

# Recording by microexplosion and two-photon reading of three-dimensional optical memory in polymethylmethacrylate films

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We report the recording of a three-dimensional (3D) pattern in bulk polymethyl methacrylate (PMMA) films by microexplosion induced by a tightly focused (numerical aperture of oil-immersion objective was 1.3) single laser shot. Recording was done by picosecond (ps) single-pulse irradiation at 532 nm and by femtosecond at a 400 nm wavelength. The light-induced damage threshold of PMMA was found at  $\sim 4 \text{ MW/cm}^2$  for ps damaging. Readout of the 3D pattern was carried out by the recording of the transmission and the photoluminescence (PL) of bits. We demonstrate the possibility exciting PL of the optically damaged area inside the PMMA by one- and two-photon absorption. © 2000 American Institute of Physics. [S0003-6951(00)03208-3]

Three-dimensional (3D) recording<sup>1</sup> is an alternative way to extend a two-dimensional recording density without the usage of more sophisticated methods of near-field optics.<sup>2</sup> 3D patterns are demonstrated in photopolymers,<sup>3,4</sup> photorefractive<sup>5,6</sup> and photochromic<sup>7-9</sup> materials, as well as in glasses.<sup>10</sup> The reflection-type confocal readout system of 3D patterns in polymethylmethacrylate (PMMA) doped by photochromic dye was demonstrated recently, pointing to the inherent features of such a setup.<sup>8</sup> One of the advantages of polymer usage as 3D recording media is the possibility of their doping by the recording light absorbing dyes. Another, obvious possibility to write a read-only 3D pattern is optical damaging of a polymer in the region of focus of laser irradiation by micro explosion.<sup>10</sup> This process has its similarities to ablation since the result of irradiation is a void formation, i.e., material removal from the irradiation spot. Again, polymers with their lower threshold of optical damage and possibility to engineer their refractive index by doping, which yield in controlled focal spot size, should demonstrate advantages as compared to amorphous transparent materials as silica.<sup>11</sup>

Our aim was to record a layered 3D pattern of optical memory inside the film of PMMA by the use of picosecond (ps) pulsed irradiation at 532 nm and femtosecond (fs) at a 400 nm wavelength. A microexplosion optically modified region was investigated with regard to the possibility of its readout by transmission and photoluminescence (PL). The readout of the bits by their PL excited in two-photon absorption (TPA) is demonstrated.

A toluene solution of PMMA (15 or 20 wt. %) was cast over a microscope cover glass to form a film, which was used as recording media. The sample was dried in an aspirator at a vacuum of  $\sim 10 \text{ mm Hg}$  for 24 h. The eventual thickness of the film was (100–150)  $\mu\text{m}$ . It was crack free and stable on the yearly scale even after the optical recording. The layers thicker than  $\sim 200 \mu\text{m}$  showed a craze formation pattern by optical observation in a microscope. A 3D

recording was made by laser irradiation through an oil-immersion objective ( $\times 100$  magnification and numerical aperture,  $\text{NA} = 1.3$ ) through the cover glass in order to avoid any oil contact with the PMMA film. An irradiation spot size can be evaluated from a diffraction-limit spot size definition (diameter of Airy disk)  $d = 1.22(\lambda/\text{NA})$ ; where  $\lambda$  is the wavelength of the fabrication laser beam and  $n$  is the refractive index of the focal point ( $d \approx 500 \pm 20 \text{ nm}$  for  $n_{\text{PMMA}} = 1.48\text{--}1.52$  in the visible range and  $\lambda = 532 \text{ nm}$ ). The procedure of fs/ps fabrication can be found elsewhere.<sup>11</sup>

Figure 1 shows transmission images of recorded layers with 7  $\mu\text{m}$  intralayer spacing, which was found to be a crosstalk-free separation for the transmission readout of a 3D pattern written by ps/fs pulses. In the case of ps-fabrication, we found that more regular bits can be written in the region, which is closer to the free surface of the sample. Probably, this region is less strained. The problem of film nonhomogeneity did not arise in fs-fabrication. High lateral bit density was achieved by the fs-fabrication yielding the most perfect spherical shape of the bits (Fig. 1) at any depth.

In Fig. 2, fabrication power dependencies of external,  $D_{\text{OUT}}$ , and internal,  $D_{\text{IN}}$ , bit sizes are presented [Fig. 2(a)] together with the transmission intensity at the center of the bit [Fig. 2(b)] for the ps-fabricated sample. It can be seen that both bits' dimensions obey the same linear power law. A temperature buildup is a source of ablation only in the case when electron-phonon interaction time, usually  $\sim \text{ps}$ , is shorter than a laser pulse.<sup>12</sup> We found the larger damage area as compared with silica<sup>11</sup> is due to the more extended region of the temperature rise,<sup>13</sup> where the temperature is higher

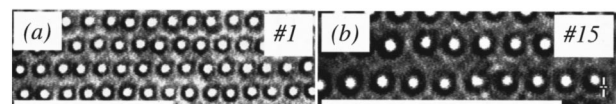


FIG. 1. Transmission images of the first (a) and seventh (b) layer of 3D optical memory in PMMA film. Bits were made by a fs single-pulse irradiation of 300 nJ/pulse energy. Scale bar, 10  $\mu\text{m}$ ; interlayer spacing was 7  $\mu\text{m}$ .

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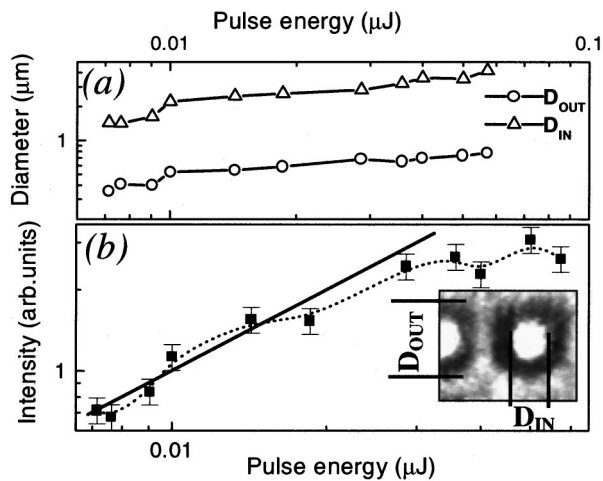


FIG. 2. Power dependency of the bit size (a) and the maximum of transmission intensity (evaluated at the bit center) for ps-fabricated bits (30 nJ/pulse). Internal bit diameter,  $D_{IN}$ , and external,  $D_{OUT}$ , are depicted on the transmission image in the inset in (b). The line in (b) corresponds to the slope 1; dotted line as a guide to the eye.

than the glass transition temperature of PMMA,  $T_g \approx 100^\circ\text{C}$ .<sup>14</sup>

The light induced damage threshold (LIDT) of PMMA was found at an energy of  $(7 \pm 1)$  nJ/pulse (corresponding intensity was  $4.3 \text{ MW/cm}^2$ ) as determined for ps-fabrication. This is when the region of changed transmission can be recognized by eye observation in the microscope. LIDT was  $\sim 7$  times smaller compared to that of silica, 50 nJ/pulse, when the same objective was used.<sup>11</sup> Thus, the LIDT of silica and PMMA is scaling approximately to corresponding melting temperatures in the absolute scale for ps-irradiation (temperature of chemical decomposition of PMMA  $\sim 250^\circ\text{C}$ ,<sup>14</sup> temperature of melting of silica  $\sim 1800^\circ\text{C}$ ). On the other hand, the difference in the LIDT for fs fabrication in silica and in PMMA was only about 1.5 times. This is related to the fs-dielectric breakdown of material by subband gap quanta irradiation (what we refer to here as the ‘‘optical damage’’), since the thermal ablation mechanism cannot be realized during the fs pulse itself due to subpicosecond energy transfer from free carriers excited by multiphoton absorption to the surrounding media.<sup>12</sup> Thermal energy is released after the end of the fs pulse, only. Thus, optical damaging is taking place through direct bond breaking rather than melting ablation.

Figure 2(b) shows single bit transmission intensity vs ps-fabrication power. Linear dependence was found to begin to saturate at the energy  $\sim 40$  nJ/pulse. For higher pulse energy or multishot irradiation the darkening of the bit center in the transmission image was observed. Most probably, it is related to the carbonization of PMMA, which further leads to the catastrophic damage due to the continuously increasing absorption of that particular area. First power law of the bit size dependence is explained by the physics of dielectric breakdown.<sup>12</sup> The region of the altered refractive index is produced in the process of single photon absorption by free carriers, which initially were created by multiphoton absorption (TPA in the case of our experiments). Even when optical damaging is made by 6–7 photon absorption, as is taking

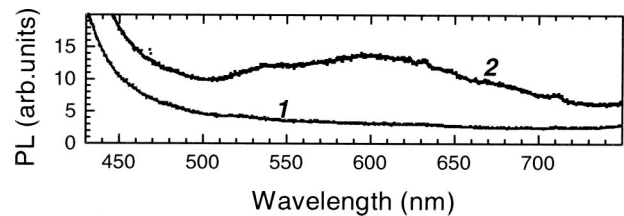


FIG. 3. Photoluminescence spectra of PMMA excited by 400 nm fs illumination of undamaged (1) and ps-irradiation damaged (2) film.

place in the silica, the first power law dependence of the bit size is observed.<sup>15</sup>

Figure 3 shows the PL spectra of PMMA. Undamaged PMMA has an absorption band starting at 300 nm and more pronounced at 275 nm with corresponding PL at 310–340 and 280 nm, respectively. Damaging PMMA with ps pulses in single shot per bit made an optical modification of it. PL from damaged regions showed broad band at 600 nm, most probably caused by the defects created by the bond scission of PMMA.<sup>16</sup> The formation of ‘‘propagating radical’’<sup>17</sup> is known as a product of photodegradation from an electron spin resonance analysis of ablated PMMA. The decomposition of PMMA by ultraviolet (UV) 193 nm surface ablation forms species as monomers, fractions of PMMA of molecular mass  $M_n = 2500$  (initial polymer was of  $M_n > 10^6$ ), CO, and CO<sub>2</sub>.<sup>18,19</sup> An increased spectra baseline after optical damaging (Fig. 3) is related to increased light scattering originated from the damaged area. A similar broad band around 600 nm was reported in spectra of a PMMA surface ablated by nanosecond multishot irradiation.<sup>16</sup>

PL of optical damaged areas can be imaged when excited by illumination of a mercury line at 365 nm. The comparison of a transmission image with that obtained by PL from the same location is presented in Fig. 4. The PL image [Figs. 4(b) and 4(c)] showed a dark centered appearance of bits. This could be expected as a consequence of cross linking of radicals in the most damaged bit-center region. An increase of C–C linkage (as opposite for C=O, C–O) was reported<sup>18</sup> in ablated regions of PMMA and could, also, cause the PL decrease at the damage center. The creation of the void, however, is the most probable explanation of the

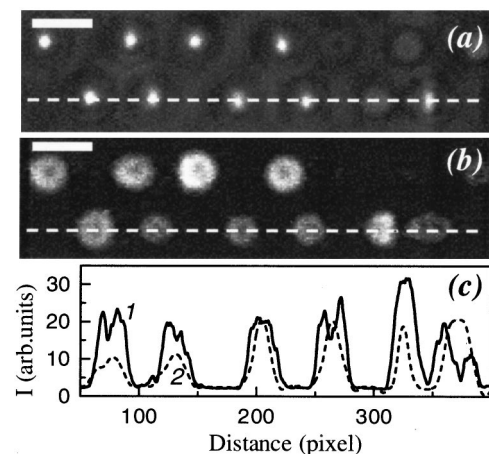


FIG. 4. Transmission (a) and PL (b) images of ps-recorded bits. PL was excited by 365 nm line of mercury lamp. PL (1) and transmission (2) intensity profiles along the same bits marked by dashed lines (c). Scale bar, 2  $\mu\text{m}$ .

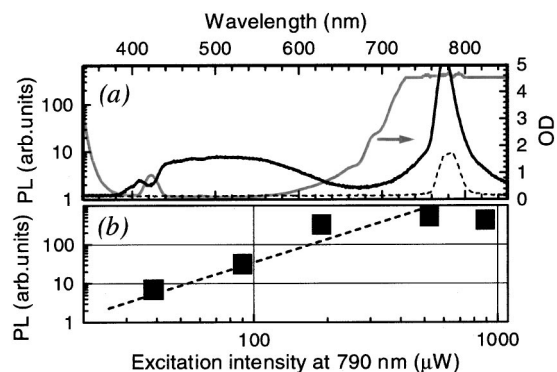


FIG. 5. (a) PL spectrum excited in TPA of 790 nm illumination (solid line). Gray line depicts spectral profile of the dichroic mirror with corresponding absorption filter, which were used in PL mapping. Dashed line is the PL of undamaged PMMA film. (b) PL of a single bit of 3D pattern (background subtracted) vs excitation intensity. Dashed line in (b) presents slope 2.

dark centered appearance of the bit in the PL image. A void in the center of the damage was found in silica.<sup>20</sup> Formation of a char or apparently carbonized shell of the damaged spot was observed when ps-fabrication pulse energy was higher than 50 nJ/pulse.

Readout of the bits in PMMA was accomplished by PL excited in TPA. Figure 5 presents a typical PL spectra [Fig. 5(a)] and power law of its excitation at 790 nm. A dynamic range of PL excitation was found very narrow, less than one order in intensity. For the higher intensities, secondary optical damage was induced, which was observable as bit size alteration and PL degradation. The possibility of TPA excitation of PL is important from an application point of view, since the high-contrast readout of the 3D pattern can be achieved without the confocal technique. Such an image is presented in Fig. 6, where PL and transmission images are presented.

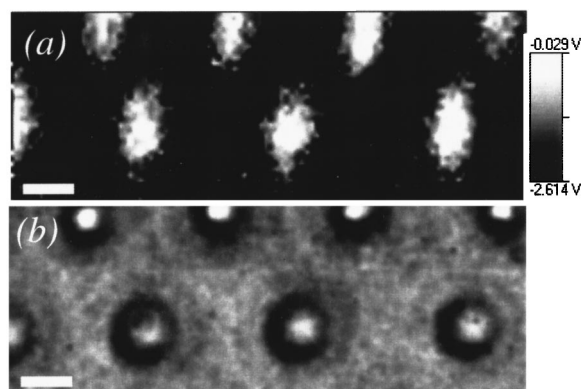


FIG. 6. (a) PL image of bits, excited by TPA at 790 nm. Gray scale on the right depicts the voltage of a photomultiplier used for the recording. The PL map is plotted in  $3\sigma$  of initial intensity distribution. (b) The transmission image of the bits. Scale bar,  $1\ \mu\text{m}$ .

Chemical functionalization of PMMA<sup>16</sup> could be achieved easier by dye doping of the film rather than that of glass. The optically damaged regions on PMMA are expected to be chemically active. Oxygen (or other gas) diffusion into the bulk of PMMA could be employed for the altering of the damaged area. This could be the way to create rewritable polymer media for 3D recording. Even higher contrast images are expected to obtain in a confocal reflection type read out.<sup>8,21</sup>

We have shown the possibility to use PMMA as recording media for 3D optical memory. 3D optical recording in PMMA can be done by fs/ps single pulses in the process of microexplosion. The readout of 3D memory could be achieved by the recording of either the transmission image or photoluminescence of the optically introduced defects. The PL of defects can be excited in one- or two-photon absorption.

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