

Wavelength dependence of thermo-optic coefficient of organically modified SiO₂-ZrO₂ hybrid films

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Thermo-optic characteristics of organically modified SiO₂-ZrO₂ films prepared by a nonhydrolytic reaction have been investigated. The thermo-optic coefficient (dn/dT) is negative on the order of $-10^{-4}/K$ and varies with the wavelength as a function of the ZrO₂ content in organically modified SiO₂ material. As the amount of ZrO₂ increases, the wavelength dependence of dn/dT gradually varies from positive to negative. The magnitude and wavelength dependence of dn/dT for organically modified SiO₂-ZrO₂ hybrid materials make these materials highly flexible for application in thermo-optic integrated devices. © 2006 American Institute of Physics.

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Temperature dependence of the refractive index (dn/dT) of optical materials is of significant importance when designing optical waveguide devices.¹ The wavelength dependence of dn/dT also makes the separation and combination of light frequencies easy in an optical multiplexing/demultiplexing system.^{2,3} Thus, the materials exhibiting both a high dn/dT and wavelength dependence of dn/dT are required for efficient and convenient thermo-optical integrated devices. According to Prod'homme's model,⁴ the dn/dT value is a property of the material and is determined by the combined influence of the temperature dependence of the density and electronic polarizability.⁵ The dn/dT value of the polymer is principally determined by the density change because the thermal expansion of these materials is significantly greater than the polarization change, resulting in a negative dn/dT . However, the dn/dT of inorganic materials is generally determined by the competition of these two factors.⁶

Recently, sol-gel derived organically modified SiO₂ has received attention as a promising candidate for thermo-optic waveguide material because of the high negative value and convenient controllability of dn/dT .⁷ We reported a negative dn/dT of an organically modified SiO₂ film (on the order of $-10^{-4}/K$) and its modification by a change in the material chemical structure.^{8,9} Because the hybrid materials have an excellent advantage of easy chemical modification, it was expected that the wavelength dependence of dn/dT could be obtained by compounding a heterometallic oxide exhibiting high wavelength dependence. In this study, we report both a high dn/dT and wavelength dependence of an organically modified SiO₂-ZrO₂ hybrid film prepared by a nonhydrolytic reaction.

The organically modified SiO₂-ZrO₂ hybrid materials were synthesized by a nonhydrolytic reaction, in which only the alcohol condensation reaction takes place using precursors having hydroxyl and alkoxy groups,¹⁰ in order to add a significant amount of ZrO₂ into the organically modified SiO₂. Zirconium dimethacrylatedibutoxide (ZDD) (25% in butanol/toluene) and diphenylsilanediol (DPSD) were used

as the precursors. The other precursor, ZDD, was chosen because ZrO₂ has a high wavelength dependence of dn/dT . As a base catalyst, barium hydroxide monohydrate [Ba(OH)₂·H₂O] was added to the solution. Due to the water sensitivity of ZDD, the blend of the precursors and catalyst was carried out in a glovebox. After 3 h of refluxing at 60 °C, the solution was cooled to room temperature and filtered using a 0.2 μm filter to remove the catalyst. The prepared solutions were spin coated onto a silicon substrate at 1000 rpm for 30 s and the resultant films were heat treated for 1 h at 150 °C. The refractive index and dn/dT of the films were measured using the prism coupling method (METRICON 2010 Prism Coupler) equipped with an auto-controlled hot stage at the prism and coupling head.⁸ Lasers of the 633, 1319, and 1553 nm TE modes were used as the light source.

Figure 1 shows the Fourier transform infrared (FTIR) absorbance spectra of the DPSD precursor and 50.0 mol % ZDD (ZDD:DPSD=1:1). The spectrum of 50.0 mol % ZDD shows the Si-(C₆H₅) vibration modes, butoxy vibration mode at 1562 cm⁻¹, and Zr-O stretching vibration at ~450 cm⁻¹. The bands at 1720 and 1640 cm⁻¹, corresponding to the carbonyl group C=O stretching mode and the

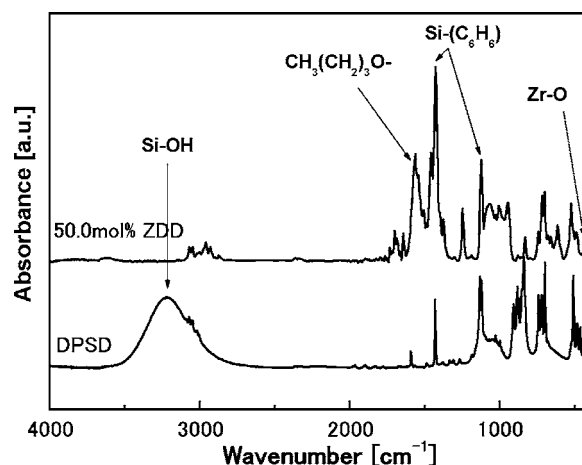


FIG. 1. FTIR absorbance spectra of the DPSD and 50.0 mol % ZDD hybrid material.

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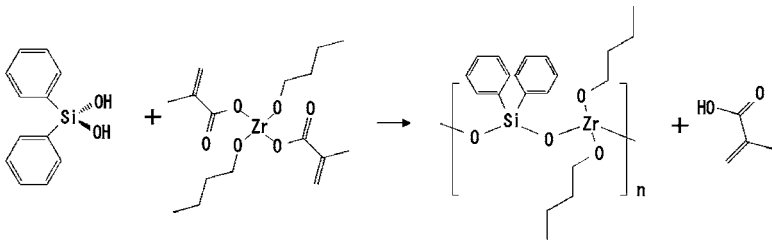


FIG. 2. Synthesis of $\text{SiO}_2\text{-ZrO}_2$ hybrid materials modified with phenyl and butoxide via nonhydrolytic reaction.

vinyl group $\text{C}=\text{C}$ stretching mode for methacrylate in ZDD, respectively, show a weak absorption, and the Si-OH vibration band has almost disappeared. In addition, it is expected that the self-condensation of DPSD is suppressed because there are no strong bands in the $1130\text{-}1000\text{ cm}^{-1}$ region corresponding to siloxane. Thus, it is suggested that the synthesized hybrid materials have the structure of the alternate $\text{SiO}_2\text{-ZrO}_2$ modified with phenyl and butoxy groups (Fig. 2).

For all the compositions and measured wavelengths, the refractive index change was linear with temperature over the measured temperature range ($30\text{-}110\text{ }^\circ\text{C}$). Figure 3(a) shows the refractive index change versus temperature of the 66.6 mol % ZDD for three wavelengths. Here, the refractive indices at $30\text{ }^\circ\text{C}$ were 1.5721, 1.5523, and 1.5519 at 633, 1319, and 1553 nm, respectively. The dn/dT of the organically modified $\text{SiO}_2\text{-ZrO}_2$ hybrid film is quite negative (on the order of -10^{-4}). The variation in dn/dT as a function of wavelength for different compositions of ZDD is shown in Fig. 3(b). The behavior of SiO_2 hybrid materials modified with phenyl and isopropenoxy via a similar nonhydrolytic process is also shown for reference, and is independent of wavelength.

As the amount of ZDD increases, the positive wavelength dependence gradually decreases, eventually resulting in a negative wavelength dependence for the 66.6 mol % ZDD. According to Ghosh's model,¹¹ which gives the wavelength dependence of dn/dT by a numerical formula, dn/dT is expressed as follows:

$$\frac{dn}{dT} = A \left(-3\alpha R - \frac{1}{E_{eg}} \frac{dE_{eg}}{dT} R^2 \right), \quad (1)$$

where $A = (n^2 - 1)/2n$, α is the linear thermal expansion coefficient, E_{eg} is the excitonic band gap, and $R = \lambda^2/(\lambda^2 - \lambda_{ig}^2)$ is the normalized dispersive wavelength (λ_{ig} : wavelength corresponding to the isentropic band gap). In the case of metal oxides or polymers, the first term related to thermal expansion is always negative because the thermal expansion coefficient is positive, and the second term is positive due to negative dE_{eg}/dT . Each parameter for SiO_2 and ZrO_2 is shown in Table I. Here, λ_{ig} of ZrO_2 is calculated from hc/E_{eg} (h : Plank's constant and c : light velocity). The dE_{eg}/dT of the yttrium stabilized ZrO_2 is used because these values are not known for our $\text{SiO}_2\text{-ZrO}_2$. The isentropic band gap is normally slightly smaller than E_{eg} . Figure 4 shows two terms of Eq. (1) for SiO_2 and ZrO_2 . A value of $-3 \times 10^{-4} AR$ is used to calculate the first term because modified organics in hybrid materials increase their thermal expansion as high as the order of $10^{-4}/\text{K}$ [e.g., $\alpha = (0.7\text{-}1.6) \times 10^{-4}/\text{K}$ for phenyl modified SiO_2 hybrid materials¹²] even though α of the inorganic materials is on the order of $10^{-6}/\text{K}$. In other words, we assumed that the first term depends on the thermal expansion of the organics and the second term is determined by

band gap change in the inorganic parts. It can be seen in Fig. 4 that the first term has a positive wavelength dependence and the second term shows a negative one, and the absolute value of the first term is always greater than the second term, thereby exhibiting a negative dn/dT for the hybrid materials. In addition, the two terms of ZrO_2 represent greater wavelength dependence than those of SiO_2 . That is the reason why the dn/dT of the SiO_2 hybrid material has negligible wavelength dependence and the $\text{SiO}_2\text{-ZrO}_2$ hybrid materials represent the wavelength dependence of dn/dT as shown in Fig. 3(b). The band gap of zirconium silicate becomes narrower as the amount of ZrO_2 is increased in SiO_2 , resulting in an increase in $1/E_{eg}$ and R^2 .¹³ Thus, the second term becomes larger with the increasing the amount of ZrO_2 in the hybrid materials, thereby increasing the negative wavelength dependence of dn/dT . Even though we assumed that all the α values in the organically modified $\text{SiO}_2\text{-ZrO}_2$ hybrid materials are $10^{-4}/\text{K}$, it can be considered that α decreases as the ZDD/DPSD ratio increases because the phenyl group, which contributes to the large thermal expansion, decreases. Then the ZrO_2 [which has a low thermal expansion ($\alpha = 6.5 \times 10^{-6}/\text{K}$)] becomes abundant, lowering the composite α , and making the wavelength dependence of the first term smaller than shown in Fig. 4. Consequently, the wavelength

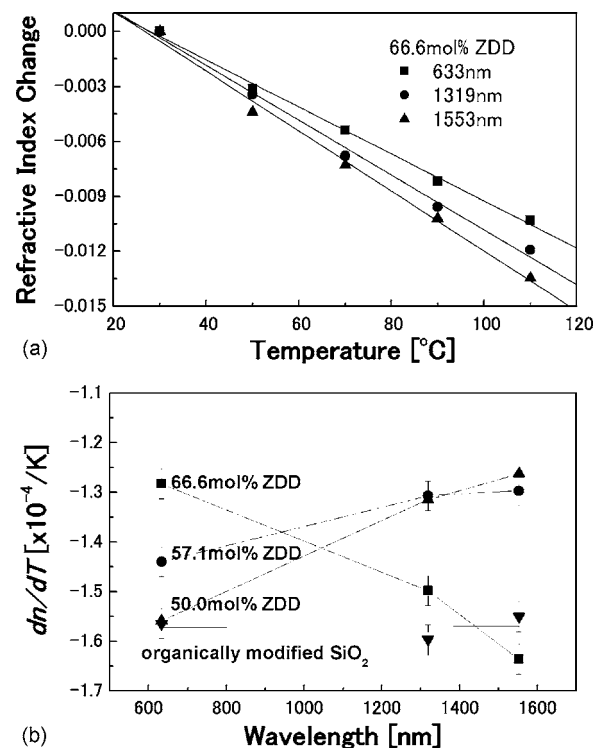


FIG. 3. (a) Refractive index variation of the 66.6 mol % ZDD hybrid material depending on temperature and measurement wavelength. (b) dn/dT change of the organically modified hybrid materials as a function of composition and measured wavelength.

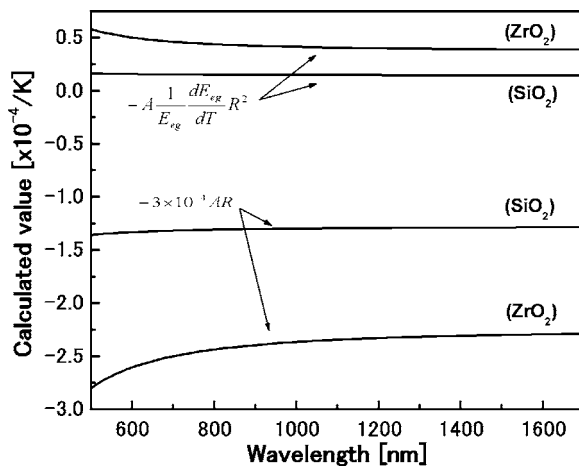
TABLE I. Parameters for Eq. (1) for SiO₂ and ZrO₂.

	A	λ_{ig} (nm)	E_{eg} (eV)	dE_{eg}/dT ($\times 10^{-4}/K$)
SiO ₂	0.427	120	8.90	-3.02
ZrO ₂	0.75	222 ^a	5.58	-2.78 ^b

^aCalculated from E_{eg} .^bValue of yttrium stabilized ZrO₂ (12% Y₂O₃).

dependence of the second term is likely to become gradually superior to that of the first term as ZrO₂ is added to the organically modified SiO₂. This causes the wavelength dependence of dn/dT to change from positive to negative.

In conclusion, dn/dT of an organically modified SiO₂-ZrO₂ hybrid film was investigated. As the amount of

FIG. 4. Calculated factors for the wavelength dependence of dn/dT .

ZrO₂ increased, the wavelength dependency in dn/dT changed from positive to negative due to the increase in wavelength dependence of the electronic polarizability. The high dn/dT values and wavelength dependence of SiO₂-ZrO₂ hybrid films make them candidates for use in thermo-optic applications and an optical multiplexing/demultiplexing system.

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