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Highly sensitive detection of transient absorption in dye-doped ultrathin polymer films by the TiO_2/K^+ composite optical waveguide method upon pulsed laser excitation

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Abstract

A composite optical waveguide (OWG) composed of a 10–18 nm thick titanium dioxide (TiO_2) film sputtered on a conventional K^+-doped optical waveguide was first applied to detect transient absorption of organic dyes in ultrathin polymer films upon excitation with ns laser. The thickness of the TiO_2 film considerably affected the relative sensitivity of the composite OWG. The composite OWG with 10 nm thick TiO_2 gave much stronger transient absorption for 30–415 nm thick polymer films containing organic dyes than that with 18 nm TiO_2. Transient absorption of phthalocyanine and spiropyran in 20–135 nm thick polymer films was detected 3–20 times more sensitively by the composite OWG with 10 nm TiO_2 than the conventional K^+-doped OWG which showed a 150-fold sensitivity as compared with the usual normal incidence method. The relative sensitivity of the composite waveguide was also affected by the thickness and refractive index of polymers.

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Keywords: Composite optical waveguide; Titanium dioxide layer; Transient absorption; Dye-doped ultrathin polymer films; Highly sensitive measurements

1. Introduction

Detection of small changes in optical properties of ultrathin films is very important in many fields such as sensing and optical data processing applications [1,2]. Optical waveguides (OWGs) are essential components of advanced photonics and integrated optics. The electric fields of light propagating through the OWG layer have an exponentially decreasing value as evanescent waves beyond both surfaces of the OWG. Evanescent waves have been used to sensitively detect and to characterize adsorbates and thin films on the OWG. Swalen et al. [3] measured optical absorption of LB films sandwiched between a glass and a polymer OWG with much higher sensitivity than usual normal incidence absorption measurements. Itoh and Fujishima [4,5] applied the K^+-doped glass optical waveguide (K^+-OWG) method to detect photodeposition of Ag from aqueous solutions onto TiO_2 by flash photolysis and to observe electrochemistry of adsorbate. Itoh and co-workers proposed to further increase the OWG sensitivity by depositing a higher refractive index layer such as Ag^+ or TiO_2 on a K^+-OWG layer utilizing tapered velocity couplers and applied them to highly sensitive biological and chemical sensors [6–14]. Quigley et al. recently reported 50 times sensitivity enhancement of integrated optical sensors by use of thin Ta_2O_5 overlays as a high refractive index layer on K^+-OWG in the channel waveguide Mach-Zehnder interferometers [15].

We have been using the K^+-OWG for sensitively detecting photoreactions by Xe–Hg lamp and transient species

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by pulsed laser excitation in Langmuir–Blodgett (LB) films or very thin spin-coated films [16–22]. We demonstrated that the K$^+$-OWG method gave the 150-fold increase in sensitivity of detecting absorption changes in steady photolysis [16,17]. The photoinduced color change in a single monolayer LB film of only 2.75 nm thick was detected by this method for 4,4′-bipyridinium salts with tetrakis[3,5-bis(trifluoromethyl)phenyl]borate upon steady irradiation by a Xe–Hg lamp [16–18]. We also evaluated the orientation of photogenerated 4,4′-bipyridinium radicals in LB films composed of a few monolayers by this method [19,20]. Transient absorption spectra and time profiles were highly sensitively detected for ultrathin films upon pulsed laser excitation by using white light or laser as a probe [21,22].

Usually fairly thick films are needed for transient absorption measurements upon pulsed laser excitation. Tran-Thi et al. [23,24] reported the transient absorption measurements in LB films containing heterodimers of cationic porphyrin and anionic phthalocyanine upon excitation with nanosecond (ns) and subpicosecond pulsed lasers. They prepared LB films with 150–400 monolayers on each side of a substrate having a total thickness of about 825–2200 nm and observed transient absorption or photobleaching with maximum absorbance changes of only about 0.02–0.08 [23,24]. For the excited triplet species of porphyrins upon pulsed laser excitation, we reported that the detection limit was two monolayers by the K$^+$-OWG method by appropriately selecting the wavelength to monitor the transient absorption [18,21]. At least about 16 monolayers of 44 nm thick were, however, necessary to obtain data with a fairly good S/N ratio to discuss the kinetics [18,21]. From these results, the K$^+$-OWG method was also proved to be much more sensitive in time-resolved measurements as compared with the usual normal incidence method. Further enhancement of the sensitivity is expected by using thin layer of a high refractive index overlay without a severe scattering loss as demonstrated for sensing applications in solutions [8–14]. In the present study, we employed the TiO$_2$/K$^+$ composite OWG method to further increase the sensitivity of detecting transient species upon ns pulsed laser excitation.

2. Materials and experimental methods

Schematic representation of the conventional and composite OWGs is shown in Fig. 1. A 10–18 nm thick TiO$_2$ layer was sputtered on the K$^+$-OWG (26 mm × 76 mm) with a flat part $G = 5$ mm and tapered parts of about 2 mm at both sides in order to transfer the guided light smoothly from the K$^+$-OWG into the TiO$_2$ layer and to achieve the stronger electric field of the evanescent wave while keeping the scattering loss as small as possible. The probe laser at 514.5 or 632.8 nm was coupled with the K$^+$-OWG by two LaSF8 (refractive index n at 632.8 nm = 1.8785) prisms.

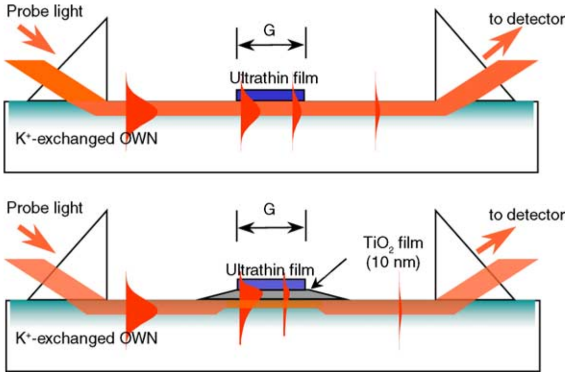

Fig. 1. Schematic representation of the zeroth-order guided mode in the conventional K$^+$-OWG and the composite OWG consisted of TiO$_2$ overlay and K$^+$-doped glass.

Aqueous solutions of zinc phthalocyaninetetrasulfonate (ZnPcS) and poly(vinyl alcohol) (PVA, $n_D = 1.520$) with a weight ratio of 1:25 or cyclohexanone solutions of photochromic spiropyran (SP) and polystyrene (PS, $n_D = 1.600$) or poly(methylmethacrylate) (PMMA, $n_D = 1.495$) with a 1:10 ratio was spin-coated on the OWGs [25]. The thickness of polymer films was controlled by changing the concentration of polymer solutions and/or the rotation speed. The thickness of the TiO$_2$ layer and polymer films was evaluated by an ellipsometry. Nanosecond OPO laser (670 nm, 0.3 mJ/pulse, B.M. Industries VEGA) or the third harmonic of YAG laser (355 nm, 8–10 ns, 0.7–1.0 mJ/pulse, B.M. Industries) was used to excite organic dyes through a cylindrical lens as schematically shown in Fig. 2. Steadt UV or visible irradiation was made through an appropriate optical filter using 150 W Xe–Hg lamp as a light source.

The calculation of the OWG absorbance (Ab$_{\text{OWG}}$) was made by the use of a multilayer approximation for a K$^+$-doped graded index type OWG with a Gaussian distribution, $n = n_s + \mathrm{d}n\,\exp(-x^2/T^2)$, where n_s is the refractive index of the substrate, dn the maximum refractive index change, x the distance (depth) and T the characteristic decay depth. The refractive index distribution was divided into 500 layers as schematically shown in Fig. 3. We calculated Ab$_{\text{OWG}}$ from the intensity of guided probe light before (I_0) and after (I_{ex}) photoirradiation using parameters shown in Fig. 4, where L_{P1}, L_{P2}, L_{C1}, L_{C2}, L_{C3} and L_{C4} are coupling losses at each prism and each part of the clad, β_{i0} and β_{iex} are the imaginary part of the propagation coefficient of polymer film before and after photoirradiation, G is the propagation length in a polymer film:

$$I_0 = L_{\text{P1}}L_{\text{C1}}L_{\text{C2}}\exp(-2\beta_{\text{i0}}G)L_{\text{C3}}L_{\text{C4}}L_{\text{P2}} \tag{1}$$

$$I_{\text{ex}} = L_{\text{P1}}L_{\text{C1}}L_{\text{C2}}\exp(-2\beta_{\text{iex}}G)L_{\text{C3}}L_{\text{C4}}L_{\text{P2}} \tag{2}$$

From these equations, Ab$_{\text{OWG}}$ is determined by β_{i0} and β_{iex} as

$$\text{Ab}_{\text{OWG}} = \log\left(\frac{I_0}{I_{\text{ex}}}\right) = \log[\exp(2(\beta_{\text{iex}} - \beta_{\text{i0}})G)] \tag{3}$$

In the complex OWG, the electric field is distorted due to the presence of a TiO$_2$ overlay. Electric field distribution

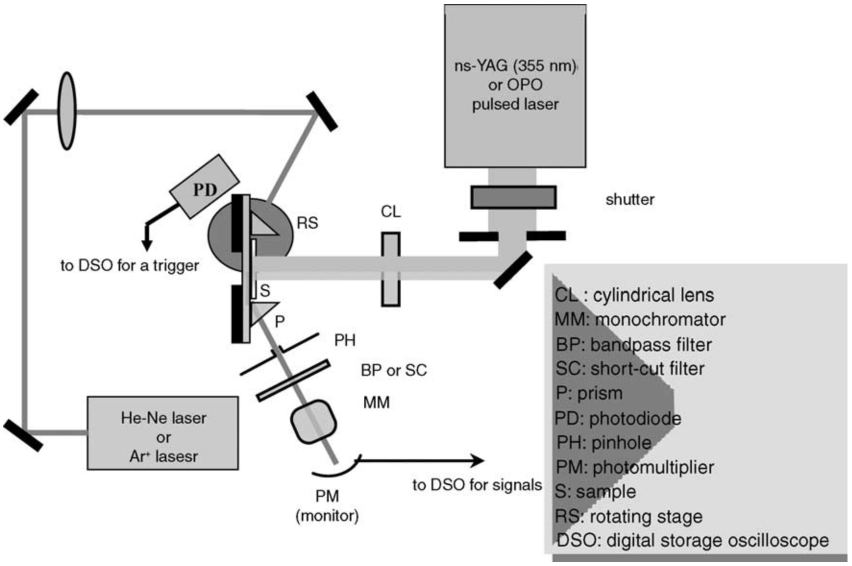

Fig. 2. The block diagram of transient absorption measurement of ultrathin organic films upon excitation with a ns laser by the OWG method.

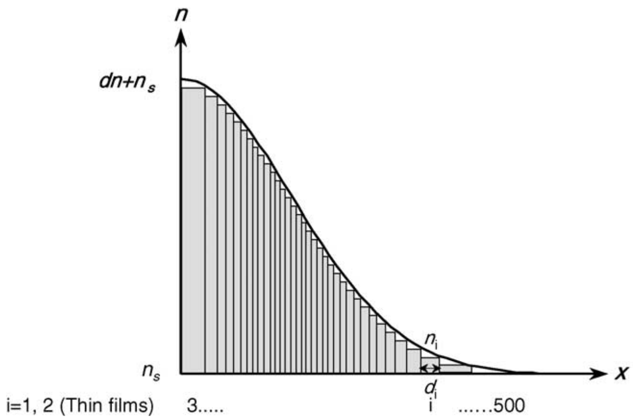

Fig. 3. Calculation of the OWG absorbance (Ab_{OWG}) by a multilayer (5 0 0) approximation for a K^+-doped graded index type OWG with a Gaussian distribution, $n = n_s + dn\exp(-x^2/T^2)$.

of evanescent wave in a thin polymer film on the OWG thus changes, which results in the increase of absorption by the polymer. The thickness of the TiO_2 overlay is an important parameter to determine the sensitivity and propagation loss. There are also other parameters to be taken into account. In order to compare the effect of the TiO_2 overlay clearly, the relative sensitivity of the composite OWG was defined in the present study as the ratio between the intensity change of a probe laser observed upon excitation of the TiO_2-covered area, as a composite OWG signal, and that observed upon excitation of the area without the TiO_2 overlay, as a conventional OWG signal.

3. Results and discussion

Calculations were first made to get information on the appropriate thickness of the TiO_2 overlay. Effective refractive index of the composite OWG is shown in Fig. 5 as a function of the TiO_2 thickness for two K^+-doped OWG layers. The effective refractive index exceeded that of K^+-doped OWG at about 24 nm. As shown in Fig. 6 which was calculated for 10 nm thick TiO_2 overlay, the electric field distribution in the polymer layer is considerably changed in the composite OWG. This result indicates that not only the evanescent wave but also the main component of the probe light starts to propagate in the TiO_2 overlay at about 10 nm. Therefore, the sensitivity of the composite OWG is expected to become higher with increasing the thickness of TiO_2 overlay until reaching the maximum. After that value, the intensity of the

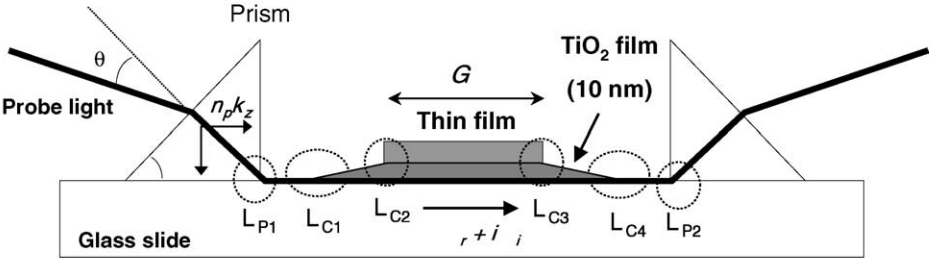

Fig. 4. Propagation of probe light through the composite OWG accompanied with various optical losses.

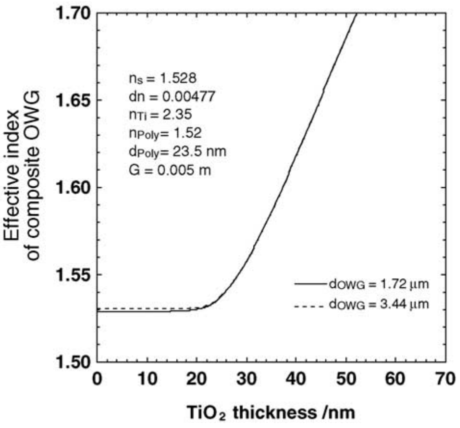

Fig. 5. Effective refractive index of the composite OWG as a function of the thickness of TiO_2 overlay for two different K^+-doped layers.

probe will become considerably lower due to absorption at the polymer film and the scattering loss in the TiO_2 overlay. In order to minimize the scattering loss yet to obtain high relative sensitivity, the thickness of TiO_2 overlay was selected to be 10–20 nm in the present experiment.

Fig. 7 shows the ground-state absorption spectrum (solid line) and the transient difference absorption spectrum (dotted line) upon excitation with ns laser at 355 nm for about 0.1 mm thick ZnPcS/PVA (1:25) cast film. Both spectra were observed by the usual normal incidence method. The transient absorption spectrum with a peak at about 560 nm and bleaching in a 600–720 nm region was attributed to the formation of excited triplet-state ZnPcS and the decrease of its ground state, respectively [26]. Fig. 8 shows the time dependence of OWG absorbance for a 134.9 nm thick ZnPcS/PVA film observed at 514.5 nm by two OWG methods upon excitation at 670 nm. The composite OWG showed much higher transient absorption than the conventional one. Both OWG absorbance decayed double-exponentially with lifetimes of 204 μs (35%) and 636 μs (65%). The lifetime of a major component corresponded with the triplet lifetime of ZnPcS [26]. The shorter lifetime of a minor component was most probably attributed to the intermolecular interactions of the excited triplet species in films due to rather high dye contents (ZnPcS:PVA = 1:25). The observed transient absorption was thus assigned to the formation and decay of the excited triplet-state ZnPcS. From these results, it is clearly demonstrated that the composite OWG method can detect the excited triplet absorption of ZnPcS in the 135 nm thick PVA film by 20 times more sensitively as compared with the conventional OWG. The observed values of normalized composite OWG absorbance at various thickness of PVA well corresponded with the calculated curve for the TiO_2 overlay of 10 nm as shown in Fig. 9. This result indicates that the calculation method employed for the composite OWG can precisely reflect the electric field in polymer films.

In order to study the effect of the refractive index of polymer films, spiropyran (SP) was dispersed in PS and PMMA films. SP is known to show photochromism between noncolored SP and colored photomerocyanine (PM) forms as shown in Fig. 10 with their absorption spectra before and after excitation at 340 nm in a PS film. PS and PMMA showed almost the same photoisomerization of SP upon UV excitation. Photochromism from SP to PM was caused by ns pulsed

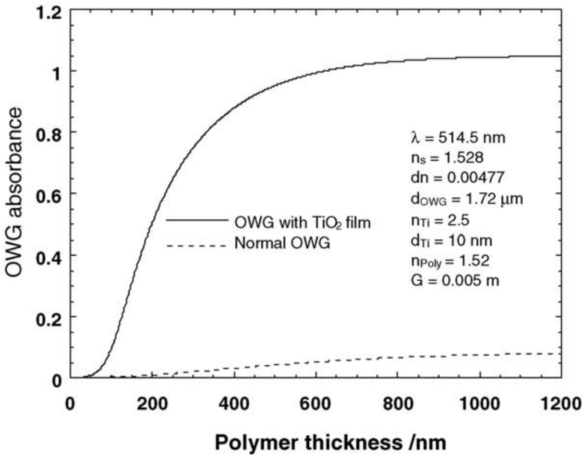

Fig. 6. Calculated OWG absorbance at 514.5 nm for conventional and composite OWGs as a function of polymer thickness with parameters given.

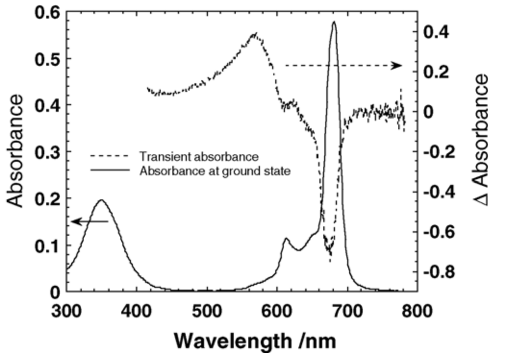

Fig. 7. Ground-state absorption spectrum (solid line) and the transient difference absorption spectrum (dotted line) observed with the usual normal incidence method upon excitation with ns laser at 355 nm for about 0.1 mm thick ZnPcS/PVA (1:25) cast film.

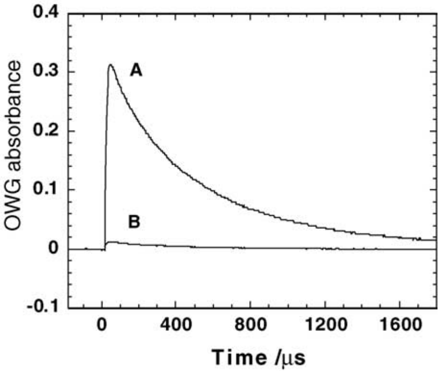

Fig. 8. Time dependence of OWG absorbance for the excited triplet state of a 134.9 nm thick ZnPcS/PVA film observed at 514.5 nm by (A) the composite and (B) conventional OWGs upon excitation with ns laser at 670 nm.

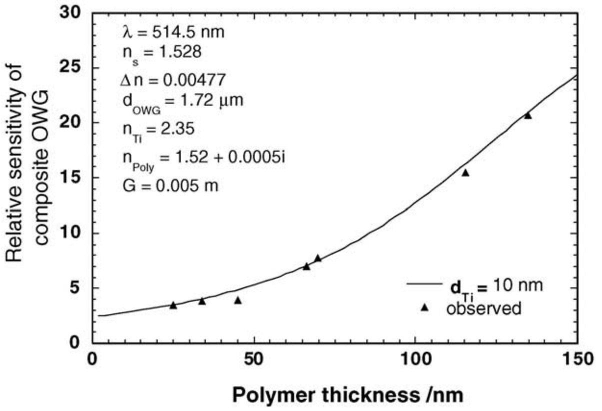

Fig. 9. Observed and calculated relative sensitivity of the composite OWG as a function of the thickness of PVA films.

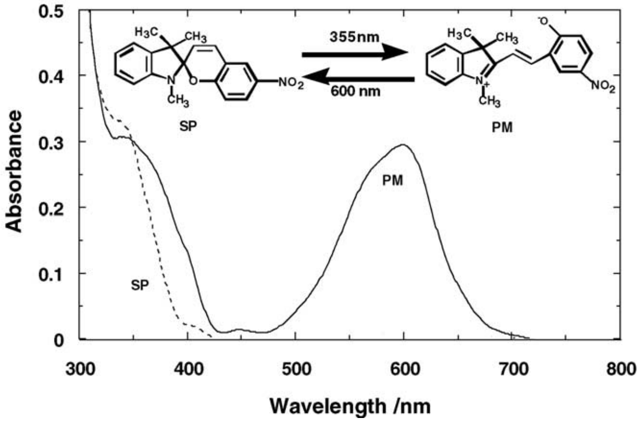

Fig. 10. Absorption spectra and structures of photochromic spiropyran (SP) and photomerocyanine (PM) upon UV and visible light irradiation. SP was dispersed in a polystyrene film (1200 nm) at 9.1 wt.%.

laser excitation at 355 nm, which was probed at 632.8 nm by He–Ne laser. Fig. 11 shows the time profiles of OWG absorbance for a 53.5 nm thick PS films containing SP upon pulsed laser excitation detected by (A) the composite and (B) conventional OWG methods. Apparent increase of noise level in the signal detected by the composite OWG is simply due to considerably decreased intensity of the probe light. Larger changes observed in the conventional OWG as compared with that for ZnPcS in PVA films shown in Fig. 8 are most probably caused by the refractive index of PS higher than the K$^+$-OWG layer. It is clearly shown that the composite OWG with 10 nm thick TiO_2 overlay detected the transient absorption by about 5 times more sensitively than the conventional OWG. Contrary to these results, the composite OWG with 18 nm thick TiO_2 overlay gave lower sensitivity than the conventional one, which was most probably due to strong absorption and/or scattering of the probe light in a thicker TiO_2 layer. The real part change of n^* estimated from the extinction coefficient change spectrum of SP (about 9 wt.%) in PS or PMMA by the Kramers-Kronig relationship is about 0.02 at 632.8 nm as reported in Ref. [30]. We actually reported reflectance change due to the complex refractive index n^* changes by photochromism of SP in 264 nm thick PS films in guided wave mode geometry [30]. In the present OWG configuration, however, the real part change of n^* is difficult to explain all the observed intensity changes at 632.8 nm due to much smaller thickness of the polymer layer as compared with the glass OWG. It may slightly change the distribution of evanescent electric field, but mainly acts as an absorbing layer for evanescent wave of propagating light in the glass OWG.

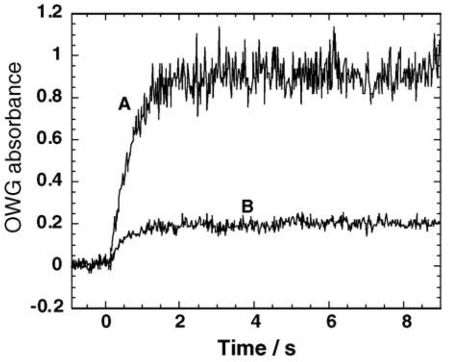

Fig. 11. Time profiles of transient absorption at 632.8 nm for spiropyran in a polystyrene film (53.5 nm) upon excitation by ns pulsed laser at 355 nm with (A) the composite and (B) conventional OWG methods.

The time dependences of OWG absorbance at 632.8 nm by (A) the composite and (B) conventional OWGs are shown in Fig. 12 for a 30 nm thick PMMA film containing SP upon pulsed laser excitation. The OWG absorbance change is expected to be about 56% from comparison of the thickness value (30 and 53.5 nm), but the observed conventional OWG absorbance was only 10% of that observed in PS. It was attributed to a smaller fraction of evanescent field absorbed by PM in PMMA due to its lower refractive index than the K$^+$-OWG layer. The relative sensitivity of the composite OWG for photochromism of SP in PMMA as compared with the

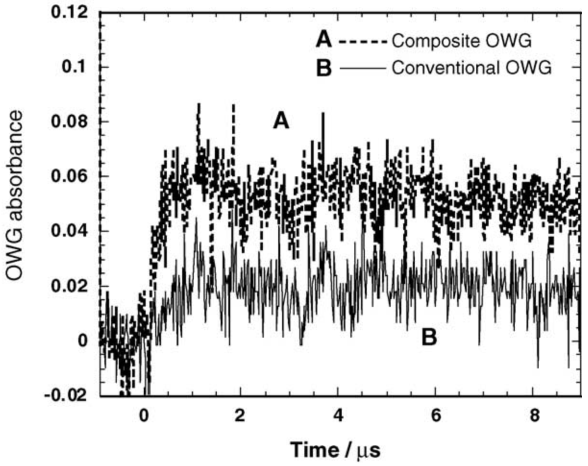

Fig. 12. Time profiles of transient absorption at 632.8 nm for spiropyran in a poly(methylmethacrylate) film (30.0 nm) upon excitation by ns pulsed laser at 355 nm with (A) the composite and (B) conventional OWG methods.

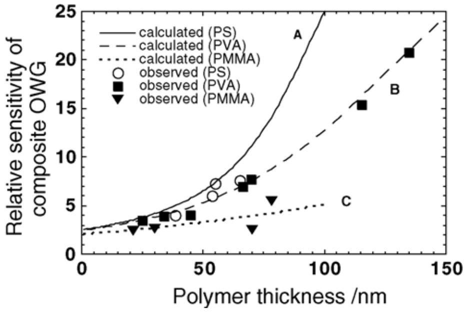

Fig. 13. Polymer thickness dependence of observed and calculated relative sensitivities of the composite OWG for detecting transient absorption upon pulsed laser excitation in (A) polystyrene, (B) poly(vinyl alcohol), and (C) poly(methylmethacrylate).

conventional one was about 2.2 times, which is also smaller than that observed in PS as shown in Fig. 11. Photochromism of SP upon steady or pulsed UV excitation hardly depended on the polymer matrix (PS or PMMA).

Fig. 13 shows the calculated and observed relative sensitivities of the composite OWG as a function of the thickness for three different polymer films deposited on it. The refractive indices employed in the calculation are 2.35, 1.528 and 1.5328 for TiO_2, the glass substrate, and K^+-OWG (the maximum value), respectively. The calculated relative sensitivity of the composite OWG increased more rapidly with increasing the thickness of PS and more slowly with increasing the thickness of PMMA as compared with PVA, which corresponded well with the observed data. The electric field distribution of guided waves is expected to be more distorted in the polymer film with increasing its thickness due to the presence of the high-refractive-index TiO_2 layer on top of the lower-refractive-index K^+-OWG layer [8]. From these results, it is concluded that the higher refractive index of PS clearly contributed to increase the relative sensitivity by assisting to increase the electric field distribution of guided waves. For polymer films with thickness smaller than about 20 nm, calculation showed that about 30 nm thick TiO_2 layer was necessary to achieve higher sensitivity.

4. Conclusion

In conclusion, very small transient absorption in ultrathin films was detected highly sensitively by the composite OWG method upon ns laser excitation. The relative sensitivity of the composite OWG method depended on the thickness and refractive index of the polymer film in addition to the thickness of the TiO_2 layer itself. We recently achieved novel very fast all-optical light modulation and switching by photoinduced complex refractive index change in a guided wave mode geometry composed of a few hundreds nm to a few μm polymer film containing organic dyes deposited on a thin metal layer [27–35]. In order to improve their performance for practical all-optical parallel processing, it is essential to evaluate photoresponses of ultrathin films and to develop materials showing large transient absorption or refractive index changes in a wide wavelength region. The present results will contribute a great deal to evaluate photoresponses of very thin films for such molecular photonics devices and also high-performance molecular sensing devices.

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