increased anharmonicity through the incorporation of the inorganic moiety in the hybrid materials provides another approach for tuning the NIR optical properties. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 1224–1228, 2005

Key words: nanocomposites; films; optics; photophysics

INTRODUCTION

Organic–inorganic hybrid materials have been recognized as a new class of optoelectronic materials.^{1–8} Molecular design on the organic or inorganic moiety of the hybrid materials produces materials with tunable optoelectronic properties.^{9–12} One promising application of the hybrid materials is optical waveguides for communication.^{11,13–16} They could improve thermal and mechanical properties over the parent organic polymers and reduce the C–H overtone vibration loss in the near-infrared (NIR) region. Previous studies^{10,11} on optical hybrid materials were mostly focused on tuning of the refractive index or reducing the C–H number density ($\rho_{\text{C-H}}$) of the organic moiety in hybrid materials. However, the effects of the inorganic moiety on tuning the near-infrared optical absorption spectra have not been fully explored yet.

Although organic polymers have been extensively studied as optical waveguide materials because of their processing, low cost, and tunable properties compared with conventional inorganic oxides,^{17–19}

thermal and mechanical properties of organic polymers are limited for their practical applications. Furthermore, the overtone vibration absorption of the chemical bond of organic polymers produces a large optical loss in the near-infrared region for optical communication.^{17–19} According to the Morse potential theory, the position of the overtone stretching vibration of a chemical bond can be expressed as the equation²⁰

$$\nu_n = \nu_0 n - \chi \nu_0 n(n + 1) \quad (1)$$

where n , ν_0 , ν_n , and χ are the vibration quantum number, the harmonic stretching frequency, the n th harmonic stretching vibration, and anharmonicity, respectively. ν_1 , ν_2 , and ν_3 are also called the fundamental, first overtone, and second overtone stretching vibration, respectively.

Note that $\nu_0 = \frac{\sqrt{k/\mu}}{2\pi c}$, where k , μ , and c are force constant, reduced mass, and velocity of light, respectively. The anharmonicity represents the deviation of the vibration from the harmonic behavior. As showed in Eq. (1), the position of the harmonic stretching vibration is determined by ν_0 and χ . For the common polymer waveguide materials, poly(methyl methacrylate) (PMMA), the optical loss results from $\nu_{2,\text{CH}}$, $\nu_{3,\text{CH}}$, and the combination of the second C–H harmonic stretching vibration and C–H bending vibration ($\nu_{2,\text{CH}} + \delta_{\text{CH}}$) in the NIR region of 1000 to 1600 nm.¹⁸ Hence, the traditional approach for reducing the optical loss of organic polymers is through reducing the C–H number density.^{17,18} Here,

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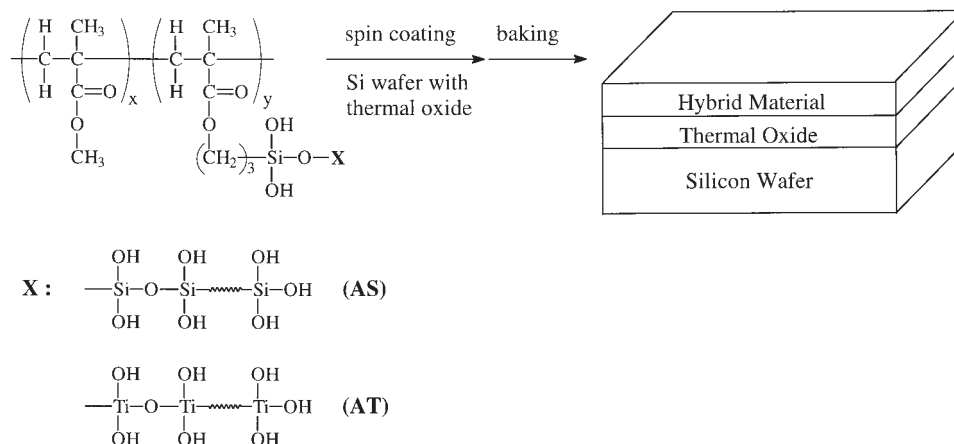


Figure 1 Preparation of optical planar waveguides based on the PMMA-silica and PMMA-titania hybrid materials.

we try to explore another possibility for tuning the NIR optical properties through the inorganic moiety in the hybrid materials.

Our laboratory has successfully prepared highly homogeneous PMMA-silica and PMMA-titania hybrid optical films.^{9,10} Thermal and mechanical properties of these prepared hybrid materials showed significant improvement in comparison with the parent PMMA. In this study, modifications of previous reaction schemes were applied to prepare optical planar waveguides based on PMMA-silica and PMMA-titania hybrid materials. The effects of the inorganic moiety on the NIR optical absorption and corresponding waveguides were studied. The variation on the anharmonicity of the C-H bond through the inorganic content was used to explain the shifting of the NIR absorption spectra.

EXPERIMENTAL

Materials

Tetrahydrofuran (THF, 99.9%, Acros) and methyl isobutylketone (MIBK, 99.5%, Acros) were purified by vacuum distillation. Methyl methacrylate (99.8%, TCI), 2,2,3,3-tetrafluoropropyl methacrylate (99%, Aldrich), 3-trimethoxysilyl propyl methacrylate (98%, Aldrich), benzoyl peroxide (75%, Acros), hydrogen chloride (Yakuri Pure Chemical), tetraethoxysilane (TEOS, 99+%, Aldrich), and titanium *n*-butoxide ($\text{Ti}(\text{OBU})_4$, 99%, TCI) were used as received. The PMMA sample for comparison with the hybrid materials was purchased from Aldrich ($M_w = 75,000$).

Processing

Figure 1 shows the schemes for preparing planar optical waveguides from PMMA-silica (AS) and PMMA-titania (AT) hybrid materials in this study. Pure

PMMA polymer-based optical planar waveguides A0 were also prepared as the reference. The denotations of ASX or ATX mean the weight percentage X of the silica precursor TEOS or titania precursor $\text{Ti}(\text{OBU})_4$ in the reaction mixture, respectively. Synthesis of AS and AT precursor solutions were through the modifications of previous reaction schemes.^{9,10} To increase film quality and thickness for the optical waveguide application, a high-boiling-point solvent MIBK was added to the precursor solutions with the weight ratio of MIBK/THF = 0.5. Then, low-boiling-point solvent THF and alcohol generated during the hydrolysis and condensation reactions were removed to form the final precursor solution by vacuum evaporation. Then, the precursor solutions were spin-coated on the top of the thermal oxide layer on 6-in. silicon wafers and cured at 110 and 150 °C for 1 h, respectively, to form the optical planar waveguides. The hybrid and thermal oxide layers were used as the guiding and cladding layers, respectively. For mid-IR and NIR spectrum analyses, the precursor solutions were spin-coated and cured on glass sheets using the same process. The prepared films were then stripped from the glass sheets for the spectrum analyses.

Characterization

The NIR absorption spectra of the prepared hybrid films were obtained using a UV-vis-NIR spectrophotometer (Jasco, Model No. V-570) in the wavelength range of 1000 to 1600 nm. The fundamental vibration, ν_1 , was obtained using a FTIR spectrophotometer (Jasco, Model No. FT/IR-410). An atomic force microscope (AFM, Digital Instrument, Inc., Model No. DI 5000) was used to probe the surface morphology and average roughness (R_a) of hybrid films. The microstructure of the prepared films was examined by a field emission scanning electron microscopy (FE-SEM,

TABLE I
Silica and Titania Content as well as Properties of the Prepared Films and Their Optical Planar Waveguides

	Silica ^a (wt %)	Titania ^a (wt %)	<i>h</i> (μm)	R_a (nm)	$\rho_{\text{C-H}}$ (mol/cm ³)	α^b (dB/cm)
A0	0	0	1.29	0.30	0.093	0.65
AS10	14.0	0	0.75	0.13	0.088	0.24
AS15	15.8	0	0.39	0.10	0.087	0.24
AS20	17.7	0	0.65	0.18	0.086	0.21
AS25	19.7	0	0.59	0.07	0.085	0.21
AS30	21.9	0	0.32	0.13	0.083	0.20
AT10	10.5	2.9	1.20	0.25	0.089	0.38
AT15	10.4	4.5	1.09	0.47	0.089	0.35
AT20	10.2	6.3	1.41	0.27	0.088	0.34
AT25	10.0	8.2	1.07	0.49	0.088	0.32
AT30	9.7	10.3	1.30	0.31	0.087	0.28

^a Theoretical content in ASX and ATX hybrids, respectively.

^b Measured at 1310 nm.

Hitachi, Model No. S-4000). Film thickness (*h*) was measured using a Prism Coupler (Metriton, Model NO. 2010). The optical losses (α) of the prepared optical planar waveguides at 1310 nm were measured by cutback method.²¹ The optical loss measurement system was designed by the Center for Measurement and Standards, Industrial Technology Research Institute (Hsinchu, Taiwan).

RESULTS AND DISCUSSION

As shown in Table I, the prepared AS and AT hybrid films have film thickness from 0.32 to 0.75 μm and 1.07 to 1.41 μm , respectively. The average roughness of AS and AT hybrid films is 0.07–0.17 nm and 0.25–0.49 nm, respectively. The average roughness in comparison with film thickness is less than 0.05% for the prepared hybrid films, which suggests excellent surface planarity for optical waveguide applications. The FE-SEM diagrams did not show any significant inor-

ganic domain larger than 20 nm in the prepared hybrid materials, which were similar to those reported previously.^{9,10} The uniform structures of the prepared hybrid materials in the AFM and SEM diagrams suggest the nanosize inorganic moiety in the hybrid materials and thus a significant scattering loss could be avoided from the prepared optical waveguides.

Figure 2 shows the near-infrared absorption spectra of the prepared films, (A0, AS10, AS30, AT10, and AT30) in the wavelength of 1000 to 1600 nm. There are two major absorption bands. The absorption band between 1100 and 1260 nm is assigned to the third C-H harmonic stretching vibration ($\nu_{3,\text{CH}}$) of the PMMA moiety. The absorption band between 1320 and 1530 nm is composed from two different sources: (1) a combination of the second C-H harmonic stretching vibration and C-H bending vibration ($\nu_{2,\text{CH}} + \delta_{\text{CH}}$) and (2) the second O-H harmonic stretching vibration ($\nu_{2,\text{OH}}$). The red-shifting trend of the spectrum is shown in Table II and Figure 2 as increasing the silica

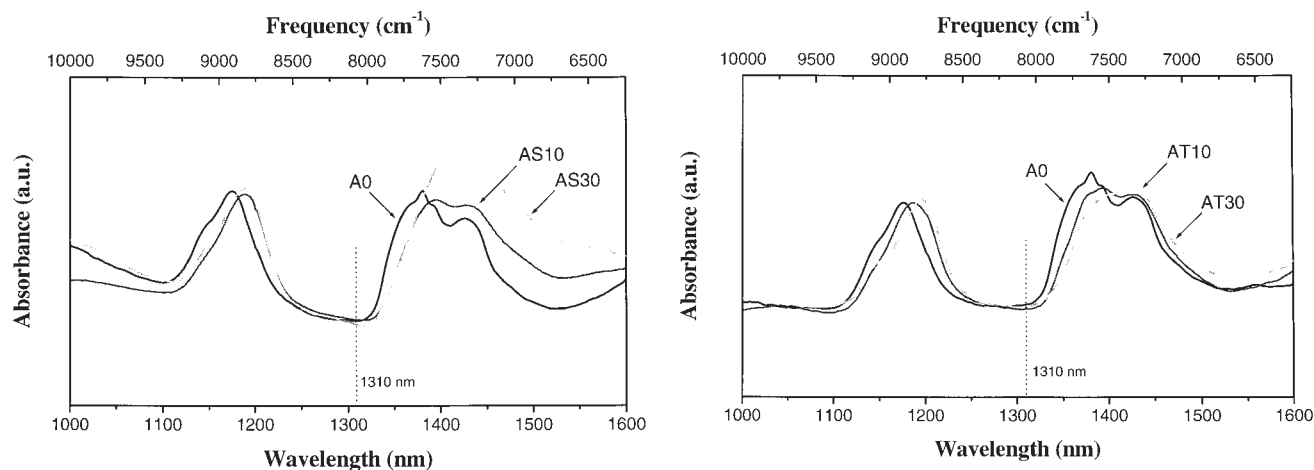


Figure 2 The NIR absorption spectra of the hybrid films (a) A0, AS10, and AS30 and (b) A0, AT10, and AT30 in the wavelength range of 1000 to 1600 nm.

TABLE II
The Harmonic Stretching Wavenumber (ν_0),
Fundamental Stretching Vibration (ν_1), Third Harmonic
Stretching Vibration (ν_3), and Anharmonicity (χ)
of the C—H Bond in the Prepared Films

	ν_0^a (cm^{-1})	ν_1 (cm^{-1}) ^b	ν_3 (cm^{-1}) ^c	χ^a
A0	3066	2952	8511 (1175nm)	0.019
AS10	3093	2951	8425 (1187nm)	0.023
AS15	3089	2951	8439 (1185nm)	0.022
AS20	3093	2951	8425 (1187nm)	0.023
AS25	3114	2952	8368 (1195nm)	0.026
AS30	3114	2952	8368 (1195nm)	0.026
AT10	3070	2950	8489 (1178nm)	0.020
AT15	3084	2950	8446 (1184nm)	0.022
AT20	3103	2950	8389 (1192nm)	0.023
AT25	3108	2950	8375 (1194nm)	0.025
AT30	3110	2951	8375 (1194nm)	0.026

^a Determined from Eq.[1] with the obtained ν_1 and ν_3 .

^b From the FTIR spectra.

^c From the UV-vis-NIR spectra. (unit conversion: wavelength (nm) = $10^7/\text{wavenumber}$ (cm^{-1})).

or titania content. For the case of AS films, $\nu_{3,\text{CH}}$ decreases from 8511 to 8368 cm^{-1} (1175 to 1195 nm) with increasing silica content. A similar trend is shown for the case of AT films. In this case, $\nu_{3,\text{CH}}$ decreases from 8511 to 8375 cm^{-1} (1175 to 1194 nm) with increasing the inorganic content. The combination band ($\nu_{2,\text{CH}} + \delta$) in Figure 2 also shows the same trend of red-shifting as that of $\nu_{3,\text{CH}}$ although it is complicated by the O-H overtone vibration.

Figure 3 shows the variation of the output transmission light intensity (I_{out}) of the prepared optical planar waveguides of A0 and AT30 with different light propagation length at 1310 nm. Linear relationships between the logarithmic value of the output intensity and the propagation length were observed. The optical losses were calculated from the slopes and are listed in Table I. Figure 4 shows the variation of the optical losses of the prepared AS and AT optical planar waveguides at 1310 nm with the silica and titania content. The optical loss of PMMA optical planar waveguide is 0.65 and reduces to 0.26 dB/cm with increasing the silica content to 21.9 wt % in AS optical planar waveguides. A similar reduction on the optical loss is shown in AT optical planar waveguides. The optical loss reduces to 0.28 dB/cm with increasing the total inorganic content to 20.1 wt %.

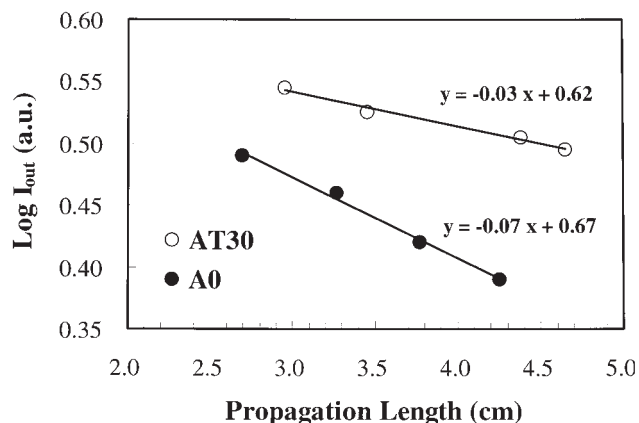


Figure 3 Variation of the transmission light intensity with the propagation length of the optical planar waveguides prepared from the hybrid film, A0 and AT30.

The ν_1 value has an insignificant variation with the inorganic content from the FTIR spectra. However, the ν_3 shows a significant variation for cases of both AS and AT hybrid materials. This suggests that the overtone frequency of the C-H bond is strongly affected by incorporating the inorganic moiety. The ν_0 and χ_{CH} shown in Eq. (1) could be calculated from ν_1 and ν_3 by applying Eq. (1). As shown in Table II, ν_0 and χ_{CH} all increase gradually to a steady value with increasing the inorganic content. The calculated ν_0 and χ_{CH} of PMMA are 3066 cm^{-1} and 0.019, respectively. The calculated ν_0 increases to 3114 cm^{-1} and χ_{CH} increases to 0.026 with increasing silica content in AS hybrids. In AT hybrids, ν_0 and χ_{CH} increase to 3110 cm^{-1} and 0.026, respectively. The increase of ν_0 and χ_{CH} suggests the increase of the force constant k and the deviation from the harmonic behavior of the stretching vibration, respectively. The increase of the C-H anharmonicity was also observed in the viscosity change

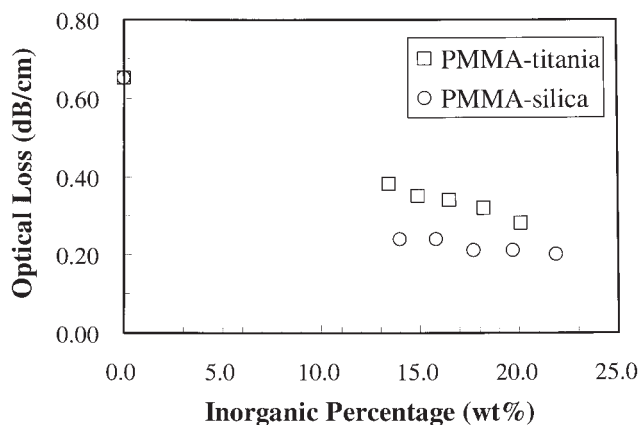


Figure 4 Variation of the optical loss of the prepared optical planar waveguide at 1310 nm with the inorganic content.

from the solid to the liquid state of 3-methylpentane since it reduces the intermolecular interaction.²² The incorporation of the inorganic moiety in the hybrid materials might also have a similar effect of reducing intermolecular interaction of the PMMA moiety. Hence, χ_{CH} increased with increasing the inorganic content in the hybrid materials.

The reduced optical loss of the optical planar waveguides with increasing the inorganic moiety in the hybrid materials might be due to the shifting of the NIR absorption spectrum and the reduction of the C-H number density. As shown in Figure 2, the transparency at 1310 nm increases with the silica and titania content due to the shifting of the overtone absorption spectra, as discussed above. Another factor of reducing the optical loss is reducing the C-H number density with the increase of the inorganic content. The calculated C-H number density of PMMA is 0.093 mol/cm³ and reduces to 0.083 mol/cm³ of AS30 and 0.087 mol/cm³ of AT30.

By replacing the PMMA segment of AT30 with the fluorinated acrylic segment, poly(2,2,3,3-tetrafluoropropyl methacrylate), in the hybrid materials, the resulted optical planar waveguide had a optical loss of 0.24 dB/cm. The obtained optical loss is similar to that of AT30. The result of the obtained optical loss also suggests that increasing the inorganic content does not result in a significant decrease on optical quality and thus the scattering loss is not significant in the prepared optical planar waveguides. This demonstrates that the current hybrid approach could achieve the same goal of reducing the optical loss as replacing the C-H bond with a C-F or C-D bond.^{20,23} Hence, the prepared hybrid materials have potential applications as waveguide materials for optical communication.

CONCLUSIONS

Low-loss optical planar waveguides were successfully prepared based on the PMMA-silica and PMMA-titania hybrid materials. The incorporation of the silica or titania segment into the PMMA segment induced an increase of the C-H anharmonicity and thus the third C-H harmonic stretching vibration absorption

was red-shifted. The C-H number density is also reduced by incorporating the inorganic moiety. Therefore, the optical loss at 1310 nm was reduced with increasing the incorporation of the inorganic segment. The increased anharmonicity through the inorganic moiety provides another approach for tuning the NIR optical properties besides reducing the C-H number density. The results also suggest that the approach of the organic-inorganic hybrid films could be waveguide materials for optical communication.

References

1. Sanchez, C.; Lebeau, B. *MRS Bull* 2001, 26, 377.
2. Chaumel, F.; Jiang, H. W.; Kakkar, A. *Chem Mater* 2001, 13, 3389.
3. Kajzar, F.; Lee, K. S.; Jen, A. K. Y. *Adv Polym Sci* 2003, 161, 1.
4. Huynh, W. U.; Dittmer, J. J.; Alivisatos, A. P. *Science* 2002, 295, 2425.
5. Arango, A. C.; Johnson, L. R.; Bliznyuk, V. N.; Schlesinger, Z.; Carter, S. A.; Hörhold, H. H. *Adv Mater* 2000, 12, 1689.
6. Huang, W. Y.; Ho, S. W.; Kwei, T. K.; Okamoto, Y. *Appl Phys Lett* 2002, 80, 1162.
7. Coakley, K. M.; McGehee, M. D. *Appl Phys Lett* 2003, 83, 3380.
8. Lin, W. J.; Chen, W. C.; Wu, W. C.; Niu, Y. H.; Jen, A. K. Y. *Macromolecules* 2004, 37, 2335.
9. Chen, W. C.; Lee, S. *J Polym J* 2000, 32, 67.
10. Lee, L. H.; Chen, W. C. *Chem Mater* 2001, 13, 1137.
11. Chang, C. C.; Chen, W. C. *Chem Mater* 2002, 14, 4242.
12. Chang, C. C.; Chen, W. C. *J Polym Sci Polym Chem* 2001, 39, 3419.
13. Xu, C. Z.; Eldada, L.; Wu, C. J.; Norwood, R. A.; Schacklette, L. W.; Yardley, J. T.; Wei, Y. *Chem Mater* 1996, 8, 2701.
14. Yen, C. T.; Chen, W. C.; Liaw, D. J.; Lu, H. Y. *Polymer* 2003, 44, 7079.
15. Innocenzi, P.; Martucci, A.; Guglielmi, M.; Armelao, L.; Pelli, S.; Righini, G. C.; Battaglin, G. C. *J Non-Cryst Solids* 1999, 259, 182.
16. Oubaha, M.; Smaïhi, M.; Etiene, P.; Coudrary, P.; Moreau, Y. *J Non-Cryst Solids* 2003, 318, 305.
17. Matsuura, T.; Ando, S.; Sasaki, S.; Yamamoto, F. *Macromolecules* 1994, 27, 6665.
18. Ma, H.; Jen, A. K. Y.; Dalton, L. R. *Adv Mater* 2002, 14, 1339.
19. Yen, C. T.; Chen, W. C. *Macromolecules* 2003, 36, 3315.
20. Groh, W. *Makromol Chem* 1988, 189, 2861.
21. Hunsperger, R. G. *Integrated Optics: Theory and Technology*, 3rd ed.; Springer-Verlag: New York, 1991.
22. Henry, B. R.; Mohammadi, M. A.; Thomson, J. A. *J Chem Phys* 1981, 75, 3165.
23. Yen, C. T.; Chang, Y.; Chen, W. C. *Jpn J Appl Phys* 2004, 43, 5297.