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Two-Dimensionally Poled Sol–Gel Processing of TiO_2 Film Doped with Organic Compounds for Nonlinear Optical Activity

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Optically nonlinear TiO_2 films containing 4-(dimethylamino)-4′-nitrostilbene (DANS) and 4-(2-(4-hydroxyphenyl)ethenyl)-*N*-methylpyridinium (HEMP) iodide were prepared by the sol–gel process under an electric field. The second-order nonlinearity was about 11 pm/V for TiO_2/DANS, and it decayed in months by the relaxation of molecular orientation in the film. When HEMP iodide was modified with a silane anchor, the declination became significantly slow.

Introduction

Utilization of organic materials as electrooptic devices has recently attracted considerable attention. Many organic compounds having a high optical nonlinearity or hyperpolarizability on their molecular level show no net nonlinearity in their native condensed phase, because the spatial molecular ordering is centrosymmetric in crystalline structure.[1] Since most of such organic molecules have large permanent dipole moments, the poling technique was proposed to fabricate second-order nonlinear optical (NLO) devices of polymer films.[2–4] Avnir and co-workers[5] pointed out that inorganic oxide glass was useful to stabilize organic molecules such as laser dyes. The sol–gel process[6] was applied to the preparation of the matrix glass. When inorganic glass is employed as a matrix in place of organic polymer, several advantages such as a higher heat resistance are expected.[5] An SiO_2 glass film doped with *p*-nitroaniline (*p*-NA) has been prepared by the sol–gel process, and its electrooptic effect was measured during the gelation under electric field.[7] Very recently, sol–gel films containing NLO dyes have been reported.[8–10] We investigated the chemical process of sol–gel reaction of metal alkoxides[11] and applied this technique to prepare dielectric $BaTiO_3$ films for fabricating a powder electroluminescent device.[12] The high dielectric constant of the matrix seems to have an advantage for ordering the molecular dipole under relativley low electric potential. In the present study, we apply the sol–gel method to prepare poled TiO_2 films containing NLO molecules. The NLO activity was evaluated by measuring the intensity of the second harmonic generation (SHG). Since the decay of the SHG activity was caused by the relaxation of the molecular orientation, an anchored NLO compound was successively employed to improve the stability.

Materials and Methods

Figure 1 shows chemical structures of the NLO molecules used in this study. From reference to the literature,[13] 4-(dimethylamino)-4′-nitrostilbene (DANS) was synthesized from 4-nitrotoluene (28 mmol) and 4-(dimethylamino)benzaldehyde (28 mmol) by refluxing in toluene (30 mL) for 24 h with piperidine (0.2 mL) as a catalyst. Similarly, 4-(2-(4-hydroxyphenyl)ethenyl)-*N*-methylpyridinum (HEMP) iodide was synthesized by the reaction of 4-methylpyridine (50 mmol) with 4-hydroxybenzaldehyde (50 mmol) in toluene with piperidine, followed by quaternarization with excess amount of methyl iodide in methanol solution. Silane-anchored HEMP, 4-(2-(4-(3-(trimethoxysilyl)propoxy)phenyl)ethenyl)-*N*-methylpyridinium (SEMP), was obtained by the following reactions. After the treated with concentrated NaOH solution, HEMP (12 mmol) was mixed with (3-chloropropyl)trimethoxysilane (60 mmol) and heated at 80 °C for 2 days. From the mixture (3-chloropropyl)trimethoxysilane was removed by the distillation under reduced pressure. The residue was washed with tetrachlorocarbon and then crystallized from diethyl ether. These NLO compounds synthesized were purified by recrystallization, and their chemical structures were checked by ^1H NMR spectroscopy.

According to the sol–gel procedure under high acidic conditions,[14] solution for the TiO_2 gel films was prepared by adding dropwise 2-propanol (PrOH) solution of HCl/H_2O into the PrOH solution of tetraisopropoxytitan (TPOT) with NLO molecules under vigorous stirring at ambient temperature. The component of the mixture was 1.0:1.0:0.5:1.88 for TPOT:PrOH:HCl:H_2O at the molar ratio. A large amount of catalyst HCl was employed to control the gelation. Chlorine is expected to form a complex with Ti atom.[14] Propylene carbonate of 3 times of TPOT in the mole amount was added to the mixture to avoid the formation of crack in the gel film. The solution was spread on a spinning ITO glass plate. The rate of spinning was adjusted to make a film having a thickness of about 1 μm. Another ITO glass plate was placed on the film and electric field was applied for a fixed duration. The sample plate was then dried in vacuo. The

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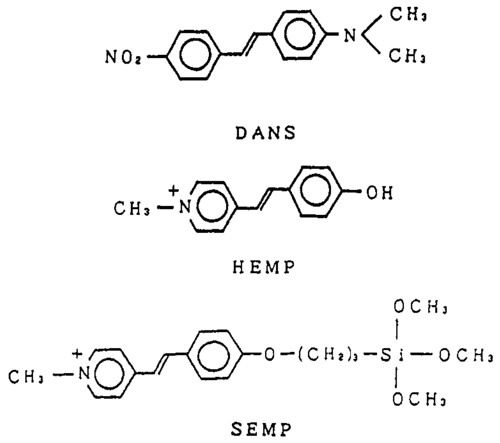

Figure 1. Chemical structure of the employed compounds having second-order nonlinear optical activity.

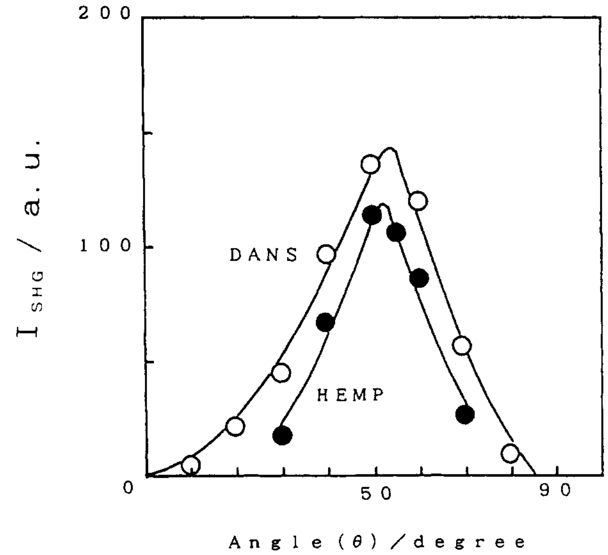

Figure 2. Intensity of second harmonic generation as a function of incident laser angle for poled TiO_2 glass film containing nonlinear optical compounds, DANS (○) and HEMP (●).

thickness of TiO_2 film was measured by an ellipsometer (Mizojiri, DVA-36L) of a Safcon thickness meter. The absorption spectra of the films were measured with a Hitachi U-3210 spectrophotometer.

For the measurements of SHG, the sample was mounted on a goniometer stage. The polarized beam of a Q-switched Nd: YAG laser (Quantaray DCR-3, operated at 10 Hz, λ = 1064 nm, pulse duration of 10 Hz, λ = 1064 nm, pulse duration of 10 ns, peak power of about 4 mW in 5-mm diameter) was passed through a 690-nm cutoff glass filter and put into the sample. The fundamental beam passed through the sample was blocked with a cyan glass filter (Toshiba, C-50S) and the second harmonic beam was monitored by a Bausch-Lomb monochromator equipped with a Hamamatsu R-928 photomultiplier tube. The output signal was averaged by accumulating with a boxcar integrator (Stanford, SR-250) or a digital storage oscilloscope (Gould, DSO-4072). The SHG intensity of the samples was standardized by referring a 0.3-mm thin layer of urea powder.[16]

Results and Discussion

Figure 2 shows the SHG intensity measured at various incident angles of the laser beam. A peak was observed at about 55° and 52° for DANS and HEMP, respectively. The angle dependence of SHG intensity is quite similar to that reported for corona-poled polymer film,[2] and the difference in the peak angle means that d_{31}/d_{33} of the DANS-doped film is larger than that of the HEMP-doped film. In the following experiments, these incident angles were conditioned for measuring the SHG activities. Without NLO molecules the poled TiO_2 film gave no SHG intensity. The peak intensity for the TiO_2 film doped with 10 wt % DANS was larger only by 15% than that for the film with 5 wt % DANS, while the peak angle remained unchanged. This observation indicates that the SHG activity of some molecules in the film becomes invalid by aggregating with each other. Since the SHG activity was not increased, the concentration of 5 wt %, which corresponds to the molar concentration of 0.17 mol/dm^3, was used in the following experiments. The same mole concentration was used for the other NLO compounds. The bulk density of 1.13 g/cm^3 reported for dry TiO_2 gel[15] was used to calculate the molar concentration.

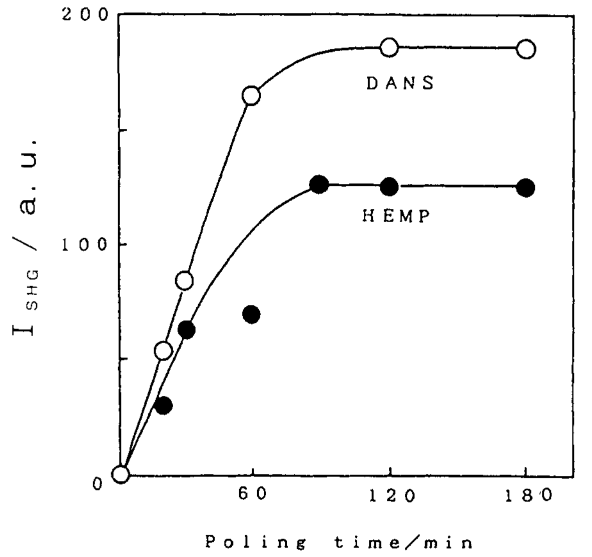

Figure 3. Intensity of second harmonic generation for DANS (○) and HEMP (●)-doped TiO_2 films prepared at different poling duration. Applied electric filed for the poling was 30 V/μm.

Dependence of the poling duration on the SHG intensities for the TiO_2 films doped with DANS and HEMP is shown in Figure 3. The SHG intensity became constant at 100 min, which may correspond to the time for finishing the gelation. When the poling was stopped in the process of the gelation, the orientation of part of the NLO molecules might be relaxed and the smaller SHG intensity resulted. Thus, the time dependence observed in Figure 3 is explained by the difference in the degree of gelation at the end of the poling process. Although finishing of the gelation could be estimated from the change in the viscosity, chemical analysis during the gelation might be helpful to confirm this explanation.

At the full poling, where the SHG intensity is expected to be proportional to the square of the molecular hyperpolarizability β, the observed SHG activity of HEMP was about 70% of that of DANS. The value of β for DANS is reported to be 450 × 10^{-30} esu,[17] while that for ionized (deprotonated) form of HEMP is 1000 × 10^{-30} esu.[18] The observed smaller SHG intensities for HEMP indicates that the chemical structure of HEMP contains the non-ionized OH group as shown in Figure 1. This structure was supported by the observation that the SEMP-doped film showed a similar SHG intensity to the HEMP-doped film as shown later.

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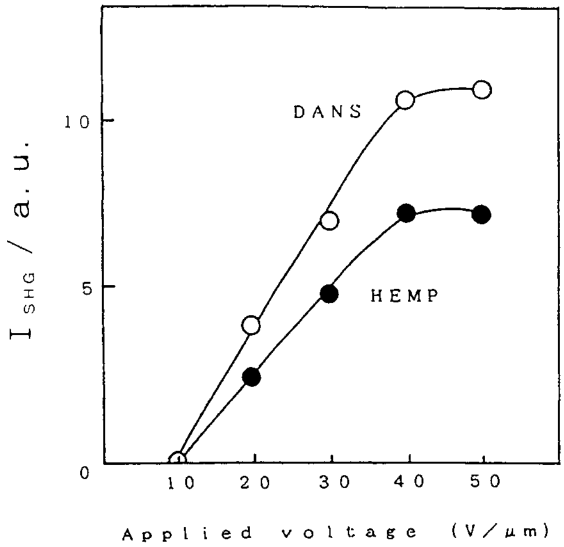

Figure 4. Intensity of second harmonic generation for DANS- (○) and HEMP- (●) doped TiO_2 films prepared at different applied electric field for poling. Duration of the poling was 120 min.

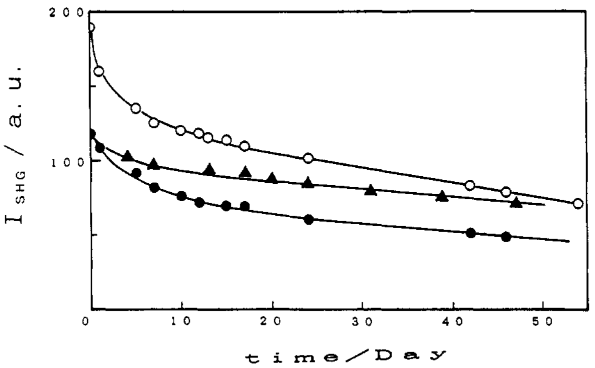

Figure 5. Stability of the second harmonic generation after the preparation for DANS- (○), HEMP- (●), and SEMP- (▲) doped TiO_2 films.

Figure 4 shows the dependence of SHG intensity on the applied electric field. The SHG intensity increased linearly with the increase of the electric field from 10 to 40 V/μm. Although the electric current flow was less than 1 mA/cm^2 at up to 40 V/μm, dielectric breakdown was observed at above 50 V/μm. In the report of SiO_2 glass films,[7] p-NA molecules are oriented under the electric field below 10 V/μm. The present result may imply that the attempt to use a low electric field for poling would have failed. The SHG activity of the DANS-doped film was 1.9 by referring the thin layer of urea powder. The absolute value for the NLO activity, d_{33}, was roughly estimated to be about 11 pm/V. This estimation is based on the d_{11} of 0.5-mm quartz plate is 0.5 pm/V and that the SHG intensity of urea powder is 400 times of quartz plate.[16] That is, $11 = 0.5 \times (1.9 \times 400 \times 0.3/0.5)^{0.5}$. The NLO activity obtained for the TiO_2 film is comparable to the well known crystal material $LiNbO_3$ which exhibit d_{33} = 30 pm/V, similarly to the poled polymer[3a] and sol–gel inorganic films.[8–10]

Stability of the SHG intensity was measured for the DANS- and HEMP-doped TiO_2 films and the result was shown in Figure 5. In the first few days the SHG intensity decays fast. Then, the rate of declination became considerably small, but decay was not ceased in the observed period of 50 days. The decay profiles of SHG activity for these dope TiO_2 are similar to that for the doped polymer.[2] Either decompositon or orientative relaxation of the NLO molecules is responsible for this declination of the SHG activity. To know the reason for the declination, we measured the absorption spectra of the samples.

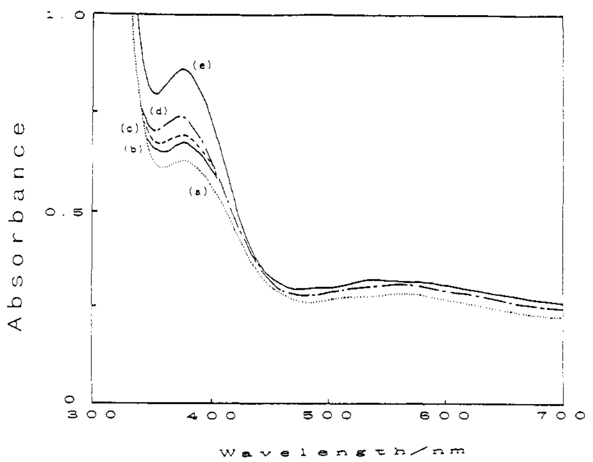

Figure 6. Time dependence of absorption spectrum of HEMP-doped TiO_2 film measured at (a) 5 min, (b) 1 day, (c) 5 days, and (d) 10 days after the preparation. Absorption spectrum of HEMP-doped TiO_2 film prepared without poling (e) is also shown for comparison.

Figure 6 shows the change in the absorption spectra of the HEMP-doped TiO_2 films at various periods after the preparation. The broad absorption at above 450 nm is based mainly on the ITO thin film. The peak absorbance at 380 nm increased with the time and approached to that of the unpoled sample. This observation indicates that the declination of SHG activity is caused by the relaxation of the molecular orientation in the TiO_2 matrix. Since the gelation occurs in 2 h in the present experimental condition, the glass film may contain pores of the size larger than that of the NLO molecules. This assumption was supported by the observation that the refractive index of the film without the NLO compounds was 1.776, which is remarkably smaller than 2.5 of crystalline TiO_2. The bulk density of 1.13 g/cm^3 for TiO_2 dry gel[15] is also smaller than 3.90 g/cm^3 for anatase crystal. Then the NLO molecules probably rotate slowly in the large cavity and the orientation changes. Therefore, formation of the chemical bond between the NLO molecule and the matrix is expected to reduce the orientative relaxation of the molecules. A novel NLO compound, SEMP, containing a silane anchor group was prepared and used in place of HEMP. The initial SHG activity was comparable to that of HEMP, but the declination became significantly small as shown in Figure 5. Although the formation of chemical bond was not confirmed experimentally, it is likely that the silane group takes a role to anchor the SHG dye to TiO_2 gel. The decomposition of the NLO molecules may be responsible for the observed slow declination, because the gel film contains the sol components such as HCl to a certain extent. Since the sample could not be calcined and the film was sandwiched between two ITO electrodes for poling, the reactants may be left in the film.

Conclusion

In the present study we showed that the sol–gel process under poling can be utilized to prepare SHG-active films. The stabilization of poled NLO molecules is easily performed by bonding a silane anchor group in the molecules. Further investigation on the fabrication procedure should be done to improve the stability of the SHG activity, which may be obtained by selecting less reactive sol components.