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Three-dimensional optical memory with rewriteable and ultrahigh density using the valence-state change of samarium ions

K. Miura[a)]
Optical Device Development Department, Central Glass Corporation, 5253 Okiube, Ube-city, Yamaguchi 755-0001, Japan and Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

Jianrong Qiu
Photon Craft Project, Japan Science and Technology Corporation, Keihanna-plaza, Super-laboratory 2-5, 1-7 hikaridai, Seika-cho, Kyoto 619-0237, Japan

S. Fujiwara and S. Sakaguchi
Optical Device Development Department, Central Glass Corporation, 5253 Okiube, Ube-city, Yamaguchi 755-0001, Japan

K. Hirao
Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

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We report the recording, readout, and erasure of a three-dimensional optical memory using the valence-state change of samarium ions to represent a bit. A photoreduction bit of 200 nm diam can be recorded with a femtosecond laser and readout clearly by detecting the fluorescence as a signal (excitation at 488 nm, 0.5 mW Ar^+ laser). A photoreduction bit that is stable at room temperature can be erased by photo-oxidation with a cw laser (514.5 nm, 10 mW Ar^+ laser). Since photoreduction bits can be spaced 150 nm apart in a layer within glass, a multilayer structure with several hundred layers could be used to record data. A memory capacity of as high as 1 Tbit could thus be achieved in a glass piece with dimensions of $10\ mm\times 10\ mm\times 1\ mm$. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1459769]

Materials processing technology by using femtosecond laser irradiation has attracted tremendous interest from both the scientific and technological communities. In particular, the use of femtosecond laser processing to write three-dimensional (3D) structures in transparent materials is technologically attractive for applications such as multilayer optical memories[1,2] and optical waveguides.[3–5] Three-dimensional optical memories have generated considerable interest in recent years for their potential application to high-density optical data storage.[6,7] Previous research on 3D optical memories using irradiation with a focused femtosecond laser has demonstrated the use of refractive-index changes or void creation in transparent materials.[8,9]

Recently, we found that rare-earth ions, such as Sm^{3+} and Eu^{3+}, in glass can be space-selectively photoreduced with an infrared femtosecond laser.[10] In this letter, we examine the possibility of achieving 3D optical data storage inside glass by using a focused femtosecond laser to permanently photoreduce of Sm^{3+} to Sm^{2+}.

The composition of the glass samples doped with samarium ions used in this study was $35AlF_3-10BaF_2-10SrF_2-20CaF_2-10MgF_2-14.5YF_3-0.5SmF_3$ (mol %). Samarium was present in the glass in the Sm^{3+} ionic state. As a recording source we employed a regeneratively amplified 800 nm Ti:sapphire laser emitting 20 Hz or 250 kHz mode-locked pulses. We tightly focused femtosecond laser pulses inside the bulk glass to locally photoreduce Sm^{3+} to Sm^{2+}. A 3D recording was made by laser irradiation through a water-immersion objective (63× magnification, NA$=$1.2) in the interior of the glass samples with an *XYZ* stage. Photoluminescence images were obtained with a three-dimensional nanometer-scanning spectroscopic microscope (Nanofinder TII) using 488 nm light from an Ar^+ laser as the readout (excitation) source. All experiments were carried out at room temperature.

Figure 1 shows photoluminescence spectra obtained by excitation at 488 nm for a laser-irradiated area (a) and nonirradiated area (b) in the interior of the glass. Comparing (a)

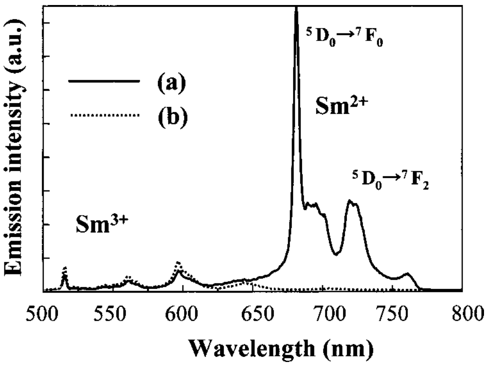

FIG. 1. Photoluminescence spectra obtained by excitation at 488 nm for a laser-irradiated area (a) and nonirradiated area (b) in the interior of the glass.

[a)] Author to whom correspondence should be addressed; electronic mail: kmiura@cgco.co.jp

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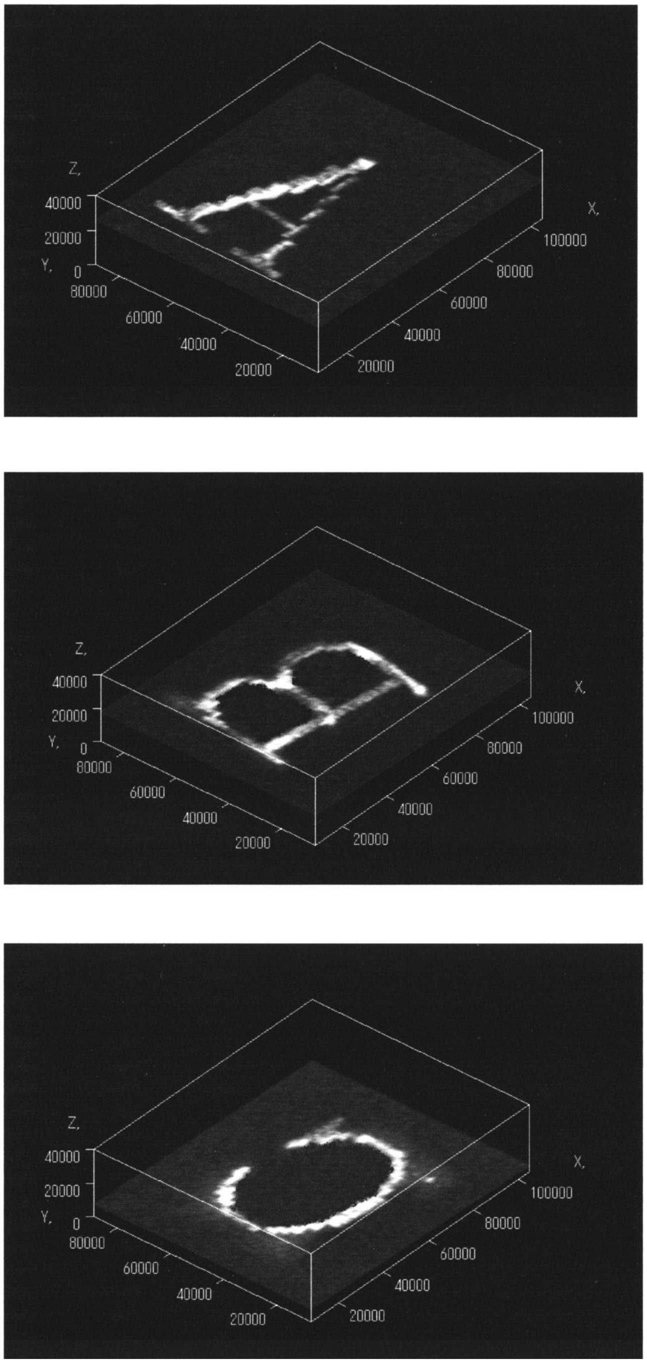

FIG. 2. Photoluminescence images of alphabetical characters recorded on different layers, which were observed by using a 40× objective lens and the 680 nm emission from Sm^{2+} with confocal detection implemented (excitation at 488 nm, 1 mW Ar^{+} laser).

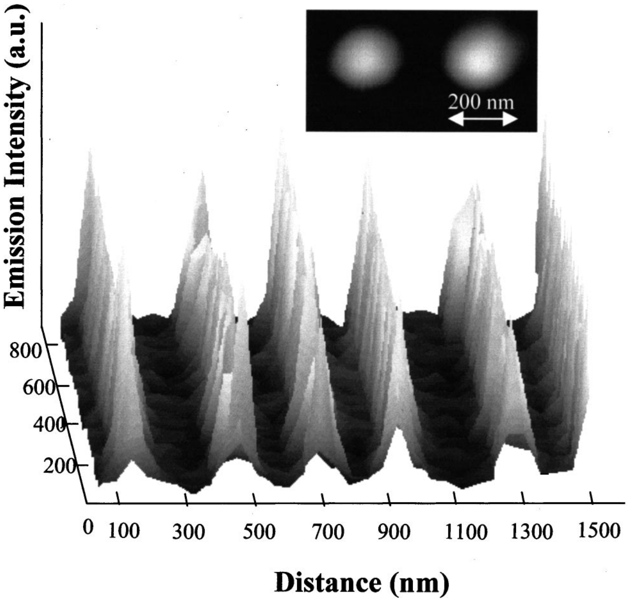

FIG. 3. Signal readout by detecting the fluorescence for photoreduction bits with a 200 nm diam.

to (b) shows that the emission in the 650–775 nm region differed appreciably. The broadbands observed around 560, 600, and 645 nm can be attributed to the $^4G_{5/2} \rightarrow {}^6H_{5/2,7/2,9/2}$ transitions, respectively, of the Sm^{3+} ions. On the other hand, the emissions at 680, 700, and 725 nm are attributed to the $^5D_0 \rightarrow {}^7F_{0,1,2}$ transitions, respectively, of the Sm^{2+} ions. This means that laser-irradiated areas (photoreduced areas) recorded inside glass can be detected only by emissions at 680, 700, or 725 nm. Although the mechanism is not fully clear at present, we suggest the mechanism of the photoreduction is as follows. Active electrons and holes were created in the glass through a multiphoton process. Holes were trapped in the active sites in the glass matrix while some of the electrons were trapped by Sm^{3+}, leading to the formation of hole-trapped defect centers and Sm^{2+}.

By using the photoreduction of Sm^{3+} to Sm^{2+}, alphabetical characters were recorded in the form of sub-micron-size bits in a three-dimensional (layered) manner in the glass samples. Here, one recorded character consisted of 300–500 photoreduction bits recorded with 5000 laser shots per bit with a repetition rate of 250 kHz. The spacing between alphabetical characters was 2 μm. The bits had a diameter of 400 nm, which was significantly smaller than the focal-beam size and the wavelength of the recording laser. Figure 2 shows photoluminescence images of alphabetical characters recorded on different layers, which were observed by using a 40× objective lens and the 680 nm emission from Sm^{2+} with confocal detection implemented. We confirmed that the spacing of 2 μm between alphabetical character planes was sufficient to prevent cross talk in the photoluminescence images. Although the 3D memory bits (photoreduced areas) were recorded with a femtosecond laser, they could be read with a cw laser at 0.5 mW.

Recording and readout in a three-dimensional memory are possible without any influence from bits in upper or lower layers recorded previously. Although obtaining a multilayer of several hundred layers has been difficult in a conventional 3D memory, it can be achieved by applying photoreduction bits to current optical memory technology. In addition, as shown in Fig. 3, photoreduction bits with a 200 nm diam could also be read out clearly by detecting the fluorescence as a signal. Since photoreduction bits can be spaced 150 nm apart on a layer in glass, a memory capacity of as high as 1 Tbit could be achieved for a glass piece with dimensions of 10 mm×10 mm×1 mm.

Another outstanding characteristic of the photoreduction of Sm^{3+} to Sm^{2+} is that stable Sm^{2+} at room temperature can be changed to Sm^{3+} by photo-oxidation with a cw laser, such as an argon-ion laser or a semiconductor laser. An example of a photoreduction bit erased by irradiation with an

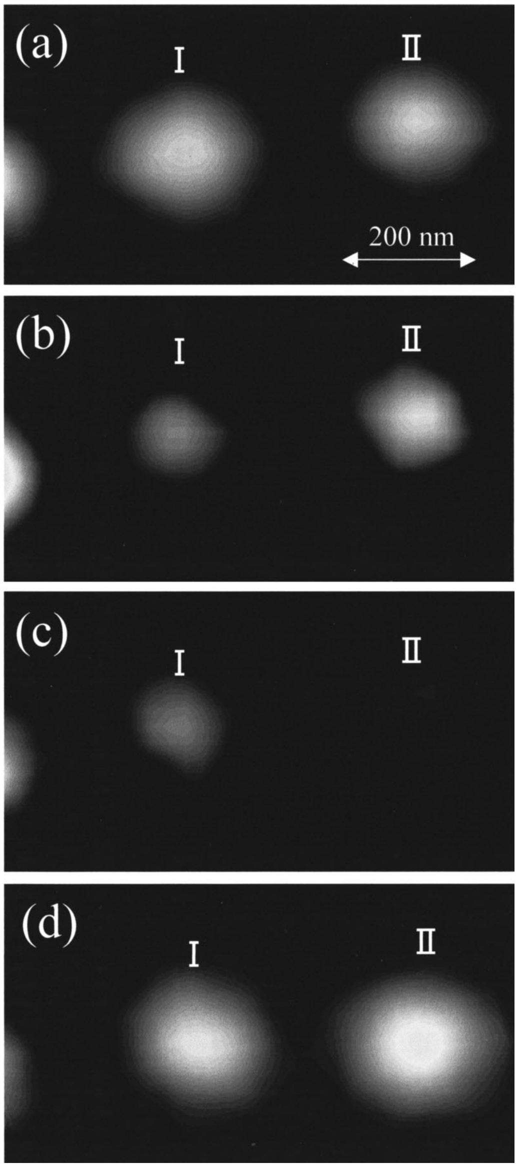

FIG. 4. Example of erasing and rewriting by irradiation with an Ar^+ laser (5 mW at 514.5 nm) and a femtosecond laser. (a) Photoluminescence image before the erasure. (b) Image after Ar^+ laser irradiation to photoreduction bit I. (c) Image after Ar^+ laser irradiation to bit II. (d) Image after femtosecond laser irradiation to areas I and II.

Ar^+ laser (10 mW at 514.5 nm) is shown in Fig. 4. Figure 5 shows the contrast achieved in readout of bits (I, II) in Fig. 4. These results indicate the possibility of achieving a three-dimensional optical memory with rewrite capability.

In summary, by using the valence-state change of samarium ions to represent a bit, data can be read out as fluorescence information and erased by irradiation with a cw laser. The ratio of the fluorescence intensity at 680 nm after and before irradiation with the femtosecond laser is limitless, so a high signal-to-noise ratio can be achieved. Moreover, it is possible to create a multilayer record of data over several hundred layers, because the recording, readout, and erasure processes for the data are not affected by layers recorded nearby. Therefore, this technique will be useful in fabricating next-generation 3D optical memory devices with an ultra-high storage density.

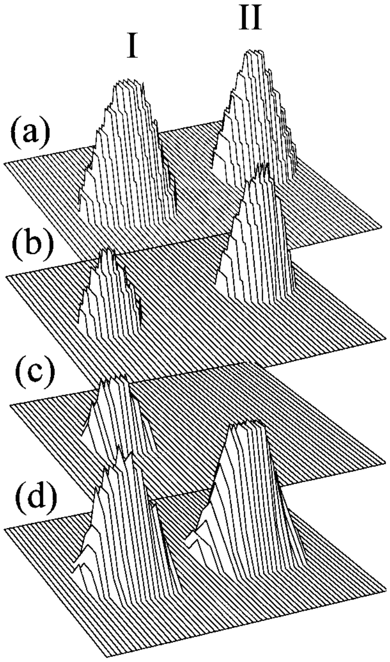

FIG. 5. Intensity distribution of the fluorescence (680 nm) for bits of I and II in Figs. 4(a), 4(b), 4(c), and 4(d).

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