Refractive Index Lithography Materials Based on Chemically Amplified Reaction

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This article is dedicated to late Dr. Ito for his distinguished invention, fantastic technology, and warmhearted humanity.

Refractive index lithography was performed on polymer films consist of a photo-acid generator (PAG), t-BOC-protected naphthazarine as an acid chromic dye. The key reaction is the chemically amplified de-protection of the t-BOC group, by which color of the material change followed by refractive index change. Naphthazarine-containing polymer was also prepared. The induced refractive index was as large as 4×10^{-3} , which is enough large to apply to optical waveguide fabrication.

Keywords: refractive index lithography / photo optical effect / naphthazarine/ chemical amplification

1. Introduction

Developing those materials whose refractive index can be directly patterned with lithographic technique is important for fabricating photonic devices, optics, optical waveguides, 3D-optical data storage media, optical computing devices and so on.¹⁾ Recently we have been developing various photo-optical materials, whose refractive indices are controlled by photochemical reactions. The photo-optical effect involves photochromic reaction of azobenzenes,²⁾ norbornadienes,³⁾ photo-rearrangement of sulfonates,⁴⁾ and two-photon-sensitized reaction⁵⁾ and so on. Change in the chemical structure during photochemical reaction is usually followed by the absorption change due to the electronic state change. And then refractive index also changes following to Kramers-Kronig's relationship. Thus, photo-optical effect is the technique that is combination of photochemistry and optical properties of the materials.

Since efficiency of the photoreaction of those materials is limited to the quantum yield of the

photochemical reaction of the materials, however, involving chemical amplification reaction is desirable for improving the photo-optical effect efficiency. Thus we designed a novel system which combines a PAG and t-BOC protected naphthazarine. The naphthazarine is a dye whose color is based on

Scheme 1 Chemically amplified photo-optical effect of t-BOC protected naphthazarine

Scheme 2 Preparation of t-BOC protected Naphthazarine, and polymer-bound t-BOC protected Naphthazarine

intramolecular conjugation involving hydrogen bonding between the hydroxyl group and quinone group. Therefore the electronic state of the naphthazarine should be controlled by the de-protection of t-BOC group with chemically amplified reaction in Scheme 1.

2. Experimental

2.1 Materials

Naphthazarine was prepared by the reaction of hydroquinone and maleic anhydride, which was then treated by di(*tert*-buthyl) carbonate to give t-BOC protected naphthazarine. Naphthazarine-containing polymer films were prepared by spin-coating of the mix solution of the t-BOC protected naphthazarine (2wt %), a photo acid generator, NAI-105 (1 wt %), and PMMA. Polymer-bound naphthazarine was prepared by the reaction of the naphthazarine and poly (acrylic acid) in the presence of a dehydration reagent, followed by repeated reprecipitation.

Photo-dynamics and photophysical process measurement was performed by electron beam pulse radiolysis with a linear accelerator (acceleration energy of 35 MeV), and a pulsed Xe lamp (pulse duration of 1μsec). Laser flash photolysis was performed with a Nd:YAG laser (10 nsec, third harmonics) as pump source and cw-Xe lamp as a monitor lamp.

Photochemical reaction was performed by photo irradiating 350 nm light from ultra-high pressure mercury lamp (Ushio SX-UI501HQ) using a monochromator.

UV/Vis absorption spectra were recorded on a Jasco V-550 spectra photometer.

Refractive indices of the samples were determined by a prism coupled m-line measurement system using 633nm light from a He-Ne laser as the probe.

Figure 1 Change in UV spectra of t-boc naphthazarine in THF solution heated at 100°C

3. Results and Discussion

3.1 Photoirradiation of Naphthazarine solution.

Fig 1 shows the spectral change of t-BOC protected naphthazarine solution in the presence of a PAG under thermal treatment after photoirradiation. Absorption with maximum at 430 nm appeared until 5 min thermal treatment, and then the absorption maximum shifted to 515 nm after then. This observation shows the de-protection of the t-BOC protect naphthazarine occurs in two steps, in which one t-BOC group eliminates within 5 min under that condition and then the other t-BOC reacts.

Similar absorption change was observed for the naphthazarine doped in PMMA film under thermal treatment at 100° C after photoirradiation. Fig. 2 shows m-line spectra of the photoirradiated sample. Seven guided modes were observed, with which refractive index of the sample film can be determined. The refractive indices of the film before and after photoirradiation are listed in Table 1

Figure 2 m-line spectra of PMMA film containing 2wt% t-boc naphthazarine and 1wt% PAG

Table 1. Refractive index of sample film before and after photo-irradiation

mode	Before Irradiation	After Irradiation	Δn
TE	1.49076	1.49069	-1×10^{-4}
TM	1.49060	1.49102	4×10^{-4}

Induced refractive index is as large as 4×10^{-3} for TM mode, which is large enough to optical waveguide manufacture. Refractive index of materials is due to polarization, and refractive index and absorption correspond to real and imaginary part of the polarization. Those absorption and refraction are related by Kramers-Kronig's relation each other, where n and κ are the refraction and extinction coefficients, ω is the observation wavelength, and P is principal value, respectively.

$$n(\omega) - 1 = \frac{2}{\pi} P \int_0^\infty \frac{\omega_1 \kappa(\omega_1)}{\omega_1^2 - \omega^2} d\omega_1$$

$$\kappa(\omega) = -\frac{2}{\pi} P \int_0^\infty \frac{\omega n(\omega_1)}{\omega_1^2 - \omega^2} d\omega_1$$

Spectral shift of the sample film after photo-irradiation and thermal treatment should be the reason for the increase in the refractive index at 633 nm.

3.2 Photo-optical effect of polymer-bound naphthazarine film.

Figure 3 shows the spectral change of the polymer-bound naphthazarine bulk film after photoirradiation of 401nm($220 \mu\text{W}/\text{cm}^2$) light and following thermal treatment at 100°C . The polymer-bound naphthazarine is chemically amplified

de-protected to show a new absorption at 550 nm. The new absorption due to naphthazarine is structureless and without peak shift because the naphthazarine is mono-substituted.

Figure 3 Spectral change of polymer-bound t-BOC protected naphthazarine film containing 1wt% PAG under thermal treatment at 100°C after photoirradiation.

Refractive indices of the film are 1.6302 for TE mode, and 1.6300 for TM mode, respectively. The average refractive index increases from 1.6301 to 1.6463 after photoirradiation, whose induced refractive index is as large as 16%.

3.3 Photophysical process of the photo-optical materials.

In order to clarify the photophysical process of the photo optical material with extraordinary large refractive index induction, photochemistry of the PAG, NAI-105, was measured. Quantum yield of photo decomposition of the PAG was 0.022 in THF solution shown in Figure 4. On the other hand the quantum yield of the NAI-105 in solid state PMMA has wide distribution ranging from 0 to 0.14 due to

Figure 4 Quantum yield distribution of PAG in THF solution and in solid state PMMA

inhomogeneity of free volume distribution in PMMA.

Figure 5 Transient absorption spectra of NAI-105 in CH_2Cl_2 by laser flash photolysis

Figure 5 shows transient absorption spectra of the NAI-105 measured by laser flash photolysis in CH_2Cl_2 solution. The absorption maximum is 480 nm and the lifetime is 7 μsec.

In order to determine the active species in the laser flash photolysis, electron beam pulse radiolysis of the sample was performed in benzene, THF, and CH_2Cl_2 solution (Figure 6). Absorption of radical anion of NAI-105 is observed at 680 nm in THF solution, and that of radical cation is at 560 nm in CH_2Cl_2 solution. Electronic excited state (T-T absorption) is also observed at 480 nm in the electron beam pulse radiolysis experiment in benzene solution. Therefore the active species of the observed transient absorption can be assigned as T-T absorption of NAI-105. Thus the rate determining step of the acid generation

Figure 6 Transient absorption spectra of NAI-105 in THF or CH_2Cl_2 solution by electron beams pulse radiolysis

reaction of NAI-105 is as long as 7 μsec compared to

the salvation dynamics of several nsec. This is quite different from the photochemical reaction of some photochromic compounds such as azobenzene and so on, whose lifetime is as short as several ps. Those compounds with shorter lifetime in their rate determining steps preserving static free volume around them even in solution, while the free volume around NAI-105 should be dynamic one in solution. Therefore NAI-105 preserves no more sufficient free volume for the photoreaction in solution that the reaction in solid state PMMA becomes preferable.

4. Conclusions

Chemically amplified photo-optical effect of t-BOC protected naphthazarine was performed to induce 16% of refractive index change with polymer-bound sample. The lifetime of the PAG in the rate-determining step was found to be 7 μsec, and the quantum yield for photoreaction is much preferable in PMMA matrix, due to preservation of static free volume. Those materials are used for refractive index lithography for waveguide or optics fabrication. And the chemical amplification is the key step for the increase in the reaction efficiency of the photo-optical effect.

5. References

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