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Multilayered optical bit storage in $Sm(DBM)_3Phen$-doped poly(methyl methacrylate) read out by fluorescence and reflection modes

Z G Nie[1,2], K S Lim[1], W Y Jang[1], H Y Lee[3], M K Lee[3] and T Kabayashi[2,4,5,6]

[1] BK21 Physics Program and Department of Physics, Chungbuk National University, Cheongju 361-763, Korea
[2] Advanced Ultrafast Laser Research Center, and Department of Engineering Science, Faculty of Informatics and Engineering, University of Electro-Communications, 1-5-1 Chofugaoka, Chofu, Tokyo 182-8585, Japan
[3] Department of Materials Science and Engineering, Yonsei University, Seoul 120-749, Korea
[4] International Cooperative Research Project, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan
[5] Department of Electrophysics, National Chiao-Tung University, Hsinchu 30010, Taiwan
[6] Institute of Laser Engineering, Osaka University, 2-6 Yamada-oka, Suita, Osaka 565-0971, Japan

E-mail: niezg@ils.uec.ac.jp

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Abstract
We report on multilayer optical data storage using $Sm(DBM)_3Phen$-doped poly(methyl methacrylate) and a tightly focused 800 nm, 1 kHz, 100 fs pulsed laser. After pulsed femtosecond laser irradiation, refractive-index change and a visible fluorescent bit were formed at the irradiated position inside the bulk sample. The photoluminescence should result from the ligands peeled from the central Sm^{3+} ions via bond scission induced by laser irradiation. Multilayer patterns recorded by tightly focusing the pulsed laser beam were read out by a reflection-type fluorescence confocal microscope, which can detect the scattered signal and also the fluorescent signal of the stored bits. The dependence of fluorescence and scattering signals on recording pulse energy was examined. The signal-to-noise ratios via two retrieval modes were compared as a function of recording depth. The detection of the fluorescence signal enables retrieval of the stored bits with a higher S/N ratio.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

As the feature sizes of two-dimensional optical memories are already close to the diffraction limit, three-dimensional (3D) optical bit storage has drawn considerable interest recently for its potential application to high density optical data storage, where the data are stored at different levels within a volume recording medium [1–17]. Femtosecond (fs) laser pulses are 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 multiphoton absorption, and the photomodified region can be well defined due to the non-thermal nature of the light–matter interaction [2, 3]. Previous works on 3D memories have mostly been carried out with the refractive-index change or void creation by fs-laser irradiation in transparent materials [2–4]. It was recently found that photoluminescence (PL) spectra of some materials can be altered space-selectively as a result of laser irradiation [5, 6]. 3D optical bit storage by detecting the fluorescent signal of

stored bits was usually expected to give rise to a much enhanced signal-to-noise (S/N) ratio, compared with the scattering signal caused by refractive-index change [5–11].

Photosensitive polymers were usually used as the data-recording media to obtain 3D optical memories in multilayered [10–14] and holographic [15–17] data-storage technologies. In this work, multilayer optical bit storage was achieved using $Sm(DBM)_3Phen$-doped poly(methyl methacrylate) (PMMA) as the recording medium. $Sm(DBM)_3Phen$, a typical rare-earth complex, shows excellent solubility in PMMA, in which dibenzoylmethane (DBM) behaves as a highly absorbing chelating reagent in the form of β-diketones [18, 19]. PMMA is an interesting material for 3D optical storage due to its high chemical resistance, advantageous optical properties and low cost [10–14]. A recent research on 3D optical memory with $Sm(DBM)_3Phen$-doped PMMA [11] demonstrated the use of micro-void formation and the void-associated PL change centred at 600 nm under multiphoton absorption excited by a focused fs-pulsed laser. The PL signal can be read out by a 514.5 nm light from an Ar^+ laser. A similar PL band has also been observed for undoped-PMMA ablated by picosecond pulses at 532 nm and the PL of irradiated areas can be excited by single-photon or two-photo absorption [10]. The induced PL band was usually considered to be from the defects created by the bond scission of PMMA [10, 11]. Here, we report a new broad PL spectrum peaked around 465 nm in $Sm(DBM)_3Phen$-doped PMMA induced by irradiation with a 100 fs pulsed laser at 800 nm. The PL increment at 600 nm reported before is also observed in this work, but it appears like an increased background. After pulsed laser irradiation, both a refractive-index bit and a fluorescent bit can be formed at the same position inside the bulk sample. The feasibility of 3D optical memory using the change in refractive index and fluorescence is demonstrated and the S/N ratios are compared.

2. Experimental

2.1. Sample preparation

$Sm(DBM)_3Phen$ was prepared basically according to the literature [20]. Its molecular structure is shown in the inset of figure 1. The central Sm^{3+} ion is bound to three dibenzoylmethane (DBM) ligands. 1,10-phenanthroline (Phen) acts as a synergic shielding ligand, which can reduce the rate of non-radiative decays and strongly enhance the fluorescence intensity of the complex [18, 19].

$Sm(DBM)_3Phen$-doped PMMA was made by a bulk polymerization technique. Firstly, a specified amount (0.3 g, this work) of $Sm(DBM)_3Phen$, 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 thermally polymerized at 60 °C for 72 h until solidification was fulfilled, followed by removing the remaining volatiles in a vacuum oven at 100 °C. The samples were cut by metal saw blade to ∼4 mm thickness and polished for all spectroscopic studies.

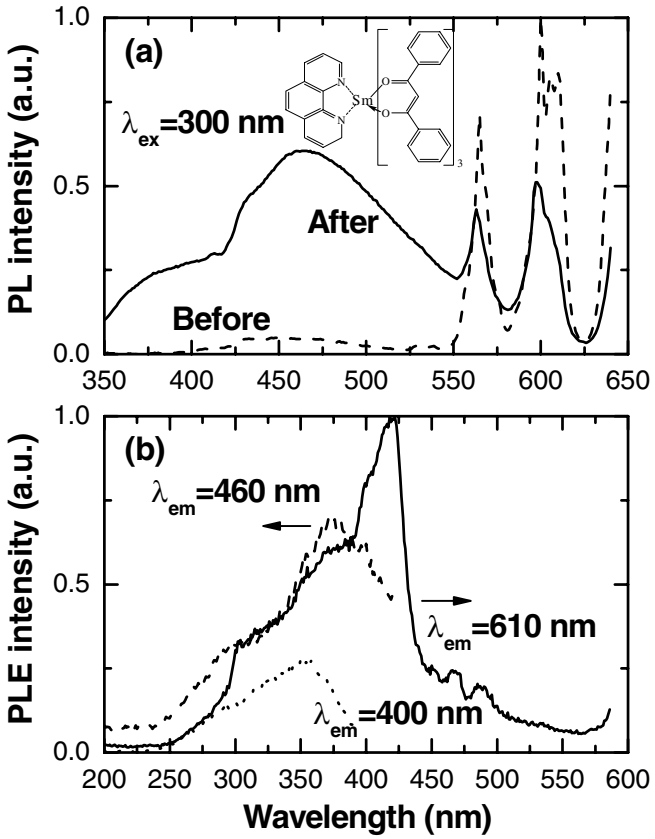

Figure 1. (*a*) PL spectra of $Sm(DBM)_3Phen$-doped PMMA under excitations at 266 nm before and after 100 fs laser irradiation. (*b*) PLE spectra measured for the emissions at 400 nm, 460 nm and 610 nm, respectively.

2.2. Characterization

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 PL spectrum was recorded on a Perkin-Elmer LS 55 fluorescence spectrophotometer. All the measurements were performed at room temperature.

3. Results and discussion

3.1. Fs-laser induced PL change in $Sm(DBM)_3Phen$-doped PMMA

First, equally spaced line patterns were made under irradiation with a 5 mW fs laser inside the sample at 100 μm under the surface within 3 mm × 3 mm area for PL measurement. Figure 1(*a*) compares the PL spectra of $Sm(DBM)_3Phen$-doped PMMA before and after fs-laser irradiation, obtained with the excitation at 300 nm. We attribute the emission lines observed at 564 nm, 610 nm and 649 nm to f–f transitions of Sm^{3+} $^4G(4)_{5/2} \rightarrow {}^6H_{5/2}$, $^6H_{7/2}$ and $^6H_{9/2}$ [19], respectively, and the broad emission at around 465 nm to the radiative transition from the lowest triplet state T_1 to the S_0 state of some uncomplexed isolated DBM [21]. Before irradiation, the PL spectrum is dominated by the strong emissions of Sm^{3+}

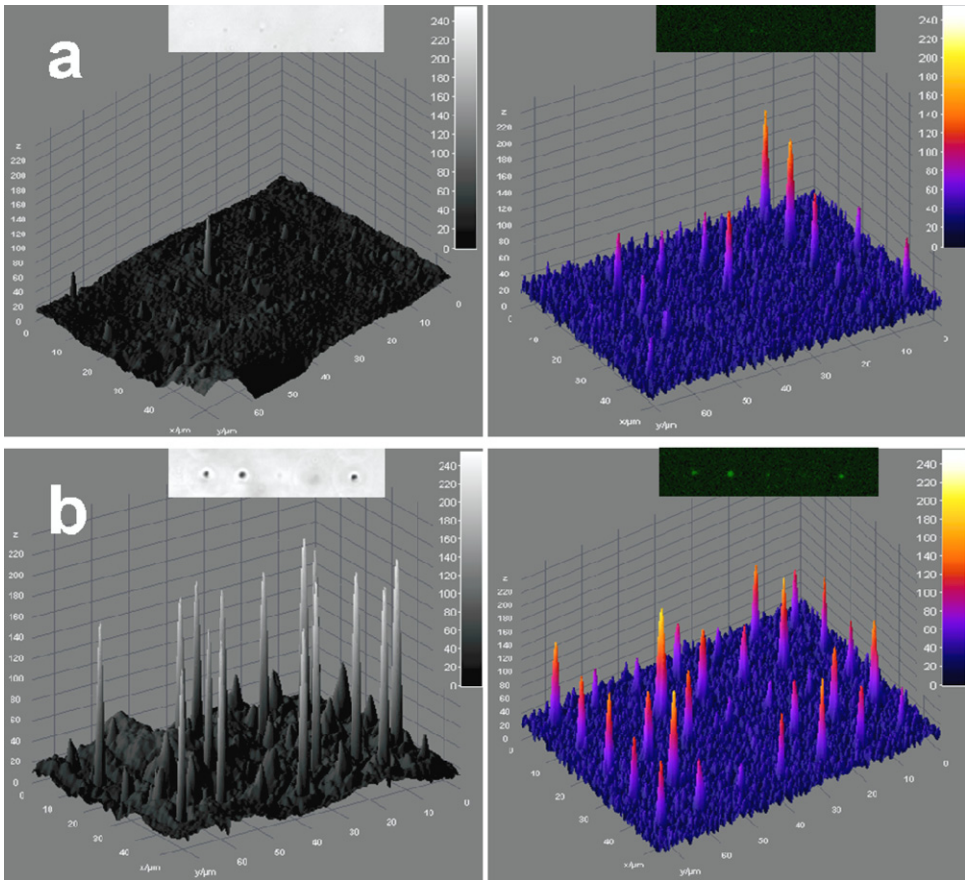

Figure 2. 3D signal view by detecting the scattering (left panels) and their corresponding fluorescence (right panels) bits recorded as a function of laser energy: (*a*) 2 μJ/pulse and (*b*) 3 μJ/pulse. A part of the scattering and the corresponding fluorescent image patterns with lateral spacing of 10 μm and layer spacing of 20 μm are shown in the insets. (Colour online.)

ions. After irradiation, the weak band emission around 465 nm increases significantly and a new emission band at around 400 nm appears, and in the meantime the emissions of Sm^{3+} decrease significantly. Figure 1(*b*) displays the PL excitation (PLE) spectra of the sample after laser irradiation. Monitoring the emission of Sm^{3+} at 610 nm, the broad excitation bands at ∼300 nm and ∼370 nm are assigned to the absorption of the DBM ligands [22, 23], and the relatively narrow peaks superposing on the broad bands at 418 nm, 467 nm and 488 nm, are attributed to the excitation from the ground state of Sm^{3+} $^6H_{5/2}$, to its various excited states $^6P_{5/2}$, $^4I(3)_{13/2}$, $^4M_{15/2}$ transitions [19], respectively. In contrast, it seems apparent that the excitation spectra of the band emissions at 400 nm and 465 nm contain only the two broad absorption bands of ligands. For the emission of 400 nm, the second excitation band is suppressed because of a cut-off filter used to block the excitation light.

According to sensitized emission theory, the excitation light is mainly absorbed by the broad bands of the ligands, and then it is followed by energy transfer from the ligands to the central Sm^{3+} ions in this material [23]. As seen in figure 1, after irradiation the increase in ligand emission is accompanied by the decrease in the line emissions of Sm^{3+}. It seems the laser irradiation destroys the effective energy transfer from the ligand to the central ions, and finally results in the emission of the ligands. Thus the bond scission after laser irradiation may mostly take place between the ligands and central ions. However, the exact mechanism of these PL changes needs to be further studied.

In principle, undoped PMMA is transparent in the near UV–visible region, though the tail of the intense UV absorption extends a little beyond 300 nm [24]. As shown in figure 1, the doping of $Sm(DBM)_3Phen$ produces strong absorption within 250–500 nm; therefore, a laser beam of an infrared wavelength at 800 nm can be used in the recording process to produce two-photon excitation at 400 nm. Since the absorption band cuts off approximately at a wavelength of 500 nm, a range of wavelengths from 500 to 750 nm can be chosen to read out the recorded data bits without significantly suffering from single-photon or two-photon excitation. The observation of PL change under excitations in the 250–500 nm range after fs-laser irradiation opens up the possibility of using fluorescence signal for multilayered optical storage.

3.2. Multilayered optical bit storage in $Sm(DBM)_3Phen$ doped PMMA

To demonstrate the feasibility of using the changes in refractive index and fluorescence associated with the bits recorded by fs-pulsed laser within $Sm(DBM)_3Phen$-doped PMMA, bit patterns were recorded as a function of pulse energy by

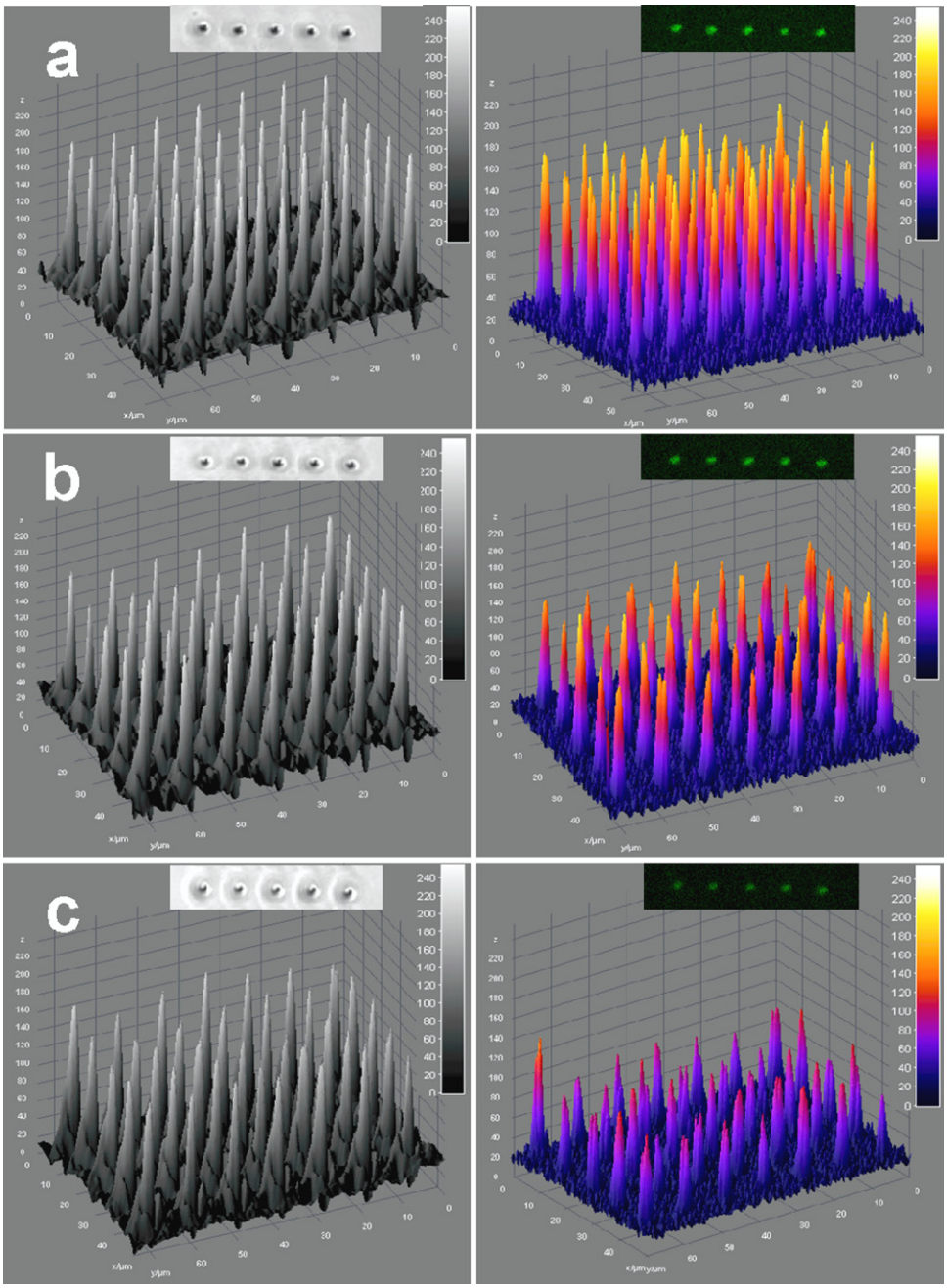

Figure 3. 3D signal distributions of the first (a), the second (b) and the forth (c) layers for the five-layer bit pattern, read out by detecting the scattering (left panels) and their corresponding fluorescence (right panels). Insets: a part of the scattering and the corresponding fluorescent image patterns with lateral spacing of 10 μm and layer spacing of 20 μm. (Colour online.)

focusing the laser beam through an objective lens (50×, NA = 0.42). The bits were formed with a single pulse under 100 μm below the surface. The recorded images were read out by a reflection-type fluorescence confocal microscope where a 405 nm LD-laser beam was used as the scanning source. The emission in the range 500–620 nm was detected as the fluorescent signal.

Figures 2(a) and (b) show the 3D view of the scattering (left panels) and their associated fluorescence signals (right panels) for two patterns (inter-spot spacing = 10 μm, inter-layer spacing = 20 μm) recorded at 2 μJ/pulse and 3 μJ/pulse, respectively. A part of bit patterns and their fluorescent images are shown in the insets. The energy threshold for the scattering and fluorescence signals is detected at 2 μJ/pulse, as displayed in figure 2(a). When the pulse energy increases to 3 μJ/pulse, as seen in figure 2(b), voids begin to be formed at some spot centres and more bits exhibit fluorescence signals, but signal distributions are still inhomogeneous. As shown in the inset, by contrast the fluorescence signal is much stronger for the bits with a minute hole at their centres. The micro-explosion at the laser focus may contribute significantly to the bond scission in the material, and then lead to the PL of the ligands. In addition, the difference in the fluorescence intensity should be caused by the inhomogeneous distribution of $Sm(DBM)_3Phen$ in PMMA, which also leads to inhomogeneous strain, and thus the difference of bit morphology.

Relatively uniform signal distributions for the two readout modes are achieved until the laser energy increases to 7 μJ/pulse, as shown in figure 3, which displays the signal distributions of scattering (left panels) and their associated fluorescence signals (right panels) of the first (a), second (b) and the forth (c) layers for a five-layer pattern. Conspicuous pattern images can be observed without inter-layer crosstalk for the two readout modes. Compared with the scattered signal, obvious decrease can be observed for the fluorescence with increasing layer number.

In the bit-type 3D optical storage, the S/N ratio is an important parameter to be considered because it is ultimately related to the storage capacity. 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 [25]. Figure 4 displays the S/N ratio of the five-layer pattern at 7 μJ/pulse as functions of recording depth and layer number. The average S/N ratios for fluorescence and reflection readout are about 20 dB and 12 dB, respectively, and degradation trends are both observed for the two readout modes. The decreasing S/N ratio is consistent with the variation of the signal intensity with increasing layer number. Interestingly, as seen in figure 3, though the fluorescence intensity begins to be lower than the scattering signal from the second layer, the S/N ratio of fluorescence mode keeps higher than the scattering one down to the deeper fifth layer. It is because the average noise level of the fluorescence mode is much lower than the reflection one. Thus the detection of the fluorescence enables retrieval of the stored bits with a relatively higher S/N ratio. However, the fluorescent signal decreases more rapidly than the scattering one with recording depth. So the reflection mode may be desirable for optical storage within much deeper layers.

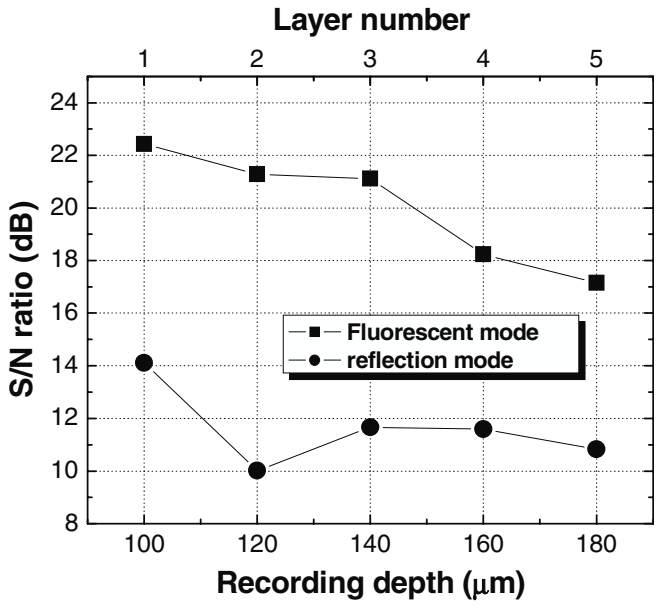

Figure 4. S/N ratio of the five-layer pattern as a function of recording depth and layer number for fluorescent mode (■) and reflection mode (●).

For the fluorescent microscopy, the number of photons entering the detector is limited by the emission filter. Thus as the bit separation and layer spacing are reduced, the S/N ratio will decrease with a simultaneous increase in crosstalk. In order to further investigate the minimum separations of adjacent bits and layers sufficient to prevent crosstalk, ten-layer bit patterns were recorded at the optimum laser energy of 7 μJ/pulse. The inter-spot spacing and layer separation were reduced down to 5 μm and 10 μm, respectively. Figure 5 shows the scattering and fluorescence signal distributions obtained from one layer. Clearly, the homogeneity of the fluorescent signal distribution decreases in comparison with the five-layer patterns recorded at the same laser energy, though high-contrast signal distributions without crosstalk can still be observed for the two readout modes. The congestion of the spots (or voids) may result in energy transfer between different luminescence and defect centres, and then leads to the quenching of some fluorescent bits.

The bit sizes used in this work are large, which leads to a relatively low capacity of 4 Gbits cm^{-3} for the ten-layer pattern. Since the fluorescent signal is fairly strong and it is possible to write even smaller bits using an objective with bigger NA, the storage density may be further increased. In addition, the high pulse energy (7 μJ/pulse) used in this work

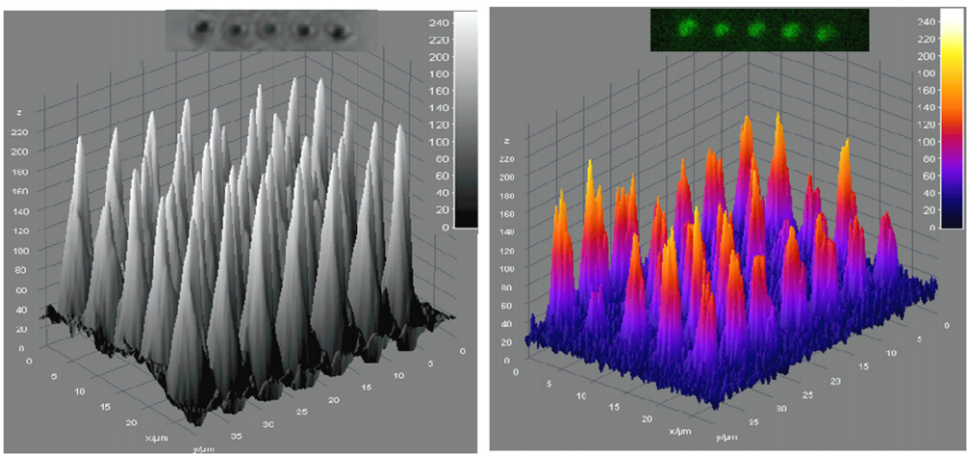

Figure 5. 3D scattering (left panel) and fluorescence (right panel) signal distributions obtained from one layer of the ten-layer bit pattern. Insets: a part of the scattering and the corresponding fluorescent image patterns with lateral spacing of 5 μm and layer spacing of 10 μm. (Colour online.)

leads to a large bit size. More works will be necessary to increase the homogeneity of the sample, which may enable us to obtain a uniform fluorescence signal and smaller bit size at a relatively lower recording energy, such as 2 or 3 μJ/pulse, and then ultimately to increase the potential storage capacity.

4. Conclusions

We examined the feasibility of multilayered optical storage inside $Sm(DBM)_3Phen$-doped PMMA using a focused 800 nm, 100 fs, 1 kHz pulsed laser. A refractive-index bit and also a fluorescent bit at the same position were formed inside the bulk sample after fs-laser irradiation. The new PL bands should result from the peeled ligands from the central Sm^{3+} ions via bond scission after laser irradiation. The fluorescence signal begins to appear after laser irradiation at 2 μJ/pulse. A five-layer pattern with spot interval of 10 μm and layer separation of 20 μm was recorded by a focused fs laser at 7 μJ/pulse and the readout was carried out without cross talk by a reflection-type fluorescent confocal microscope. The detection of the fluorescent signal enables retrieval of the stored bits with a relatively higher S/N ratio for the layers at high levels (recording depth $<$180 μm, this work) below the surface.

Acknowledgments

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