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Femtosecond laser induced photoluminescence in poly(methyl methacrylate) and three-dimensional optical storage

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ABSTRACT

We report on a femtosecond-laser induced photoluminescence (PL) in poly(methyl methacrylate) and its potential application to three-dimensional optical storage. Irradiation with a focused 800 nm, 1 kHz, 100 fs pulsed laser induced a strong PL change in UV–visible region. Absorption spectra and Fourier-transform infrared spectra before and after laser irradiation indicate the PL may result from the emissive oxidized products of photo-degradation reaction of PMMA. This makes it possible to read out the stored data by detecting the PL change. The pulse energy threshold of the light-induced PL change of PMMA is found to be at ~2 μJ/pulse and the optimal recording energy is ~3 μJ/pulse. A ten-layer pattern inside the bulk sample recorded by tightly focusing a pulsed laser beam was read out by a reflection-type fluorescent confocal microscope, which detected the emission in visible range as the signal. High-contract fluorescent images with a much higher signal-to-noise ratio were obtained without crosstalk in comparison with the ordinary reflection mode.

1. Introduction

Many efforts have been made to realize three-dimensional (3D) optical storage in recent years for their potential applications to high density optical data memories [1–20]. Femtosecond (fs) laser pulse is a prospective tool for 3D fabrication since the ultrashort pulse duration and extremely high local intensity make it possible to fabricate 3D structures of sub-wavelength scale even in transparent materials through multi-photon absorption, and the photo-modified region can be well defined due to the non-thermal nature of the light-matter interaction [13–20].

Poly(methyl methacrylate), PMMA, is an interesting material for 3D optical storage due to its high chemical resistance, advantageous optical properties and low cost [9–12]. The detection of stored bits is usually done by means of a refractive index change or a fluorescent signal. The use of the latter can give rise to a much enhanced signal-to-noise (S/N) ratio, compared to the former [15–20]. Previous research on 3D optical memories with PMMA-based material has demonstrated the use of refractive-index modification [9], micro-voids formation, [10,11], and photoluminescence (PL) change [11,12]. Yamasaki et al. [12] have reported that voids can be formed in PMMA by single-shot ultrashort pulses at 400 nm and these voids can be read out under two-photon excitation. It has also been shown that damaged PMMA with picosecond pulses at 532 nm causes a broad PL band centered at 600 nm and that PL of irradiated areas can be imaged when excited by single-photon or two-photo absorption. Here, we report a new PL spectrum in UV–visible range induced by irradiation with a 100-fs pulsed laser at 800 nm. The strong PL change makes it possible to achieve 3D optical bit memory with a much higher high *S*/*N* ratio than that of the ordinary refractive mode.

2. Experimental procedures

PMMA used in this work was made by a bulk polymerization technique. 0.05 g of 2,2-azobisisobutyronitrile (AIBN, Aldrich, 98%) as an initiator were dissolved in 10 ml of purified methyl methacrylate (MMA, Aldrich, 99%). Then this solution was thermal polymerized at 60 °C for 72 h until solidification was fulfilled and followed by removing remaining volatiles in vacuum oven at 100 °C. The samples were cut to 3.7 mm thickness and polished

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for all spectroscopic studies. A regeneratively amplified 800 nm Ti:sapphire laser system (Quantronix) with 1 kHz repetition rate and 100 fs pulse duration was employed for this study. A pulsed laser beam was focused by a lens inside the sample on the x–y–z stage. The absorption spectra were measured on a Cary 5000 UV/VIS/NIR spectrophotometer. The background due to light-scattering center in the absorption spectra after fs-laser irradiation was carefully subtracted. The Fourier-transform infrared (FTIR) spectra were acquired with a NICOLET 510 FTIR spectrometer.

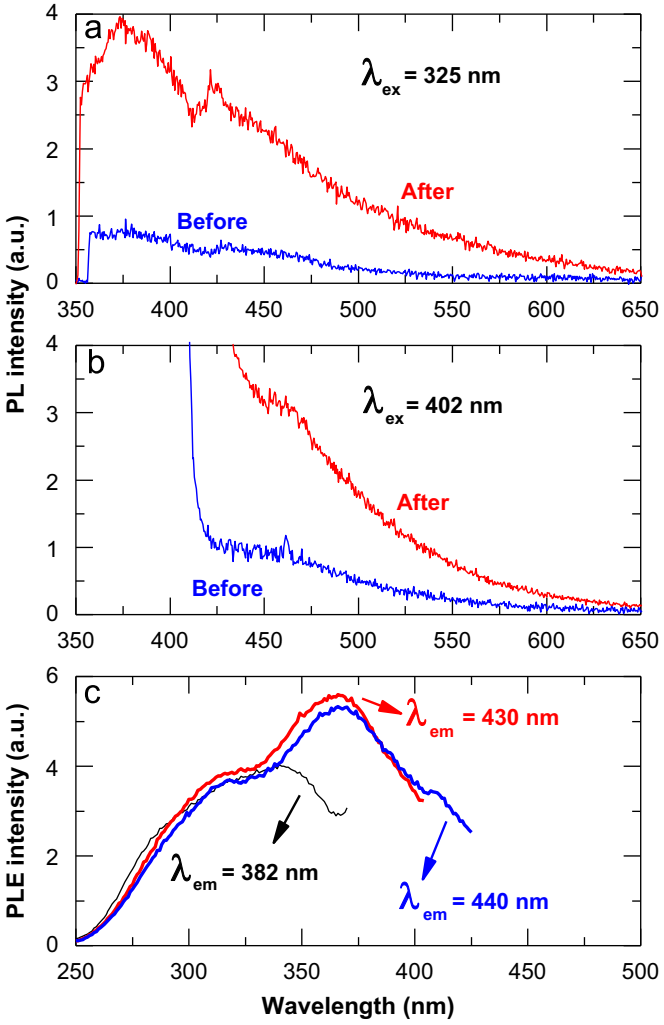

Fig. 1. PL spectra of PMMA before and after fs-laser irradiation (3 mW) under excitations at (a) 325 nm and (b) 402 nm, respectively. (c) PL excitation (PLE) spectra measured for the emissions at 382, 430 and 440 nm.

3. Results and discussions

3.1. Fs-laser induced PL change in PMMA

First, equally spaced line patterns were made under irradiation with 3 mW laser inside the sample (line interval: 15 μm, depth of focusing: >100 μm) within 3×3 mm^2 area for PL measurement. Fig. 1(a) and (b) compare the PL spectra before and after laser irradiation. A 325 nm He–Cd laser source was used as the excitation source. Before irradiation, the sample is fluorescent weak at UV to visible wavelength with an emission band extending into 600 nm. As a result of fs-laser irradiation, a strong PL spectrum was generated, appearing to consist of two overlapping bands at 380 and 430 nm. A similar emission occurs under excitation of 402 nm (see Fig. 1(b)). The PL increment at 600 nm reported before is also observed in this work, but it appears like an increased background. So the induced PL band has a different origin from the background one. Fig. 1(c) presents the excitation spectra measured for the emissions at 380, 430, and 460 nm, respectively, after irradiation. The excitation spectra have a same band at about 300 nm, which is the host absorption band [21]. For the emissions at 430 and 460 nm, the second excitation band with a maximum excitation at ~375 nm, which is usually ascribed to the absorption of some unsaturated aldehyde or ketone groups, undergoing $n\rightarrow\pi^*$ transitions near 380 nm [22], while for the emission of 380 nm, the second excitation band is suppressed because of a cut-off filter used to block the excitation light.

The single-layer line patterns used for PL measurement are shown in Fig. 2a, which was read out by scanning a 405 nm laser-diode beam focused by an objective lens ($20\times$, NA=0.4) into the sample. The PL signal was fed into the monochromator adjusted to the region of 410–480 nm and subsequently sent to a CCD detector. As illustrated in Fig. 2b, the detected fluorescent signal for this recorded line pattern achieves a high S/N ratio. This observation opens up the possibility of using such materials for 3D optical storage.

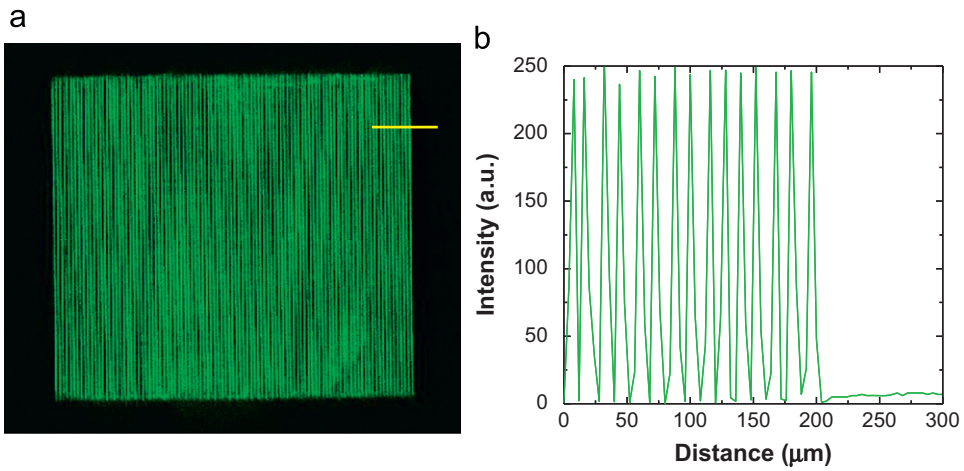

Fig. 2. (a) Single-layer line patterns read out by scanning a 405 nm laser-diode beam focused by an objective lens ($20\times$, NA=0.4) into the sample. (b) Fluorescent signal in 410–480 nm regions measured along the marked line.

3.2. Photochemical reaction in PMMA under fs-laser irradiation

Absorption spectra and FTIR spectra of the samples with and without fs-laser irradiation are shown in Fig. 3(a) and (b), respectively. As seen in Fig. 3(a), the irradiation causes an increase of absorbance in 300–400 nm range. In principle, PMMA is transparent (or has little chromophore activity) in the UV–visible region, though the tail of the intense UV absorption of the ester group near 240 nm extends a little beyond 300 nm [23]. Thus, the increase of absorption in 300–400 nm region can be explained by formations of new unsaturated groups, such as aldehyde or keto groups, as a result of fs-laser irradiation [22]. Since PMMA is also a transparent material in infrared region [9], nonlinear properties such as multi-photon absorption at 800 nm is required to create the optically damaged region, making it chemically active. In the FTIR spectra, a slight increase was observed for the relative absorption intensity of C=O ($\sim$1730 cm^{-1}) to C–O ($\sim$1190 cm^{-1}) vibrations, which indicates that oxidation reactions may take place. It is probably due to the fact that the laser irradiation was realized in ambient air and the diffusion molecule oxygen is smaller than the holes comprising the free volume in the polymer [22], and then leads especially to the increase of band intensities of polar groups, such as carbonyl one (C=O) [22–25]. It has been reported that photo-degradation of PMMA produces some oxidized products, which are stable and can be emissive by virtue of the energy levels they possess [21]. The energy level properties of these oxidized products reported are in accord with the excitation spectra of PMMA after irradiation in this work [21,22]. Thus, the PL change may result from the emissive oxidized products of photo-degradation reaction in PMMA. However, the exact products and mechanism of the photo-degradation reaction of PMMA needs to be further studied.

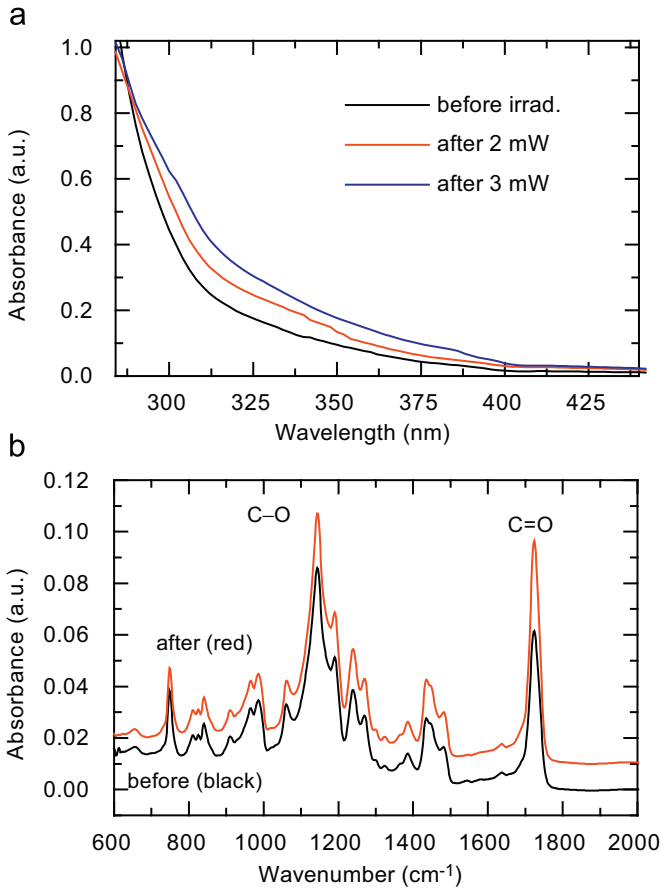

Fig. 3. (a) Absorption spectra change of PMMA before and after fs-laser irradiation with increase in laser power. (b) FTIR spectra change of PMMA before and after fs-laser irradiation (3 mW).

3.3. 3D optical storage by fs-laser induced PL change in PMMA

To investigate the availability of the induced emission as the detection signal for 3D optical storage, single-layer bit patterns were first recorded inside the PMMA (> 100 μm under the surface) as a function of recording energy by focusing a laser beam through an objective lens (50 ×, NA=0.42). Each bit was formed with a single pulse. The recorded images were read out by a reflection-type confocal microscope where a 405 nm laser beam was used as the scanning source. The emission in the range of 410–510 nm was detected as the fluorescent signal. Fig. 4 shows the recording pulse energy dependence of patterns and their associated fluorescent images, read out by a reflection-type confocal microscope. As a whole the recorded spots can be observed by reflection signal at all the recording energies, while their corresponding fluorescent signals can be detected only from the spot with a void at its center. As seen in Fig. 4(a), at the 1 μJ/pulse energy no void could be created and the fluorescent image of the bits shows nothing. This situation is similar to that reported by Day and Gu [10], who reported a similar phenomenon in PMMA using an average laser power less than 2 μJ/pulse. When the pulse energy is 2 μJ/pulse, voids began to

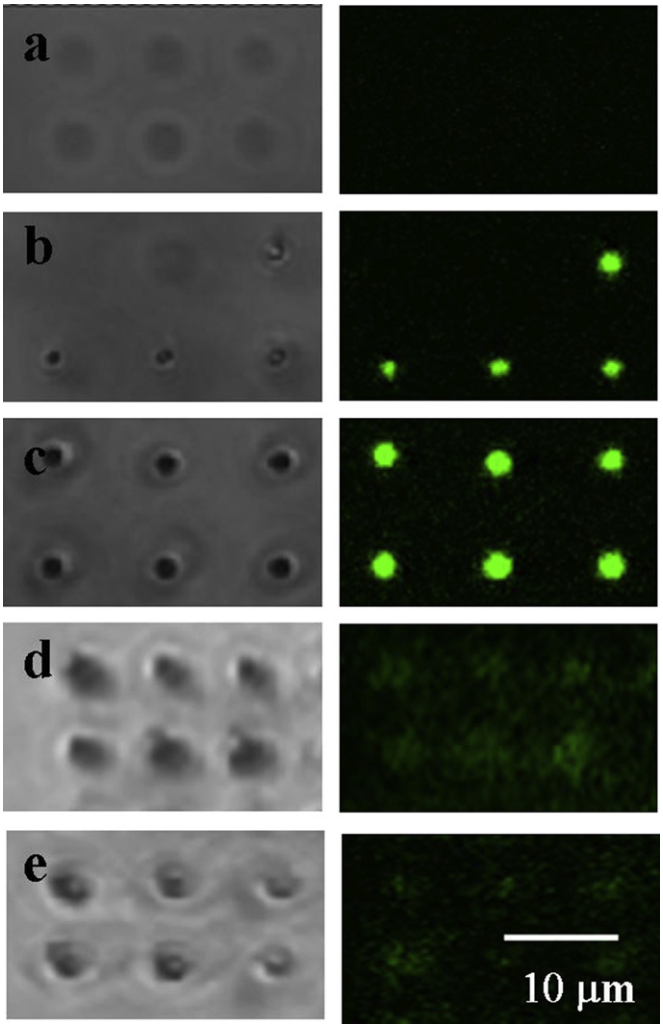

Fig. 4. Patterns (left panes) and their associated fluorescent images (right panes) as a function of recording laser energy: (a) 1 μJ/pulse, (b) 2 μJ/pulse, (c) 3 μJ/pulse, (d) 5 μJ/pulse, and (e) 8 μJ/pulse.

form at some spot centers with associated fluorescent signals in Fig. 4(b). So the induced PL is from the focal region, where the deposited energy exceeds the threshold of PL change and also is high enough to create a void by micro-explosion. The energy corresponding to this threshold is 2 μJ/pulse for the employed laser. As the pulse energy is less than the threshold, the bit is formed as a result of melting or relaxation of the polymer, and the associated refractive index change is large enough to produce a weak reflection signal but not enough to produce a fluorescent signal. As the energy increases to 3 μJ/pulse, a relatively uniform bit morphology and PL signal was achieved, as shown in Fig. 4(c). However, after the pulse energy exceeds this optimal value, the PL signal decreases greatly even though the void created by the laser pulse turns larger and some cracks begin to appear, as displayed in Fig. 4(d) and (e), in which the patterns are recorded at 5 and 8 μJ/pulse, respectively. The decrease of PL may be due to the negative quenching effect of defects created by micro-explosion.

A ten-layer bit pattern was then recorded inside PMMA (>100 μm under the surface) by single-shot irradiation with the optimum laser energy of 3 μJ/pulse. The inter-spot spacing and the layer separation were fabricated to be 10 μm. Fig. 5 shows 3D view of the fluorescent signal (left panel) and reflection signal (right panes) distributions of the first (a), fifth (b) and tenth (c) layers for the ten-layer pattern. Although conspicuous pattern images can be observed without inter-layer crosstalk in the reflection mode, the contrast remains relatively low as compared with the fluorescent mode. The material can be crack free and PL stable on the yearly scale at room temperature after the optical recording.

The S/N ratio is typically defined as S/N ratio (dB)$=20\log_{10}[V_S/V_N]$, where V_S is the signal amplitude and V_N the average noise level.

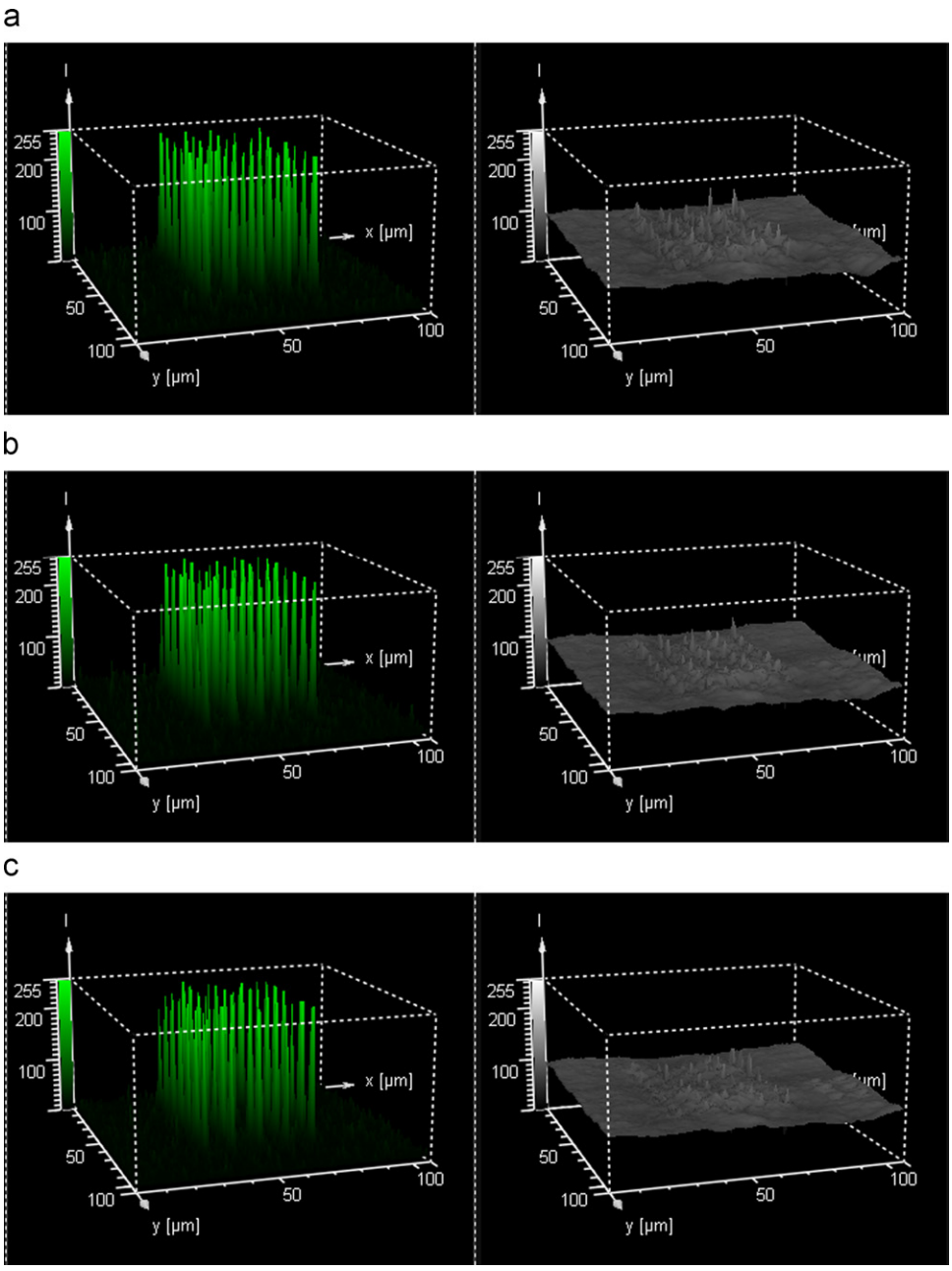

Fig. 5. 3D view of the fluorescent signal (left panels) and reflection signal (right panes) of the first (a), the fifth (b) and the tenth (c) layers for the ten-layer pattern. All bits were formed by single-shot irradiation with the energy of 3 μJ/pulse.

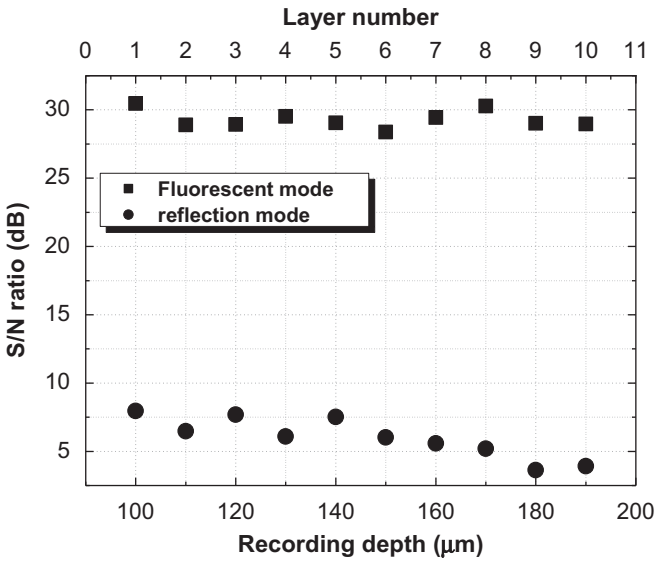

Fig. 6. *S*/*N* ratio of the ten-layer pattern as a function of recording depth and layer number for fluorescent signal mode (■) and reflection signal mode (●).

Fig. 6 displays the *S*/*N* ratio of the ten-layer pattern as a function of recording depth and layer number. The first layer detected in the reflection mode showed an *S*/*N* ratio of 7.96 dB and a degraded value of 3.92 dB was observed for the tenth layer. The average *S*/*N* ratio for fluorescent read out was about 29.29 dB and no obvious degradation was detected as a function of the layer depth. Clearly, the detection of the fluorescent signal enables retrieval of the stored bits with a much higher *S*/*N* ratio.

The minimum bit size and layer separation sufficient to prevent cross talk in PMMA need to be further studied. They will be affected by the recording system and the material property, especially the strength of PL change. The bits used in the current work are large and spaced widely apart, thus leading to a relatively low capacity of 1.0 Gbits/cm^3. However, the fluorescent signal is fairly strong and no cross talk exists between the layers in this work. So it is possible to write even smaller bit size by using an objective with bigger NA, and then the storage density can be further increased.

4. Conclusions

In summary, we have achieved 3D optical memory with undoped PMMA. Irradiation with an infrared 100-fs pulsed laser induced two overlapping PL bands near 380 and 430 nm. The emissive oxidized products of photo-degradation reaction under fs-laser irradiation may be responsible for the PL change. The dependence of fluorescence on the laser pulse energy indicates that the threshold of the PL change is ~2 μJ/pulse, and the optimal recording energy is ~3 μJ/pulse. A ten-layer pattern (spot interval = 10 μm, layer separation = 10 μm) was recorded by the focused fs laser and the read out was carried out by a fluorescent confocal microscope. High contrast pattern images were obtained without cross talk, implying that PMMA organic glass can be a potential medium for realizing a high-density 3D fluorescent storage.

Acknowledgements

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