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Effects of TiO_2 and ZrO_2 on optical properties of organic–inorganic hybrid polymers and thin films

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Abstract TiO_2- and ZrO_2-doped hybrid polymers were prepared by an anhydrous sol–gel process, and their optical properties were studied. Incorporation of TiO_2 and ZrO_2 was found useful in promoting sol–gel condensation reactions and reducing the OH absorption and optical losses of the hybrid polymers. The thermo-optic properties of the TiO_2- and ZrO_2-doped hybrid polymer thin films were measured, and linear functions were observed for the changes in film thickness and refractive index during thermal scanning tests. The photosensitivity of the hybrid materials upon UV irradiation was observed to increase with the increase of the content of TiO_2 and ZrO_2, and the mechanisms for TiO_2 and ZrO_2 enhancing the photosensitivity of the hybrid polymers are discussed.

1 Introduction

Titania and zirconia are widely used as dopants for modifying the properties of optical materials due to their exceptional properties, such as high refractive index, and excellent chemical and mechanical stability [1–3]. Using TiO_2 and ZrO_2 to tune the properties of hybrid polymers for integrated optical planar waveguide applications has also been extensively studied [4, 5]. Sol–gel processing of TiO_2 and ZrO_2-doped hybrid polymers with the conventional system (i.e. the aqueous sol–gel process) usually faces two obstacles: the homogeneity of TiO_2 and ZrO_2 in the hybrid material network and intrinsic optical losses due to high levels of residual OH groups. The first obstacle is due to the significant differences between the hydrolysis rates of titanium/zirconium and silicon alkoxides. Titanium and zirconium alkoxides are generally highly reactive with water, thus it is difficult to avoid the formation of precipitates or clusters when these alkoxides directly react with water. Stabilization of titanium/zirconium alkoxides by a chelating agent is useful to improve the uniformity of their Sol–gel reactions with water, but the process is normally quite complicated. The organic groups from the chelating agents may also result in additional absorption due to C-H vibrations. The second obstacle is due to the intrinsic limit of the aqueous sol–gel process. The remaining OH groups that are bonded with Zr and Ti atoms tend to be difficult to condense further, resulting in a high proportion of OH species at the end of the material synthesis [6]. The formation of ≡Zr-OH and ≡Ti-OH species in the water-based system is inevitable because of the high sensitivity of zirconium and titanium alkoxides to the hydrolysis reaction.

In this paper, a two-step anhydrous sol–gel process has been developed for synthesizing hybrid polymers containing the hetero-linkages, ≡Si-O-Ti≡ and ≡Si-O-Zr≡. Optical characterizations for the hybrid polymers have been performed, and the results show that highly homogeneous TiO_2- and ZrO_2-doped organic–inorganic hybrid polymers with low –OH contamination can be synthesized using this two-step anhydrous sol–gel process. The photosensitivity of TiO_2- and ZrO_2-doped hybrid polymeric films upon UV irradiations is also investigated, and the photosensitive mechanisms have been discussed.

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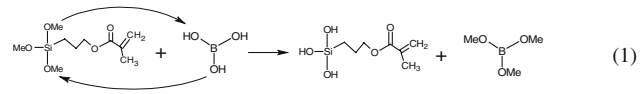
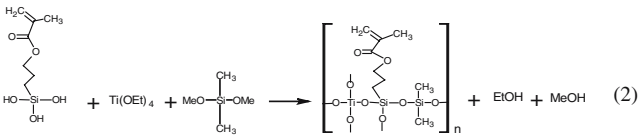
2 Experimental details

To improve the homogeneity of TiO_2 and ZrO_2 in the hybrid material network and to reduce the optical losses due to a high concentration of OH residuals, we have developed a two-step anhydrous sol–gel process [7, 8]. Briefly, the two-step anhydrous sol–gel process consists of a hydrolysis reaction (1) and a condensation reaction (2):



(1)



(2)

In reaction (1), MEMO (3-methacryloxypropyltrimethoxysilane) and boric acid were mixed using methanol as a mutual solvent. The hydrolysis of MEMO was achieved through a ligand exchange reaction under reflux conditions (oil bath set at 80 °C) for 2 h, 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 min, giving a highly viscous resin. In the condensation reaction (2), TET (titanium tetraethoxide) and DMDMS (dimethyldimethoxysilane) were added to the hydrolyzed MEMO, and the mixture was refluxed at 80 °C for 1 h under nitrogen. TET and DMDMS can be substituted by other alkoxides, such as TPZ (zirconium isopropoxide) and DPhDMS (diphenyldimethoxysilane), for tuning the refractive index of the resulting polymer. Adding a catalyst (a base or an acid) for the condensation reaction was found unnecessary because TET or TPZ was observed to show a self-catalyzing effect. The by-products from the condensation, such as methanol and ethanol, were removed with a rotary evaporator at 80 °C under vacuum conditions (1 mbar), and the resulting organically modified hybrid polymer was passed through a 0.2 micron filter before optical characterization. All chemicals were obtained from Sigma Aldrich.

To measure the optical properties (such as thermo-optical coefficient and optical film forming property) of the hybrid polymer, thin films were prepared by a spin-coating process. The polymer resin had 1 wt% IRGACURE-369 (from CIBA) added as a photo-initiator and was diluted with cyclohexanone in a weight ratio of resin /solvent = 6:1. The solution was passed through a 0.2 μm filter before coating onto substrates, such as fused silica glass and silicon wafers. The thin films were exposed to UV irradiation using a mercury lamp (350–380 nm) at a power intensity of 0.5 mW/cm^2, and then baked at 160 °C for 10 h under vacuum conditions. The UV-induced changes in the refractive indices of thin films were measured using a SCI Filmtek 4000 system, and the thermo-optic properties of the hybrid thin films were evaluated by mapping the variations of film thickness and refractive index as a function of temperature. UV-Vis-IR spectra of polymer resins and thin films were measured on a Cary 5000 spectrometer, and FT-IR spectra were recorded using a Perkin Elmer 2000 FT-IR spectrometer.

3 Results and discussion

Figure 1 shows the UV-Vis-IR spectra of the hybrid polymer resins containing different content of TiO_2 and ZrO_2. It can be seen that the OH residuals in the hybrid materials decrease as the increase of the concentration of TiO_2 and ZrO_2. The low OH absorption in these hybrid polymers indicates that TET and TPZ are effective in condensation with silanols. The effect of TET and TPZ on promoting condensation reaction (2) was further supported by the FT-IR spectra shown in Fig. 2, where a strong OH absorption peak disappeared after adding TET and TPZ.

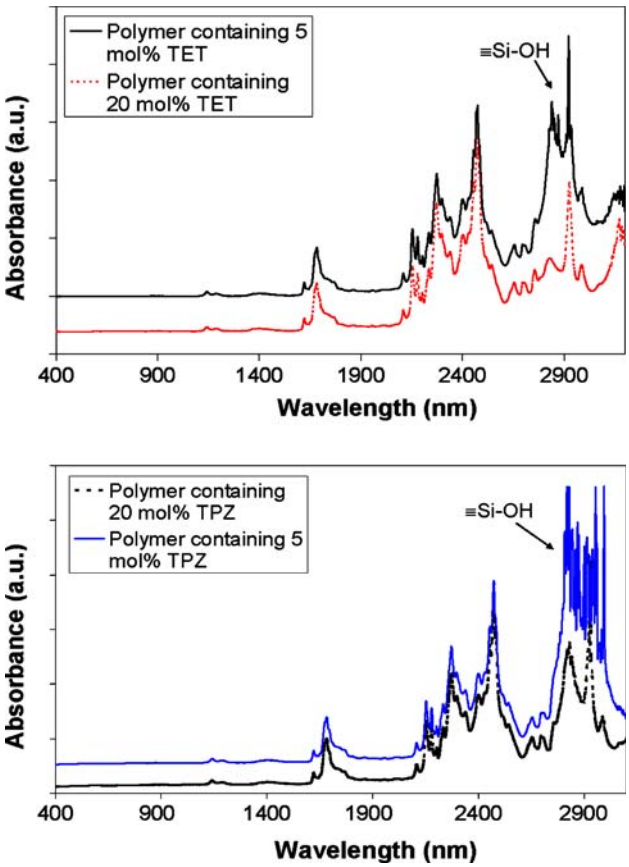


Fig. 1 UV-Vis-IR spectra of TiO_2- and ZrO_2-doped hybrid polymers

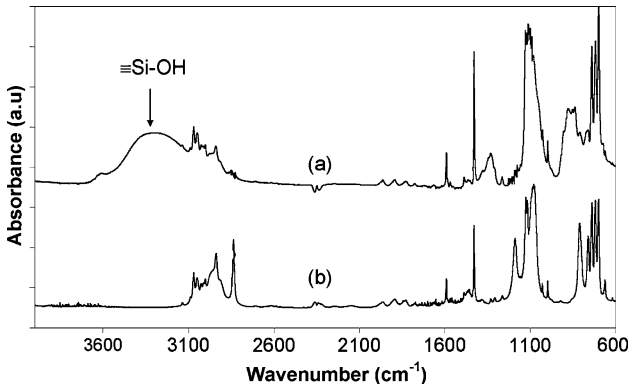


Fig. 2 FT-IR spectra of hydrolysed MEMO: before (**a**) and after (**b**) condensation with TET

An important advantage of photosensitive polymers for integrated optical applications is the potential for waveguide fabrication by direct UV writing process. To achieve this purpose, the polymers must possess some functional groups which can be readily polymerized by UV irradiation [4]. Therefore, the photosensitivity of the methacrylate groups (C=C) in the TiO_2- and ZrO_2-doped polymers upon UV irradiation is of interest. The UV-induced changes in refractive index of the hybrid thin films as a function irradiation dose is shown in Fig. 3. It can be seen that the refractive index of hybrid film increases with the progress of conversion of C=C groups into polyacrylate chains and finally reaches a saturated plateau. The total growth in the refractive index produced from UV exposure increases with the increase of the concentration of TiO_2 and ZrO_2, but the time required to reach the saturated state decreases. In the films containing 20 mol% TiO_2 and ZrO_2, the saturated refractive index (corresponding to an increase of ~0.006) was achieved within less than 2 min UV exposure, while a growth of 0.004 in refractive index took 10 mins for the films containing 5 mol% TiO_2 and ZrO_2. Comparing with ZrO_2, TiO_2 seems more effective in promoting the photosensitivity of the hybrid polymers as the TiO_2-doped samples showed larger refractive index increase within a shorter exposure time. Nevertheless, these results suggest that both TiO_2 and ZrO_2 have a catalytic effect on promoting the polymerization of C=C groups.

The mechanism for TiO_2 and ZrO_2 enhancing the polymerization of C=C groups in the hybrid polymers may be attributed to an inter-valence band transition produced by photo-reduction during UV exposure. The photo-chromic phenomenon, an inter-valence band transition induced by photo-excitation, in mixed-valence clusters was reported in [9, 10], and solutions containing titanium-oxo clusters are known to have photo-chromic properties [11]. The polymerization of acrylate groups induced by titanium-oxo clusters upon UV irradiation in hybrid sol–gel glasses containing TiO_2 with no photo-initiator was observed by Soppera et al. [12], which was proposed to be due to the same mechanism that occurred in the photo-chromic phenomenon. Mixed valence titanium (Ti^{4+} and Ti^{3+}) was supposed to exist in the titanium-oxo clusters, and Ti^{4+} may be reduced to Ti^{3+} upon UV irradiation, from which radicals are formed, thus promoting polymerization reactions with free acrylate radicals. Evidence for the reduction of Ti^{4+} to Ti^{3+} upon UV irradiation was revealed by the UV-Vis spectra in Fig. 4, showing that UV irradiation has induced marked red shifts in the absorption band in the region 200–400 nm. There is not much existing knowledge concerning polymerization of acrylate C=C groups initiated by ZrO_2 clusters in the literature. Since the responses to UV irradiation in the ZrO_2-doped and TiO_2-doped samples do not differ much, it is tentatively proposed that the UV-induced polymerization of C=C groups in the ZrO_2-doped thin films is also due to the photo-reduction mechanism. More details about the photo-reduction and polymerization

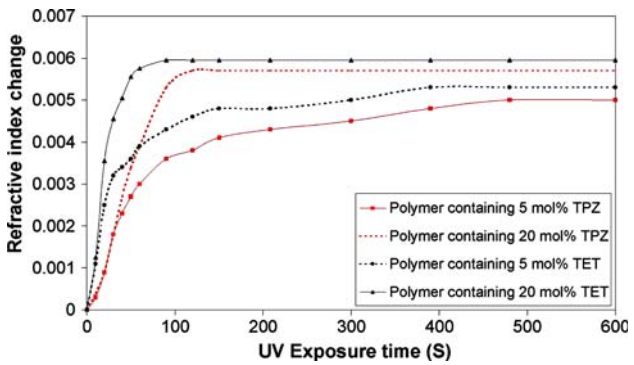


Fig. 3 Variations of refractive index in the TiO_2- and ZrO_2-doped hybrid polymer thin films during UV exposure

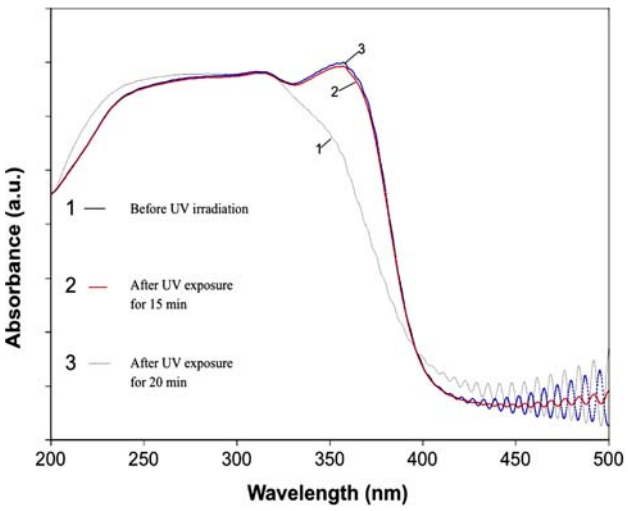


Fig. 4 Changes of the UV-Vis spectra of TiO_2-doped thin films upon UV irradiation

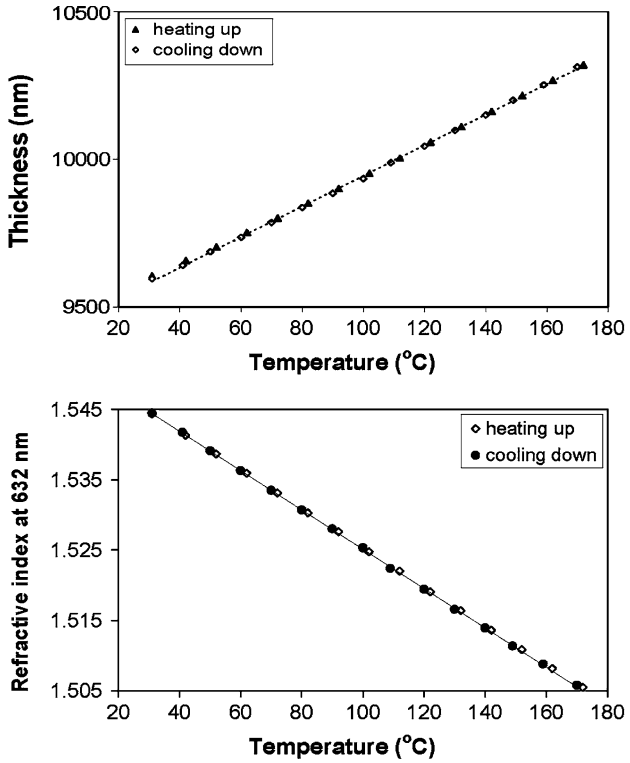


Fig. 5 Changes in film thickness and refractive index of the baked hybrid polymer thin films during heating and cooling treatment

kinetics in the hybrid polymers during UV exposure and thermal curing will be reported in our next paper.

The refractive index, birefringence and thickness of the thin film were measured with a SCI Filmtek 4000 system, and the values from different positions over the wafers are plotted to evaluate the optical quality of the film. This mapping technique is useful for comprehensively understanding the uniformity of the film. The hybrid polymer thin films were found to have excellent optical properties (low birefringence $< 1.3 \times 10^{-4}$; and good uniformity in refractive index and film thickness with fluctuations, <0.1% and <0.2% respectively, across the whole film surface). XRD measurements did not show the existence of TiO_2 and ZrO_2 nano-crystals in the films, further suggesting that TiO_2 and ZrO_2 were homogeneously incorporated into the silica network.

Figure 5 shows that the variations in film thickness and refractive index of the hybrid polymers as a function of temperature. It can be seen that the thermal expansion coefficient of the hybrid polymers was around 5.3×10^{-4} /°C, which was calculated by $\frac{dl}{dT} \times \frac{1}{L_0}$, where L_0 and l represent the film thickness at the initial point and at the temperature T. The thermo-optic coefficient (dn/dT) of the hybrid polymers was obtained to be around -2.7×10^{-4}/°C. The thermal scanning measurements in Fig. 5 were repeated with heating-up (from room temperature to high temperature) and cooling-down (from high temperature to room temperature) modes, and the results showed that the graphs obtained from both modes were perfectly repeatable without any hysteresis, clearly indicating that the film thickness and refractive index vary linearly with temperature. These properties are highly desirable for fabricating thermo-optic devices (no evidence of glass transition behaviour in the range of measurement).

4 Conclusion

In this study, organic–inorganic hybrid polymers containing ZrO_2 and TiO_2 were prepared with a two-step anhydrous sol–gel process. The incorporation of ZrO_2 and TiO_2 into the hybrid matrix using this anhydrous process does not need stabilization of titanium and zirconium precursors, and the direct condensation of silanols with titanium and zirconium alkoxides under anhydrous conditions provides the capability for improving the homogeneity of ZrO_2 and TiO_2 and reducing the OH contamination in the material network. Optical characterization showed that the ZrO_2- and TiO_2-doped hybrid polymers have low OH absorption and good thermo-optic linearity. The photosensitivity of the hybrid polymers upon UV irradiation increases with the increase of the content of ZrO_2 and TiO_2, thus the hybrid polymers with incorporation of these dopants are promising for low-cost fabrication of integrated optics components and devices.

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