Two-photon Sensitized Recording Materials for Multi-layer Optical Disk

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Abstract

Two types of novel two-photon sensitized recording material writable at 405 nm and 522nm were developed. The fluorescent dye generation type (F-type) material consists of at least two-photon absorption dye (TPAD) and fluorescent dye precursor (FDP), which is non-fluorescent before two-photon recording and fluorescent after two-photon recording due to fluorescent dye generation. The fluorescence quench type (Q-type) material, on the other hand, consists of at least TPAD, fluorescent dye (FD) and fluorescent quencher precursor (QP), which is fluorescent before two-photon recording and the fluorescence intensity is reduced after two-photon recording at the recorded spot due to fluorescent quencher generation. Both types of material showed quadratic dependency on recording light intensity. A twenty-layer two-photon recording media was fabricated with the fluorescence quench-type material, and two-photon recording and one-photon fluorescent signal readout was successfully conducted.

1. Introduction

Volumetric optical disks for recording, which store data in three dimensions inside the disk, has been attracting attention as the next generation optical data storage media that meet the demands for even greater capacity and for reducing power consumption for the recording of data, and for this, there have been proposals of materials for nonlinear void formation[1)], heat-mode material with linear absorption[2)], and two-photon absorption recording material[3)].

Two-photon absorption recording utilizes the simultaneous absorption of two photons. This is a three dimensional nonlinear optical effect, and it is a way of recording particularly suitable for volumetric recording. The reason is that the recording light can reach deep inside the recording media without attenuation because it is possible to use a long wavelength light that is not linearly absorbed by the recording media material, and further because it is possible in principle to record three dimensionally merely by changing the focal point along the depth direction, since absorption is limited only to the area with strong light intensity, near the focal point.

Data storage media that utilize two-photon absorption must have efficient two-photon absorption which causes desired physical changes in such properties as absorption and fluorescence. A spiropyran derivative[4)] was the first photochromic material reported to have both of these functions in a single molecule, and since then various photochromic materials have been used for two-photon recording material. Generally speaking, the two-photon absorption cross section of photochromic material is very small and it is extremely difficult to make the two-photon absorption cross section large while preserving the ability of photochromism, and therefore it is not practical to implement two-photon absorption recording using photochromic material. Instead, based on the idea that it is possible first to separate the two required functions and use an independent compound for each of them, making it possible to obtain a highly efficient two-photon recording material by combining a compound which has large two-photon absorption cross section and a compound whose physical properties change in the desired manner, we have been working on the development of separate-function composite two-photon sensitized recording material[5)].

In this article, we first demonstrate the possibility of achieving the recording density required for practical application (recording capacity per recording layer 25 GB, equivalent to a Blue-ray disk, hereafter BD), and then report the details of an experiment where we successfully conducted two-photon three dimensional recording on a twenty layer medium.

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2. Recording/Readout Evaluation System

Prior to performance evaluation of two-photon absorption recording material, we built an evaluation system for two-photon recording and readout. We used FUJIFILM's newly developed ultra-compact femtosecond pulsed laser F-1A[6] (pulse width 490 fs, pulse frequency 3 GHz, maximum peak power 50 W) for two-photon recording at 522 nm, and a Ti : sapphire laser (Spectra-Physics, pulse width 200 fs, pulse frequency 8 MHz, maximum peak power 200 W) for two-photon recording at 405 nm. In this article, we mainly report on the results of recording/readout experiments using the Fujifilm laser. For reading out the recorded marks formed by two-photon recording we used a 633 nm He-Ne laser or a 405 nm semiconductor laser.

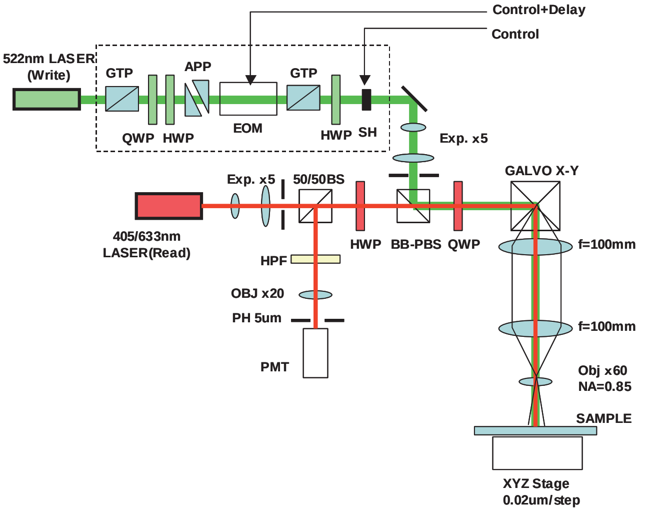

Fig. 1 The optical setup for two-photon absorption recording and one-photon fluorescence readout.

3. Two-photon Absorption Recording Material

3.1 Material Design Principle

In developing highly sensitive two-photon absorption recording material, we chose the idea of two-photon sensitization as the principle. Two-photon sensitization is obtained by combining materials with different functions, namely a two-photon absorption compound and a compound that exhibits the desired physical change (modulating material). This is an excellent material design principle, as the use of a compound with large two-photon absorption cross section provides high sensitivity, while the use of modulating material that exhibits the desired change in physical properties allows necessary flexible adaptation to signal configurations. In this article, we report on a fluorescent dye generation type material in which when an area is two-photon recorded, fluorescent dye is generated and fluorescence intensity increases, and on a fluorescence quenching type material in which when an area is two-photon recorded, fluorescent quencher is generated and fluorescence intensity decreases.

3.2 Fluorescent Dye Generation Type Material

Fluorescent dye generation type material consists of two-photon absorption dye (TPAD) and fluorescent dye precursor (FDP). As shown in Fig. 2, this is a non-fluorescent material which has no linear absorption in the wavelength region longer than 400 nm in an unrecorded area. When this recording material is irradiated using a 405 nm or 522 nm pulsed laser as two-photon recording light, two photons are absorbed in the irradiated area causing excitation of TPAD. Excited TPAD induces photoinduced electron-transfer reactions with the FDP also present, and radical cations of FDP are generated, followed by oxidization reactions that generate fluorescent dye (FD) that has an absorption peak around 650 nm. For readout of the recorded signals, first the generated FD is excited using a 633 He-Ne laser whose wavelength is in the absorption range of the FD, and then the induced fluorescence is detected.

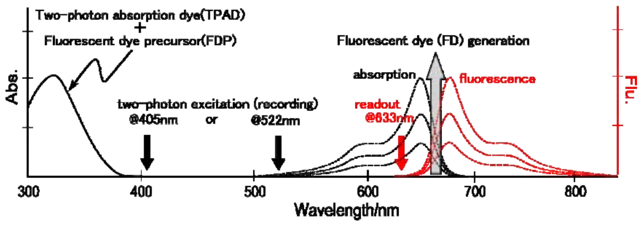

Fig. 2 Absorption and fluorescence spectral change of the F-type material upon two-photon recording.

Fig. 3 shows the behavior of the signals obtained when the recorded marks created by two-photon recording on a spin coated single layer recording film consisting of fluorescent dye generation type recording material were read out by irradiating 633 nm continuous wave light from an He-Ne laser with the average power of 0.3 – 0.5 mW.

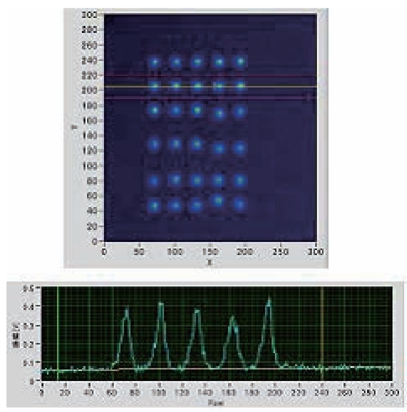

Fig. 3 Two-photon recorded pits (top) and signals from the two-photon recorded pits on the monolayer media (bottom). These signals are recorded via two-photon absorption at 522 nm and read by one-photon excitation at 633 nm.

This recording material provides low-to-high recording where fluorescent signals can be expressed since fluorescent dye is generated in an area where the recording light is irradiated, and this is surrounded by a non-fluorescent background.

3.3 Fluorescence Quenching Type Material

Since the diffraction limit of two photons is $1/\sqrt{2}$ times that of one photon, it is expected that by using 522 nm recording light and two photon recording, it should be possible to achieve recording density equivalent to one-photon recording at 373 nm which is close to that of BD, where one-photon recording at 405 nm is used. On the other hand, with the fluorescent dye generating type recording material we discussed in the previous section, the signal readout is a bottleneck for achieving BD quality recording density because the absorption of the fluorescent dye at 633 nm is the signal that is readout. Therefore, we developed a fluorescence quenching type material that allows readout at 405 nm, aiming for higher recording density by enabling signal readout at a shorter wavelength.

The fluorescence quenching type material is composed of three components; two-photon absorption dye (TPAD), fluorescence quencher precursor (QP) and fluorescent dye (FD). For the TPAD and QP, we used the same compounds as the TPAD and FPD, respectively, of the fluorescent dye generating type material. The FD we used is fluorescent dye that originally has a absorption at 405 nm, the readout wavelength, and generates intense fluorescence. This fluorescence is quenched by the quencher (Q) generated by irradiation of recording light (Fig. 4).

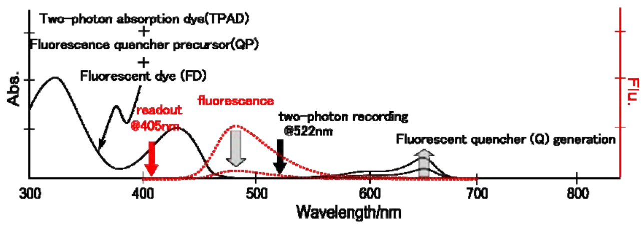

Fig. 4 Absorption and fluorescence spectral change of the Q-type material upon two-photon recording.

Fig. 5 shows the behavior of the signals obtained when the recorded marks created by two-photon recording were read out by irradiating 405 nm continuous wave light from a semiconductor laser on a spin-coated single layer recording film consisting of fluorescence quenching type recording material.

This recording material provides high-to-low recording where darker signals with less fluorescence appear on a bright fluorescent background since the original fluorescence is quenched by the fluorescent quencher generated in the area where the recording light is irradiated.

This result demonstrates that two-photon recording is possible at a recording density equivalent to that of BD, and that one-photon readout signal readout is possible at a short wavelength which is effectively the same level as BD, 405 nm.

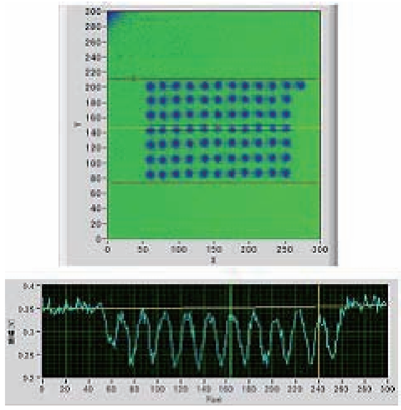

Fig. 5 Two-photon recorded pits (top) and signals from the monolayer recording media (bottom). These signals are recorded by two-photon absorption at 522 nm and read by one-photon excitation at 405 nm.

3.4 Characteristics of Two-photon Recording

Fig. 6 shows the relation between the recording light intensity and the signal intensity (in the case of the fluorescent dye generating material) and the relation between the recording light intensity and the modulation factor (in the case of the fluorescence quenching type material). The wavelength of the two-photon recording is 522 nm for both cases, and the readout wavelength is 633 nm for the fluorescent dye generating material and 405 nm for the fluorescence quenching type material.

The results shown in Fig. 6 clearly demonstrate that the signal intensity and the modulation factor are proportional to the square of the recording light intensity, which confirms that the recording pits were formed by simultaneous two-photon absorption.

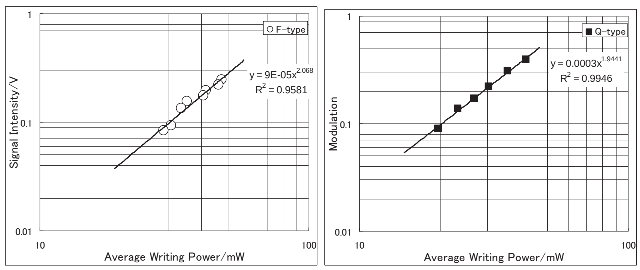

Fig. 6 Relationship between average writing power vs. signal intensity for the F-type material (left) or modulation for the Q-type material (right). The signals were recorded 522 nm of pulsed laser with 50 µs of exposure time. Recorded signals were read at 633 nm for the F-type material and 405 nm for the Q-type material.

3.5 Verification with Twenty Layer Recording Media

For the purpose of confirming the possibility of three dimensional recording using two-photon absorption, we fabricated multilayer media consisting of twenty recording layers using the fluorescence quenching type material and carried out two-photon recording and one-photon readout at each layer. The fabricated media had a structure in which 1 μm recording layers are sandwiched by 10 μm intermediate layers. Fig. 7 shows the result of the multilayer recording experiment. The dark areas surrounding the alphabetical letters are the recorded marks created by two-photon recording. For the sake of the ease of layer identification, we adjusted the recording light irradiation positions so that each layer has a different letter shape left as the non-recorded area.

Fig. 7 clearly shows that we could observe very clear, well separated signals in each of the twenty layers, with effectively no leakage of signals recorded in neighboring recording layers (interlayer cross talk).

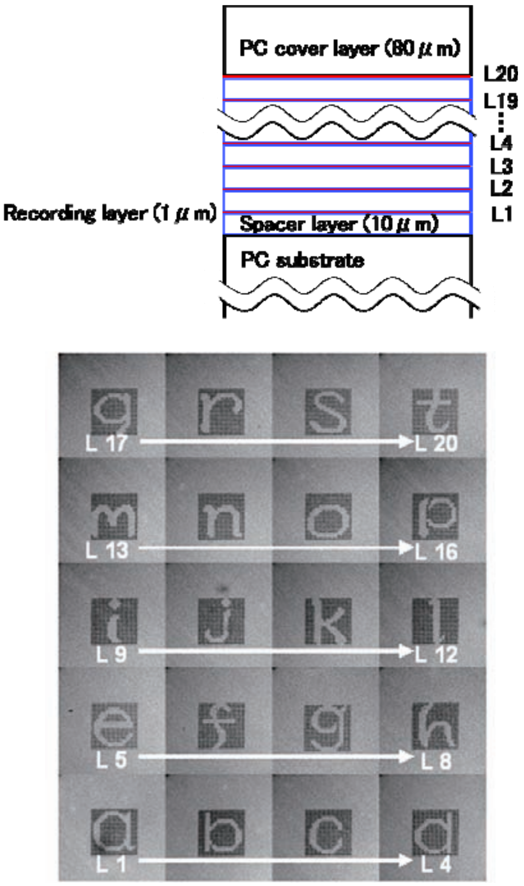

Fig. 7 The structure of the fabricated twenty-layer two-photon recording media (left) and the two-photon recorded signals in each layer (right).

4. Conclusion

We developed a two-photon absorption recording material that has a recording density capability in principle equivalent to that of BD, based on the concept of achieving different functions by combining different materials. This material clearly exhibits square dependence on the intensity of recording light, which clearly shows that the recording is due to simultaneous two-photon absorption. In addition, we empirically demonstrated three dimensional recording in a twenty layer recording media consisting of fluorescence quenching type material, showing that it has excellent three dimensional recording characteristics with no cross talk between neighboring recording layers.

We plan to work on further improvement of sensitivity and of recording characteristics in preparation for practical applications.

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