Transient Light-Induced Refractive Index Change Made by Laser Microfabrication in Nitroaniline-Doped PMMA Film

Kazuhiko Yamasaki*, Saulius Juodkazis**, Mitsuru Watanebe*, Shigeki Matsuo*, Kenji Kamada***, Koji Ohta, and Hiroaki Misawa*

*Graduate School of Engineering, The University of Tokushima, 2-1 Minamijyosanjima, Tokushima 770-8506, Japan
E-mail: misawa@eco.tokushima-u.ac.jp (Corresponding author: Hiroaki Misawa)
**SVBL, The University of Tokushima, 2-1 Minamijyosanjima, Tokushima 770-8506, Japan
***Osaka National Research Institute, 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

Keywords: PMMA, nonlinear properties, optical memory, laser microfabrication, light-induced damage threshold

We report the observation of high light-induced change in refractive index (recognizable by observation in conventional microscope) in PMMA film doped with an optically non-linear dye 2-nitroaniline (NO2(C6H4)NH2 abbreviated as 2NA). The optically altered micrometer-sized regions were fabricated by single-shot irradiation of 120 fs laser pulses into doped PMMA film using high numerical aperture 1.3 and high magnification x100 objective lens. The doping of films can be achieved in a wide range of 2NA concentrations (up to 40 wt%) without precipitation. This allows to control a storage time of an optically altered region up to one month by the adjusting the energy of the femtosecond (fs) recording pulse at 800 nm. Typical recording energy was 10-80 nJ/pulse at the point of irradiation. Total recovery of transmission of the PMMA[2NA film was confirmed by optical transmission measurements in microscope. The light induced damage threshold (LIDT) (for permanent damage) was increased more than by 4 times (up to 40 nJ/pulse) when 2NA doping were ca. 13 wt%. While the LIDT for transient damage was decreased by 1.5-2 times. Total optical recovery was observed single exponential with decay time of ca. 0.5-1 min for moderate irradiation intensities (0.1xLIDT of permanent damage). The damage induced with at the higher intensities lasts up to month, but the recovery was not total (residual transmission changes were observable).

The phenomenon can be applied for the optical memory, photonic crystal, and micro-mechanical applications. The underlying mechanism of the phenomenon is discussed in terms of anelastic α- and β-relaxation (polymer backbone and side chain relaxation, respectively).

1. Introduction

Polymethylmethacrylate (PMMA) is gaining an interest in the field of optical applications due to its high optical transmission in visible, easy dye-doping, preparation and processing including the laser ablation and controllable photo-modification. A three-dimensional (3-D) optical memory1 and an optical waveguide2 have been demonstrated recently. On the part of optical 3-D memory various approaches have been proposed: a bacteriorhodopsin protein-based two-photon absorption (TPA) induced write/read memory,3 femtosecond (fs) pulse induced micro-explosion recording,4 photorefractive,5 photochromic6 and photopolymer7 materials have been used as recording media.

Here we demonstrate a novel mechanism of 3-D recording, which is transient with controllable duration of recording (10^3-10^7 s) made by a single pulse fs-irradiation of PMMA film doped with 2-nitroaniline, NO2(C6H4)NH2. The dye was responsible for TPA of 795 nm illumination and lowered the light induced damage threshold (LIDT) of PMMA. The recovery of optical transmission was explained in terms of viscoelastic α- and β-relaxations of PMMA.

2. Experimental

2-nitroaniline (2NA) was introduced into chloroform solution of PMMA (15 wt.%) then casted over a microscope cover glass to form a film, which was used as recording media. The 2NA doping up to 40 wt.% was precipitation free. Samples were dried in a desiccator at a vacuum of ~10 mm Hg for 24 h. Eventual thickness of the film was ca. 150-300 μm. It was crack free and stable on the yearly scale even after the optical recording. 3-D recording was made by laser...
irradiation through an oil-immersion objective (x100 magnification and numerical aperture, NA = 1.3) through the cover glass in order to avoid any oil contact with PMMA film. An irradiation spot (lateral size) can be evaluated as diffraction-limited spot size (diameter of Airy disk) \( d = 1.22\lambda/NA = 746 \text{ nm} \) and the corresponding axial size was \( z = 2n\lambda/NA^2 = 701 \text{ nm} \), where \( \lambda = 795 \text{ nm} \) is the wavelength of fabrication laser pulse, \( n \) is the refractive index at focal point \( (n_{\text{PMMA}} = 1.49 \text{ at } 600-800 \text{ nm}) \). The sample was translated in the focal plane during irradiation. Every single bit seen as an optically-altered transmission region was recorded in a single shot of 120 fs duration.

### 3. Results

Permanent optical damage (bit) can be recorded in PMMA film as we reported earlier, when the pulse energy density is higher than LIDT of material. For undoped PMMA, we found it ca. 2.3 J/cm\(^2\) (10 nJ) for 795 nm, 120 fs pulses. This determination was made from an optical transmission, when the bit is recognizable by observation in 100-times magnification, NA = 1.35 objective. The recovery of the transmission of irradiated spot was observed (Fig. 1), when the pulse energy was smaller than 1×LIDT and PMMA film was doped with 2NA. The sequence of snap shots in Fig. 1 allow to trace the recovery of transmission of selected bits A, B and C on a time scale on tens-of-seconds as depicted in Fig. 2. The transmission at the center of the bits showed single-exponential recovery with time constant \( \tau_0 = 10-30 \text{ s} \) (Fig. 2(a)). More complicated recovery can be observed when the average transmission on a square of 1×1 \( \mu \text{m}^2 \) was plotted over time (Fig. 2(b)). It can be seen from Fig. 1 that the bit was enlarging while its transmission was decaying. The increase in average transmission up to 10-15 % was observed at irradiated spot immediately after fabrication in PMMA\(2\text{NA-32 wt.\%} \) film, when the pulse energy was 12

![Fig. 1. Time series (a-c) of optical transmission recovery after irradiation of 15 nJ (3.4 J/cm\(^2\)) pulses (120fs at 795nm). The film was PMMA\(2\text{NA-32wt.\%} \) (307 \( \mu \text{m}\)-thick). Scale bar 7 \( \mu \text{m} \).](image)

![Fig. 2. Time decay of maximum (background subtracted (a)) and average (b) bit transmission. (a) the bits A, B, and C corresponds to those in Fig. 1. (b) averaging was made on 40-by-40 pixels. BKG marks the background transmission.](image)

![Fig. 3. Absorbtion spectra of fresh PMMA\(2\text{NA-30wt.\%} \) film (dashed line) and during the recovery \( (\tau_0 = 1-3 \text{ h}) \) of optical damage (shifted upwards by 0.25). Thickness of film was 157 \( \mu \text{m} \).](image)
4. Discussion

Optical alteration of materials is usually considered in terms of refractive index changes, directly related to the local mass-density modifications or in terms of an absorption of optically induced defects, which are, in turn, causing the changes of refractive index via Kramers-Kronig relation. Astonishing high refractive index changes (> 5x10⁻²) were reported made by microexplosion in silica and sapphire. Indeed, if one is measuring the diffraction efficiency of a grating written by microexplosions and if the absorption is considered negligible the effect of diffraction on thin sinusoidal grating gives overestimated values of refractive index changes. The transmission contrast such as in Fig. 2(a) gives the value of ca. 0.02 for the grating written in silica (similar value would be found in PMMA). We should properly address the refraction, absorption and scattering to get insight into transmission image formation in order to understand the images such as in Fig. 1 (identical images can be observed in silica, sapphire, TiO₂-rutile).

Obviously, when the optically altered volume is of the size comparable with the wavelength of the image forming light (550 nm mid-wavelength of condensor illumination in a microscope) the light scattering is one of the most important factors. To look at a near-field distribution of the light passing through a small sphere of decreased and increased refractive index as compared with the index of sphere's ambience, we carried out numerical simulations according the code developed by Barber and Hill. The program allows to calculate the light intensity inside and outside sphere, when incident plane wave has intensity I. The central part of the bit was considered of decreased refractive index and the diameter is given by fabrication spot radius of 373 nm. This can be described as a light scattering sphere, which relative refractive index is defined by \( m = n/\n_0 < 1 \), where \( n \) is the refractive index of the void-like sphere and \( \n_0 \) is that of sphere's surrounding. Another sphere considered for calculations was of increased index, \( m > 1 \), and the diameter was twice larger than that of the void-like sphere's. This simulates the real structure of the bit, which is void-like inside and surrounded by densified shell. In the following part we will show how the employed values of \( m \) are justified (\( m = 0.998 \) for the void-like sphere and \( m = 1.002 \) for the higher density shell). The results of simulations in Fig. 5 shows, that the center of the sphere with \( m > 1 \) appears bright centered in transmission (Fig. 5(a)), while the void-like sphere should give an opposite contrast. Also, the larger sphere of \( m > 1 \) caused larger intensity contrast as compared with that of sphere with \( m < 1 \). This qualitatively explains the observed transmission of 3-D memory written in PMMA, although the real bit structure was treated simplified as two separate spheres.

To answer the question, what is the refractive index of densified and dilated regions of bit, let us compare our observed recovery time of transmission of 1-100 s with creep compliance data in the experiments of dielectric
cooling and strain release). Are the amorphous polymers responding as a glass or as a rubber the matter of time and temperature. Such a strain is already larger than typical limit of elasticity of ca. 0.2% even in ductile polymers. The strain, as a measure of $\Delta V/V$, there $V$ is the volume, is directly related to the refractive index. Yoldas, derived the relation between porosity and refractive index, which we can adopt for the densified/dilated material:

$$\frac{\Delta V}{V} = \text{Strain} \equiv 1 - \frac{n^2_{\text{diluted}} - 1}{n^2_{\text{diluted}}}.$$  \hspace{1cm} (1)

The relation does not depend on the elastic response of material and can be applied to microexplosion altered material. By taking $\text{Strain} \approx 0.8\%$ (plateau in Fig. 6) we find corresponding refractive index changes of $3.3 \times 10^{-3}$. When unperturbed index of film was taken as that of PMMA, namely 1.490. The relative refractive index values of $m = 1.002$ and 0.998, for the densified and dilated regions can be found. These are the values employed in the modelization of light scattering (Fig. 5). If the absorption needs to be taken into account, the numerical simulations are done with complex refractive index $m$ (the calculations in Fig. 5 were obtained without consideration of absorption). Typical result of absorption on the transmission intensity is the lowered contrast. The direct evaluation of transmission without consideration of scattering is straight forward $I = I_0(1-R)e^{-\alpha d}$, where $R$ is reflectance, which for the right angle incidence is given by: $R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}$, where $k = \alpha l/4\pi$.  \hspace{1cm} (2)

Here, the absorption coefficient can be considered proportional to the strain, since more material is encountered in the light pass in denser region and vice versa for dilated one. When pure relaxation mechanism of transmission recovery is considered, the absorption coefficient is $\alpha = 0$ cm$^{-1}$. Even then a realistic transmission image can be reconstructed by taking into account light scattering (Fig. 5).

Glass-rubber transition is mainly due to $\beta$-relaxation (also known as Johari-Goldstein), i.e. a side chain kinematic movement. At high power of irradiation the temperature can be higher than glass transition of PMMA at $T_g = 105^\circ C$ at irradiation spot (then $\alpha$-relaxation is involved during recovery time is widely varied by the doping concentration and fs-laser pulse energy. The mechanism of optical recovery, most probably, is caused by an anelastic dielectric relaxation, mainly $\beta$-relaxation. The phenomenon can find applications in the micro-systems as fluid pumps (driven by strain), optically controlled capacitance (driven by dielectric constant), and temperature sensors (temperature control over transmission). The phenomenon can be expected to be found in other polymers as well.

5. Conclusions

We have demonstrated for the first time the 3-D transient optical memory in PMMA:2NA dye doped films. The recovery time is widely varied by the doping concentration and fs-laser pulse energy. The mechanism of optical recovery, most probably, is caused by an anelastic dielectric relaxation, mainly $\beta$-relaxation. The phenomenon can find applications in the micro-systems as fluid pumps (driven by strain), optically controlled capacitance (driven by dielectric constant), and temperature sensors (temperature control over transmission). The phenomenon can be expected to be found in other polymers as well.

References