1. Introduction

A second-order nonlinear optical effect is used for photonic devices, and many kinds of effects have been reported in their applications, for instance, second-harmonic generation (SHG), electrooptic light modulation, etc. Some organic dyes show high nonlinearity, and among them, the azo-dye chromophore is one of the most probable candidates because of its high second-order nonlinear optical susceptibility. Some polymers grafted with azo-dye have been intensively studied so far. The second-order process is normally dipole forbidden in centrosymmetric materials. A non-centrosymmetric order for polymer film has to be achieved to obtain second-order nonlinearity, and many studies have been carried out using electric poling. Poled polymers have crucial problems, for example, the nonlinearity decreases with time because of the orientation relaxation. With a sol–gel method, the organic dye can be doped in a higher concentration into a strong inorganic matrix in which the dye can be fixed and stabilized for a long-term. Sugihara et al. reported that azo-dye doped silica film made by a sol–gel method with an electric poling technique had high second-order nonlinear optical and long-term stability. However, an electric poling technique has difficulty controlling the poling state of devices, for example, the SHG in optical waveguides requires severe phase control. Meanwhile, optical-poling techniques can develop non-centrosymmetric structures and automatically achieve phase matching for SHG. In an electric poling technique, an azo-dye with a dipole in a sample is rotated and oriented by the dc electric field applied between electrodes. On the other hand, physical mechanism of optical-poling techniques consists of two processes: the orientational hole-burning and the reorientation of azo-dye molecules. Under the excitation of a fundamental beam together with its second-harmonic (SH) beam, an orientational hole-burning of azo-dye molecules occurs through the interference of two-photon absorption at the fundamental frequency and one-photon absorption at the doubling frequency. The orientational hole-burning is followed by a momentary trans-cis-trans photo-isomerization (Fig. 1), which leads finally to a net permanent poled orientation of molecules. The orientation with the largest excitation probability is depopulated in favor of the opposite orientation. Fiorini et al. prepared phase matched azo-dye grafted polymer films by this technique. Si et al. investigated the light-induced SHG of azo-dye grafted polyimide films, and showed the ascendancy of optical poling over electric poling with an optical storage demonstration. The present authors have optimized the preparation of optical-poled DR1 doped silica films made by sol–gel method. The thermal evolution of the gel and the term stability of the photo-induced SHG of the films have been investigated, and we found that the rigid silica matrix prevented the relaxation of polarized structure.

2. Experimental procedure

2.1 Preparation of sols and films

Tetraethyl orthosilicate \((\text{C}_2\text{H}_5\text{O})_4\text{Si}\); Nacalai Tesque, Kyoto, Japan) and 4-[N-ethyl-N-(2-hydroxyethyl)] amino-4-nitro-azobenzene (Disperse Red 1, DR1; Aldrich, Milwaukee, USA) were used as starting materials. The sol procedure is illustrated in Fig. 2, based on an approach reported by Izawa et al. First, 1.432 g of tetraethyl orthosilicate and 1.005 g of N,N-dimethylformamidine (HCON(CH_3)_2; Nacalai Tesque) were put into 0.633 g of ethanol (Nacalai Tesque). Then, 0.108 g of DR1 was dissolved in the solution at 25°C. Finally, the mixed solution consisting of 0.633 g of ethanol, 0.072 g of 35% hydrochloric acid (Nacalai Tesque), and 0.696 g of deionized water was added to the dye mixed solution. After stirring for 30 min at 25°C, sols were obtained. Gel films were spin coated on alkali-free glass substrates (AF-45, Schott Japan, Japan). Immediately after spin coating, the gel films were directly heat-treated to build a polarized structure for second-order optical nonlinearity. Two seed beams at 1064 and 532 nm wavelengths from a Q-switched Nd : YAG laser were coaxially applied to the films. Second-harmonic generation was observed from the films after the optical-poling. We found that the rigid silica matrix prevented the relaxation of polarized structure.

Key-words: Optical-poling, Azo-dye, Hybrid, Sol–gel, Second-harmonic generation
put into an oven and dried at 150°C for 20 min to remove solvents for 1-time-coating films. In 2-time-coating films, the first and second dry times were for 5 and 20 min, respectively.

2.2 Measurements

Differential thermal analysis/thermogravimetry (DTA/TG) measurements were performed on gel film dried in an oven at 150°C for 20 min. The samples were scratched the films off the glass substrates and performed on DR1. The measurement of each powder was conducted in air while heated at 5°C·min⁻¹ with a differential thermal analyzer (Model Thermo Plus TG8110, Rigaku Co.). Thicknesses of films were measured using a surface roughness measure (Model Surfcorder SE-2300, Kosaka Laboratory), where parts of the films were scratched away from the glass substrates and measured. Refractive indices of heated films were measured using an ellipsometer (Model DVA-36VW, Mizojiri), where gel films were coated on alkali-free glass substrates, dried in an oven at 150°C for 20 min, and heat-treated at 210-250°C for 10 min. The measurement was carried out at 1064 nm.

The experimental setup shown in Fig. 3 was used in the preparation and the measurements on SHG relaxation of the optical-poled films. First, the dried films were treated by optical-poling without or with heat treatment at 210-250°C for 10 min to build the polarized structure. Two seed beams for the optical-poling of 1064 nm (pulse width 3.5 ns, fluence 1.09 J·cm⁻²) and 532 nm (3.0 ns, 5.48×10⁻³ J·cm⁻²) from a Q-switched Nd: YAG laser (50 Hz) were coaxially applied to the films with heat treatment at 210-250°C for 10 min, then the polarized lights of the two seed beams were aligned. Next, the seed beams were eliminated from the samples and the temperature of the oven was reduced to 25°C. The SHG intensity was consecutively measured by applying the 1064 nm beam. The SHG intensity was compared with the second harmonic generated by a Y-cut quartz crystal. Ultraviolet (UV) and visible (VIS) absorption spectra of optical-poled films were measured using an ultraviolet and visible light spectrophotometer (Model V-570, Jasco).

3. Results

3.1 DTA/TG curves of the gel film

Figures 4(a) and (b) show the DTA/TG curves of DR1 and the gel film with DR1 dried at 150°C for 20 min, respectively. Two endothermic peaks attributed to the melting point were observed at 141 and 164°C without weight loss in the DTA curve of (a) DR1. A gradual weight loss from approximately 200°C and a sharp weight loss from approx-
Optical-Poling of an Azo-Dye Chromophore Doped Silica Hybrid Thin Films

524

immediately 250°C were observed in the TG curve of (a), accompanied by an exothermic behavior at higher than approximately 240°C. On the other hand, a slight exothermic peak at approximately 210°C was observed, followed by a monotonous endothermic behavior in the DTA curve of (b). Figure 4(c) shows the DTA/TG curves of a silica gel film without DR1. The measurement was performed from room temperature to 500°C. A monotonous weight decreasing behavior in the TG curve and a slight exothermic peak position in the DTA curve were similar to those of the gel film containing DR1. A constant weight decreasing was observed from 300 to 500°C in the TG curve of (c).

3.2 Thickness and refractive indices of the gel-derived films

Thickness and refractive indices of the gel-derived films are shown in Table 1. The thickness and the refractive indices decreased when the heat treatment temperatures increased. The thickness of the film-coated repetition numbers two was more than twice as thick as that of coated repetition numbers one.

3.3 SHG relaxation of the optical-polied films

Figure 5 shows the laser shot dependence of second-harmonic \( \frac{\chi_{\text{eff}}}{\chi_q} \) of the optical-poled films heat-treated at various temperatures, where \( \chi_{\text{eff}} \) is the effective second-order susceptibility and \( \chi_q \) is the second-order susceptibility of quartz. The values of \( \chi_{\text{eff}}/\chi_q \) are shown as,

\[
\frac{\chi_{\text{eff}}}{\chi_q} = \frac{2L_{\text{qc}}T_1^{1/2}n_3^{3/2} \cos \theta_s \sqrt{I_{2s}/I_q^{2u}}}{\pi L_s \sinh \left[ \alpha_s L_s/2 \right] \exp \left( -\alpha_s L_s/2 \right) n_3^{3/2} T_1^{1/2}}
\]

where \( L_{\text{qc}} \) is the coherence length of quartz (\( L_{\text{qc}} = 20 \mu \text{m at } 1.063 \mu \text{m}^{16} \)), \( T \) is transmittance of fundamental and second-harmonic waves, \( n \) is the refractive index at 1.064 \( \mu \text{m} (n_q=1.55^{37}) \), \( \theta_s \) is the angle between the boundary normal and the direction of phase propagation inside the film\((\theta_s=0)\), \( L_s \) is the sample thickness, \( \sinh(x) = \sinh(x)/x \) and \( x \) is the attenuation constant. The subscripts \( s \) and \( q \) refer to the sample and quartz, respectively. The second-harmonic intensity \( I_{2s} \) of the optical-poled films was measured, where \( I_{2s} \) and \( I_q \) are the sample and quartz intensities, respectively. As shown in Fig. 5, the second-harmonics \( \chi_{\text{eff}}/\chi_q \) of the optical-poled films heat-treated at 210 and 230°C were higher than that of the optical-poled film heat-treated at 250°C. Moreover, the SHG relaxation rate of the poled films decreased with increasing the heat treatment temperature.

In the plots of the \( \chi_{\text{eff}}/\chi_q \) heat-treated at 210 and 230°C slight increasing behaviors of \( \chi_{\text{eff}}/\chi_q \) were observed at the beginning, and then the signals decreased. While applying the two seed beams with heat treatment, the optical-poled films were observed to shift from red to orange. A similar color shift was observed when a gel film was heat-treated in the oven without applying the seed beams. To investigate the differences between the optical-poling and an electrical poling, a corona poling was performed applying a high voltage of 8 kV·cm⁻¹ with the same heat treatment condition as the sample optical-poled at 250°C. The value of \( \chi_{\text{eff}}/\chi_q \) and the relaxation of SHG were measured with the same experimental set up as shown in Fig. 3 by rotating the sample stage (the oven) against the 1064 nm beam. The \( \chi_{\text{eff}}/\chi_q \) value was measured to be 0.20, no measurable difference between the relaxation plots of the optical-poling and electrical poling was observed.

3.4 Absorption spectra of optical-poled films

Figure 6 shows the absorption spectra of gel-derived films optical-poled at different heat treatment temperatures. As shown in Fig. 6 and Table 1, the reduction of peak heights and the blue shifts of the absorption spectra were observed, and when the heat treatment temperature was increased, the peak height decreased and shifted to shorter wavelength. Moreover, a new peak at approximately 350–400 nm was observed.
SHG relaxation rate of the poled films decreased (Fig. 5). From these results, it is possible that the polarized DR1 was fixed in the silica matrix and the matrix was made tougher through polycondensation as a result of the heat treatment. In the rigid matrix, the polarized structure might be stabilized.

On the other hand, the SHG intensity was reduced as the heat treatment increased temperatures, as shown in Fig. 5. As mentioned above, the absorption at 532nm beam is needed for the photo-isomerization between trans and cis in this azo-dye doped system. The degree of the photo-isomerization reaction depends on the resonance absorption of the azo-dye, so the more the absorbance at 532 nm, the easier the dipole rotation and the DR1 orientation. As shown in Fig. 6, the absorbance at 532 nm was reduced as the heat treatment temperatures increased. Therefore, we suggest that the difference in the SHG intensity was caused by the absorption degree of the film.

In the plots of the $\chi_{eff}/\chi_0$ heat-treated at 210 and 230°C, slight increases of the $\chi_{eff}/\chi_0$ were observed at the beginning, and the color shift from red to orange was observed when a gel film was heat-treated in the oven without applying the seed beams. Temperature increase in the films could be caused by a thermal effect from the pulses of 1064 nm beam. The color shift could lead to a decreased absorption of green. The absorption for the SHG might be reduced because of the thermal effect of the 1064 nm beam. Therefore, the appearance of an increase in $\chi_{eff}/\chi_0$ could be observed.

It is difficult to specifically describe the nanoscopic structure of this DR1/silica system. However, there are some keys in the absorption spectra and other previous studies. The reduction of peak heights, blue shifts, and the new peak at about 350–400 nm were observed in Fig. 6. Films made by sol–gel method have many pores when the films are heat-treated at a low temperature. DR1 could have evaporated through the pores. Nakamishi et al. reported the UV exposure of DR1/silica films made with a sol–gel method. They studied the absorption spectra of the exposed films. From thin-layer $\mathrm{H-NMR}$ studies, they determined the structure where DR1 changed into two materials, and one had a $p$-nitroaniline-like structure with an absorption peak near 370 nm. A similar decomposition was made with the heat treatment. Besides, another structure change might have occurred as follows. DR1 has a hydroxy group. Si–O–C chemical bonds can be produced during the hydrolysis of TEOS and polycondensation between the hydroxy group of DR1 and hydrolyzed TEOS. The Si–O–C bonds can be hydrolyzed again, but some parts of bonds that hold in the dense silica matrix remain after the heat treatment. A reverse reaction can not be made because of the lack of water. DR1 has a donor group ($-\text{N(CH}_2\text{CH}_3\text{)}$) and an acceptor group ($-\text{NO}_2$) at (CH$_2$CH$_2$OH)) and an acceptor group ($-\text{NO}_2$) at separated positions, respectively. Charge transfer is caused by an absorption band at from approximately 400–600 nm in a DR1 molecule. If the new chemical bond is produced between DR1 and the silica matrix, the structure change of the donor can cause a decreased electron-release behavior and change the resonance absorption. As a result, a reduction of peak heights and blue shifts can possibly occur.

5. Conclusion

DR1 doped silica films were prepared from the solution of tetraethyl orthosilicate and DR1 using the sol–gel method. Optical-poling with heat treatment was applied to the films. SHG from the polarized films was observed. The results of the thermal analysis and the measurements of SHG relaxation included the following.

(1) A polarized structure of DR1 could be made in...
silica films with the optical-poling technique.

(2) A rigid silica matrix could be made with the heat treatment.

(3) The rigid silica matrix prevented the relaxation of the polarized structure.

Acknowledgments The authors thank S. Fujiwara, Dr. T. Suzuki and Y. Kondo (Hirao Active Glass Project) for their help in some experiments.

References