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FEATURE ARTICLE

Two-Photon Three-Dimensional Optical Storage Memory

A. S. Dvornikov, E. P. Walker, and P. M. Rentzepis*

Department of Chemistry, University of California at Irvine, Irvine, California 92697

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We describe the design and construction of ultrahigh capacity three-dimensional, 3D, optical storage devices that operate by two-photon absorption. The molecular systems and their properties that are used as two photon media for writing and one photon for accessing the stored information within the volume of the device are presented in some detail and the nonlinear two-photon absorption mechanism is briefly visited. The optical system and its components, which facilitated writing and reading, are also described and the bit density, bit error rate, store and access speeds, cycle times, and stability of the materials under various experimental conditions are also topics addressed in this review. The first ever storage of terabyte data in a removable storage disk is described in detail.

1. Introduction

Computer technology continues to progress at such an increasing rate that it creates an even larger need for high-performance storage devices that must store, retrieve, and process huge volumes of data at extremely high speeds. Improvements in silicon technology are bringing computer performance to a point where the memory capacity and input−output rates are becoming the limiting factors; consequently, the major component that will modulate the practical limits of high-speed computing is thought to be the memory that stores the huge amount of data the industry and government generate. To accomplish these tasks needed for the parallel execution of tasks, the necessity of a reliable compact and terabyte capacity memory is becoming almost mandatory.

To that effect, research to find means to store large amounts of information in small volumes, capable of large bandwidths and parallel access continues in many fronts and three-dimensional (3D) storage has the promise to provide a solution to these needs. Basic research and applied efforts that may lead to 3D information storage include mainly phase holograms[1,2] and two-photon processes.[3−9] This paper will be confined only to 3D storage by means of two-photon absorption and in particular is a review of our studies and result in the conception, design and construction of two-photon 3D terabyte storage devices.

To ensure a quantum jump in storage density and processing, the input−output speed must include parallel processing, which most probably means that an all-optical storage device must be advanced and utilized. In the case of two-photon 3D storage the density of information stored is dependent upon the reciprocal of the wavelength λ to the power of the dimension used to store information. For example, if the information is stored in one dimension, then the density is proportionally $1/\lambda$. This relationship also suggests that the information storage density is much higher at short, UV wavelengths than visible light. For example, the theoretical storage density for a 2D device that operates at 200 nm is 2.5×10^9 bits/cm^2, whereas for a similar 3D storage memory the density may be as high as 1.2×10^{14} bits/cm^3.

In the following sections we present the basic two-photon absorption mechanism and method for writing and retrieving information stored within the bulk of the device. In addition, a number of the materials and their relevant properties that are used as two photon 3D media are presented and the system(s) employed for storing Terabytes of data in a DVD-type disks described.

2. Two-Photon Mechanism

The theoretical bases for two-photon processes were established in the early 1930s.[10,11] The probability for a two-photon

* Corresponding author. Tel.: (949) 824-5934. Fax: (949) 824-2761. E-mail: pmrentze@uci.edu.

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Alexander S. Dvornikov graduated from Moscow State University, Russia, in 1976 and received his Ph.D. in physical chemistry from the Institute of Chemical Physics Academy of Sciences, Moscow, in 1983. He was a researcher at the Institute of Chemical Physics from 1976, where he studied the mechanism and kinetics of photochemical reactions of organic dyes and photochromic materials. He joined the staff of the University of California, Irvine in 1989. In 1995, he also joined Call/Recall, Inc., where he was a Head of Materials Division and VP, involved in developing 3-D optical memory technology. He has published over 100 research papers in scientific journals and books and holds several patents.

Edwin P. Walker received his Ph.D. in Optical Sciences from the University of Arizona in 1998. His work includes optical system design and prototyping, optical testing and system alignment, optical data storage, focus and tracking servo systems, deformable mirror system integration, design/tolerancing/ prototyping/integrating state of the art high performance optical systems. Recently he is working at Boeing as a Senior Optical Scientist/Engineer. He also performed 7 years of pioneering research and development on volumetric optical data storage systems and recording/ readout system integration with Call/Recall. He has over 20 publications in the optics area, 1 patent and some pending, including 1 book chapter published.

Peter M. Rentzepis received the Ph.D. degree in physics and chemistry from the University of Cambridge, U.K. He joined Bell Laboratories, Murray Hill, NJ, as a Member of the Technical Staff and later as Head of the Physical and Inorganic Chemistry Department. He was appointed Presidential Chair and Professor of Chemistry and Electrical Engineering and Computer Science at UCI in 1985. He is a Founder of Call/Recall Inc. He pioneered two-photon 3D optical storage and has published over 400 papers, 5 books, and has over 80 patents. Dr. Rentzepis has received several awards in chemistry and physics and is a member of several scientific societies including the U.S. National Academy of Sciences and of other countries.

transition to occur may be expressed as a function of three parameters: line profile, transition probability for all possible two-photon processes, and light intensity. These factors are related by

$$P_{if} \cong \frac{\gamma_{if}}{[\omega_{if} - \omega_1 - \omega_2 - v\cdot(k_1 + k_2)]^2 + (\gamma_{if}/2)^2}$$

$$\mathrm{X}\left|\sum_k \frac{R_{ik}\cdot e_1 \cdot R_{kf}\cdot e_2}{(\omega_{ki} - \omega_1 - k_1\cdot v)} + \frac{R_{ik}\cdot e_2 \cdot R_{kf}\cdot e_1}{(\omega_{ki} - \omega_2 - k_2\cdot v)}\right|^2 \cdot I_1 I_2$$

where γ_{if} is the spectral width; i, k, and f are the initial, intermediate, and final states, respectively; 1 and 2 refer to the two laser beams; R_{ik} and R_{kf} are matrix elements; I_1 and I_2 are the intensities of the two laser beams; k_1 and k_2 are wave vectors; e_1 and e_2 are polarization vectors; ω_{ki} is the center frequency; v is velocity; and P_{if} is the two-photon transition probability.

These two-photon transitions may also allow for the population of molecular levels that are forbidden for one-photon processes such as g → g and u → u in contrast to the g → u and u → g transitions that are allowed for one-photon processes. The first factor describes the spectral profile of a two-photon transition and corresponds to a single-photon transition at a center frequency with a homogeneous width γ_{if}. The second factor describes the transition probability for the two-photon transition. This second factor is the sum of products of matrix elements $R_{ik}R_{kf}$ for transitions between the initial state i and the intermediate molecular level k or between k and the final state f. Often a virtual level is introduced to describe the two-photon transition. The frequencies of ω_1 and ω_2 can be selected in such a way that the virtual level is close to a real molecular state. This greatly enhances the transition probability, and it is, therefore, sometimes advantageous to populate the final level E_f by means of two different energy photons with $\omega_1 + \omega_2 = (E_f - E_i)/h$ rather than by two equal photons. The third factor shows that the transition probability depends upon the product of the intensities I_1 and I_2. In the case where the photons are of the same wavelength, the transition probability depends upon I^2, it will therefore be advantageous to utilize short pulses that such as picosecond and femtosecond pulses.

Such a two-photon absorption process makes it possible to preferentially excite molecules inside a volume rather than the surface, which is the case for most storage devices. This is possible because the wavelength of each photon alone is longer, has less energy than the energy gap between the ground state and first allowed electronic level. However, if two photons collide simultaneously at any point within the volume of the storage media and the energy sum of the two laser photons is equal to or larger than the energy gap of the transition, then absorption will take place. It is also important to note that there is no real level at the wavelength of either beam; therefore, neither photon may be absorbed alone. When two such photons collide at a point within the volume, absorption occurs only at the place of pulse overlap. At the point where the two beams interact, the absorption induces a molecular change in structure

and in effect creates a new molecule that is distinct from the unexcited molecules. The two molecular structures, the original and the one created by the two-photon absorption, become the write and read forms of a 3D optical storage memory, respectively.

3. Writing and Reading in a 3D Format

A 3D memory provides several desirable properties that may not be found in today's electrooptic information storage devices:

1. Immense information storage capacity, $\sim 10^{13}$ bits/cm^3.
2. Random and parallel access.
3. Fast writing and reading rates (nanosecond range).
4. Small size and low cost.
5. Minimal cross talk between adjacent bits.
6. High reading sensitivity.

The operations that enable one to store, retrieve, and erase information within a 3D volume are:

1. Writing: information is recorded by two-photon absorption at any preselected place within the volume of the 3D medium.
2. Reading: information is retrieved from the memory in bit or parallel form.
3. Erasing: information recorded in any part of the memory may be erased and new information stored using the appropriate wavelength.

Currently, computer information is stored and read in the form of binary code. The two stages of the binary code: zero, 0, and one, 1, in our case they may be thought to be the photochemical changes that lead to two distinct structures of the particular molecular species used as the storage medium. An example is provided by the changes in molecular structure occurring in photochromic materials such as spiropyrans after the simultaneous absorption of two photons. The structure of a typical material used has two distinct forms: the write, closed form, and the read, open form. These two distinct forms provide the two states necessary for storage information in a binary format. Specifically, the original closed form designates zero, whereas the open form designates one.

To write information in a 3D device, the media are excited by two-photon absorption of either a 1064 nm photon and a 532 nm photon equivalent to one 355 nm photon or two 532 nm photons, corresponding to a 266 nm photon.

Figure 1b displays the energy level diagram along with the molecular structures of the write and read forms of one of the molecules that we used to store data. By using laser beams with the wavelengths, shown in Figure 1, and by translating the beam along the axes of the memory device, which may be in the form of a cube or a disk, Figure 1a, we store the data in the form of spots within the volume of the memory device. The information can be stored in a page 2D disk format with many disks stored next to each other within a memory volume. Excitation and storage may be achieved also by using one tightly focused beam inside the volume of the 3D device, Figure 1a.

A complication may arise from the presence of fluorescence from the excited, closed zero form which, if absorbed by adjacent molecules, would subsequently transform them to the read form and thus introduce cross talk between adjacent bits. To avoid such effects, molecules are chosen such that the write form neither absorbs the fluorescence wavelengths of the read form nor it emits fluorescence.

The read cycle operates in a manner similar to that for the write cycle except that the read form absorbs at longer wavelengths than the write form; therefore, the reading laser source wavelength is longer than the write. Following excitation of the written bits the fluorescence is detected by a photodiode

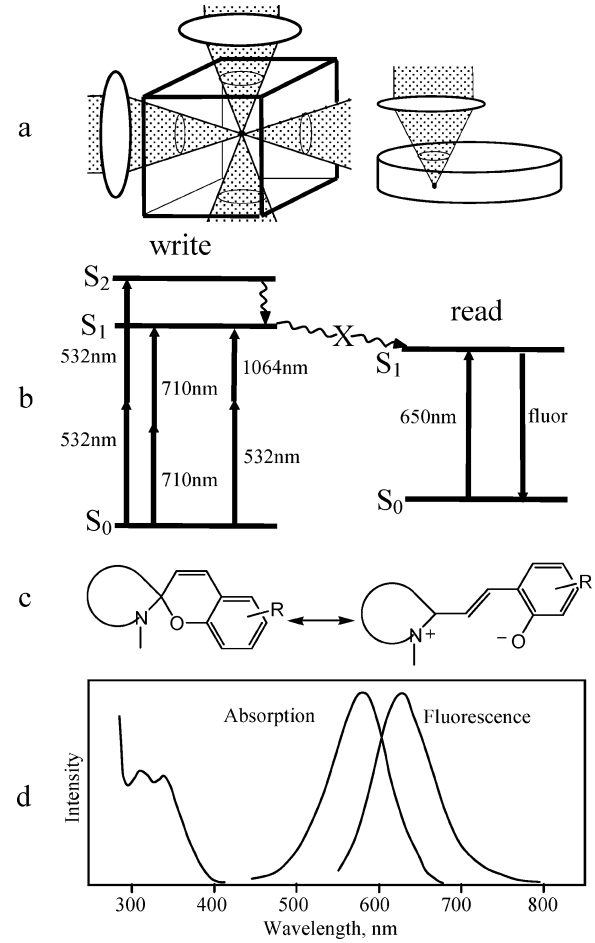
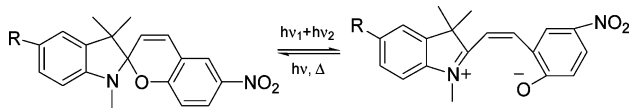


Figure 1. (a) Cube and disk storage devices. (b) Two-photon process schematic diagram. (c) Photochromic reaction, write and read forms. (d) Spectra of write and read forms.

array or charge-coupled device (CCD) and is processed as 1 in the binary code. The longer wavelengths of the reading light ensure that only the written molecules will absorb this radiation. Absorption of the two forms and the fluorescence spectrum of a written bit are shown in Figure 1d. Self-absorption of the fluorescence by adjacent written molecules does not affect the reading process because the largest segment of the fluorescence is emitted at longer wavelengths than the absorption band. Because reading is based on fluorescence, a zero background process, this method has the advantage of a high reading sensitivity. Light detection by means of photomultipliers or photodiode arrays makes possible single-photon detection measurements. The fluorescence was found to decay with ~ 5 ns lifetime, which in essence is the speed of the reading process.

Information can be stored not only at a bit at a time rate but also in a page format. Passing one beam of the written laser pulse through an SLM (Spatial Light Modulator) that contains the information to be stored in a 2D page format and image inside the cube where the plane of the other beam intersect it yields a two-photon process that results in the writing of a complete 2D page in the bulk of the cube or disk. In the case where the information of an entire page is to be accessed at once, rather than in a bit by bit mode, a single low intensity thin plane beam is used to illuminate the entire written 2D page to induce fluorescence by one photon process of the entire 2D page. The fluorescence is picked-up by a CCD and processed.

SCHEME 1



4. Materials

A vast number of molecules may be used as materials for 3D devices, including photochromic materials, phosphors, photoisomers, and semiconductors. One of the most important properties that a two-photon medium must have is high two-photon cross-section. Excellent progress has been made in this area by several researchers,[6,7,12−15] where very high two photon cross-section materials were designed and synthesized.

A few types of the molecules that have been used as 3 D storage media are described in the next section.

4.1. Spiropyrans. One of the first memory materials that we utilized for recording information in 3D format by two-photon absorption were photochromic spiropyrans (SP).[3,16] Spiropyran molecules may exist in two isomeric forms: cyclic spiro form A and open merocyanine form B, Scheme 1. Exposure of the colorless form A to UV light results in the heterolitic cleavage of the C−O bond followed by isomerization to the colored merocyanine from B. Typical absorption spectra of forms A and B and the fluorescence spectrum of form B are shown in Figure 1d.

The spiro form A that corresponds to zero in the binary code is stable; however, the written merocyanine form is thermally unstable and reverts back to the original form after a few hours at room temperature. The most direct and simplest means for stabilizing this structure is to lower the temperature below the −30 °C activation energy; however, low temperatures are not desirable for practical applications.

4.2. Reversible Dimerization of Polycyclic Aromatic Compounds. Other photochromic materials studied in our laboratories that show promise for use as 3D memory devices are dimers of polycyclic molecules such as anthracenes.[17]

The photodimers are formed by excitation of the corresponding monomers, and the dimers revert back to monomers when exposed to UV light, Figure 2. The dissociation of the dimer, write form, results in the regeneration of a conjugated double bond molecule that exhibits a red-shifted absorption band. The monomer, written form, has its long wavelength absorption band

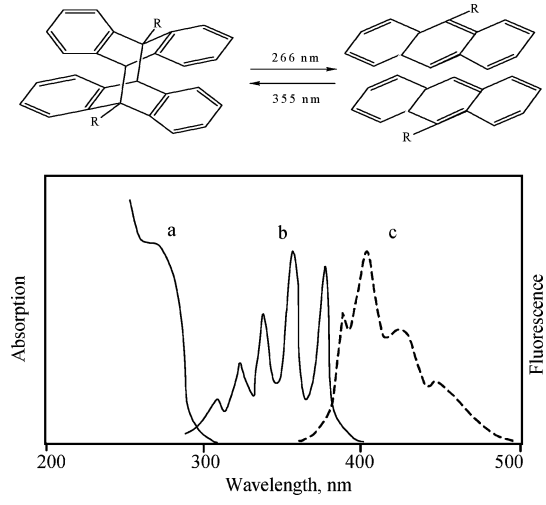
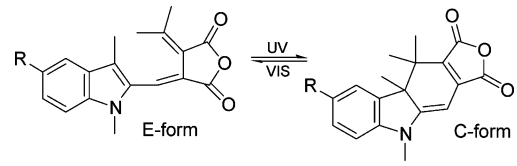


Figure 2. Reaction scheme and absorption spectra of (a) dimer, (b) monomer, and (c) fluorescence spectrum of anthracene monomer in PMMA.

SCHEME 2



in the 300−400 nm region, while the dimer is blue-shifted and has practically no absorption at wavelengths longer than 300 nm. The monomer, written form emits with a fluorescence quantum yield of 0.3, while the dimers are practically void of any fluorescence. Because both dimer and monomer forms are stable and possess the high absorption cross-section and high quantum efficiency for both dissociation of dimers and monomer fluorescence, this photochromic system is potentially attractive as media for 3D memory and other optical devices.

4.3. Fulgides and Fulgimides. Photochromic fulgides, a class of organic compounds known to be capable of reversible light induced change in their structure[18,19] are thermally stable in both forms and exhibit high photoreaction efficiency and high fatigue resistance to repeated writing−reading−erasing cycles. Photochromic fulgides are promising candidates for many technological applications including use in recording media, particularly in erasable 3D optical storage devices. However, because photochromic fulgides do not fluoresce in either form we synthesized the fluorescing fulgides, shown in Scheme 2, which undergoes reversible photoisomerization that generates the cyclic structure C that fluoresces,[20] Figure 3.

The absorption spectrum of the colored C form, Figure 3, is red-shifted by 130 nm compared to the open, E, form and in addition the C form exhibits a very low absorption in the region of 330−400 nm. Because of the significant Stokes shift of the spectra, we were able to convert the open form, almost quantitatively, into the cyclic, closed, colored form by light excitation at 350 nm. The colored form can be reversed to the open form by excitation at ∼500 nm. During the photoinduced process, only the formation of the E form was observed, which is the preferred configuration for the cyclization process. The coloration/bleaching cycles that correspond to the write and read forms can be repeated many times without noticeable decomposition of the material, Figure 4.

All isomeric forms of these 2-indolylfulgides show excellent long-term, room temperature, thermal stability. In contrast to other previously investigated fulgides, the colored, read form C, of the 2-indolylfulgides emits a broad-band fluorescence with maximum intensity at about 610 nm, Figure 3. The fluorescence spectrum is Stokes shifted by approximately 100 nm from the absorption. No fluorescence from the E form was detected.

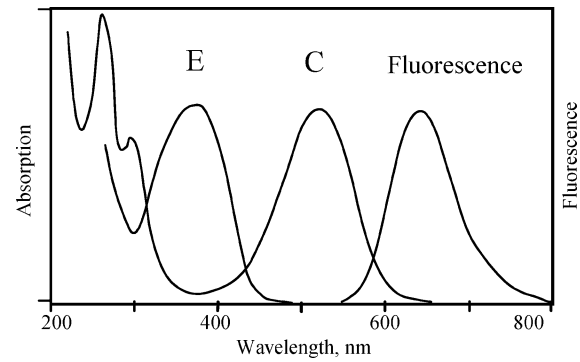


Figure 3. Absorption and fluorescence spectra of isomeric forms of 2-indolylfulgide.

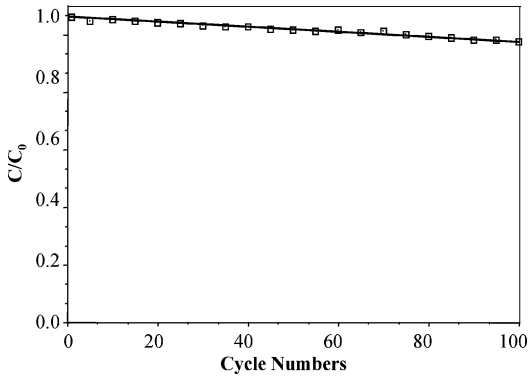
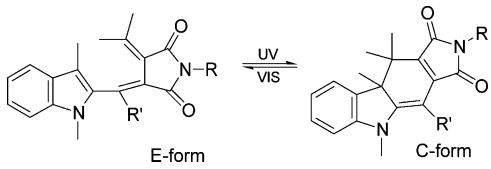
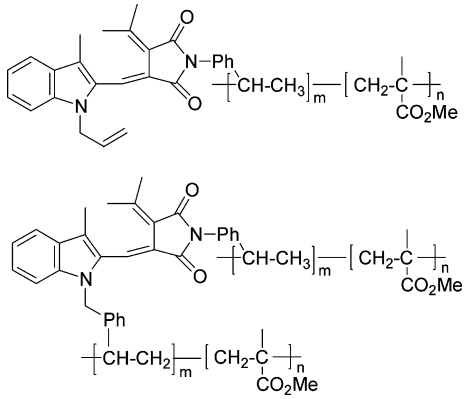


Figure 4. Fatigue resistance of 2-indolylfulgides to repeated coloration/bleaching cycles.

SCHEME 3



SCHEME 4



Not only do fulgimides,[21] Scheme 3, which are derivatives of fulgides, exhibit the excellent photochromic properties of their precursor fulgides, but in contrast to fulgides, they are also chemically stable to acid or base-catalyzed hydrolysis. In addition, a very attractive aspect of these fulgimides is that the introduction of various substituents at the nitrogen atom position of the imide ring can be used as a linking group to prepare photochromic copolymers, photochromic liquid crystals, photoregulated binding of proteins, and photochromic Langmuir–Blodgett films.[22−25]

4.4. Photochromic Copolymers. For molecules to be suitable as storage media they must be uniformly dispersed in a polymer matrix at relatively high concentration $\sim 10^{-1}$ M. A desirable means to achieve uniform dispersion and high concentration of the storage media is to form a photochromic cross-linked copolymer. We have synthesized such copolymers by copolymerization of the photochromic molecule and the corresponding monomer.[26] To this effect, we polymerized methyl methacrylate monomer and the photochromic 2-indolylfulgimides containing groups capable to copolymerization and formed the optically clear photochromic cross-linked copolymer, shown in Scheme 4.

These copolymers were found to be photochromic and exhibit photoinduced reversible transformation from the write to read form, and the written bits emitted intense fluorescence. Similar to the case for the colored forms of the pure fulgimides, we also determined that the efficiency of the write/read cycle in the copolymer was essentially the same as for unpolymerized fulgimide molecule in solution.

4.5. Nondestructive Readout Molecular Memory. There is a common problem associated with rewritable optical memory materials: destructive readout. In most if not all photochromic molecules proposed so far, the read and erase states have the same absorption band; therefore, some erasing, while reading, is unavoidable. This is expected because the vast majority of photochemical reactions and the onset of emission, in condense media, proceed from the same lowest electronic-excited state of the molecule.

Several reviews[6,7,27−30] have described materials to be used for 3D storage applications and a number of papers are found in the literature that describe means for overcoming destructive optical readout. One approach suggests that the written information may be accessed by the detection of the changes in refractive index[31] or IR spectra[32] of the material. The advantage of this approach is that the photons used to induce index or IR changes are not sufficiently energetic to initiate the erasing process. However, the absorption cross-section of these processes is small and also most polymer matrices absorb in the IR region. In addition, index change detection in such systems and volumetric storage may be rather expensive and complicated, which might render them impractical. Another approach invokes the stabilization of the "read" form by reaction with an acid or a base.[33] Because such bimolecular reactions are diffusion controlled, they are very slow and perhaps they may be used in liquid media, but rather improbable for commercial solid-state optical devices. Two methods have been advanced that are capable of reading information with very small amount of erasing. The first relies on accessing the information by illuminating chromophoric materials at the long wavelength tail of their "read" form absorption band and detecting the induced fluorescence.[34] Because of the low absorption cross-section at this spectral region only a small amount of the stored data is erased; however, such weak absorption also induces a proportionally very weak fluorescence readout signal and consequently a very low readout performance. The second method[35,36] is based on modulation of the fluorescence or phosphorescence intensity emitted by the storage material. Excitation at the region where this material has very small absorption intensity may be used to induce fluorescence and thus access the information stored. As in the previous case, at these wavelengths where the absorption is weak, the photochemical reactions are also less efficient; therefore, readout causes very little erasing. However, the reading signal is also very weak since both processes operate on the same wavelength of the absorption band. Alternatively, employing phosphorescence as the readout signal may have the same disadvantages, plus a slow access rate because of the slow triplet singlet radiative transition rate and the need to maintain an oxygen free device.

To avoid this generally occurring destructive readout process, we have designed and synthesized a molecule that has the absorption bands of its write, read, and erase forms distinct and well separated from each other. This molecule was synthesized by chemically bonding benzophenoxazin dye and *N*-(4-aminophenyl)fulgimide. We have shown that this new molecule fulfills all the chemical, optical, and performance requirements imposed to rewritable optical storage devices with nondestructive readout.

This material that we synthesized consists of two chemically bonded components. One of the two components, referred to as the "driver", is photochromic and may be reversibly

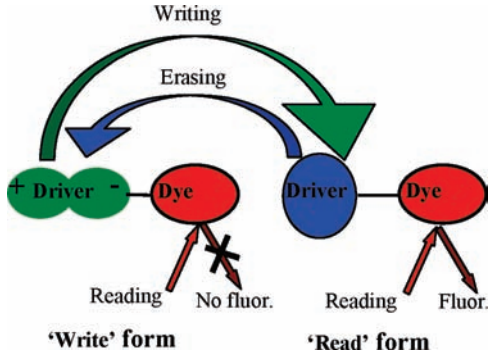
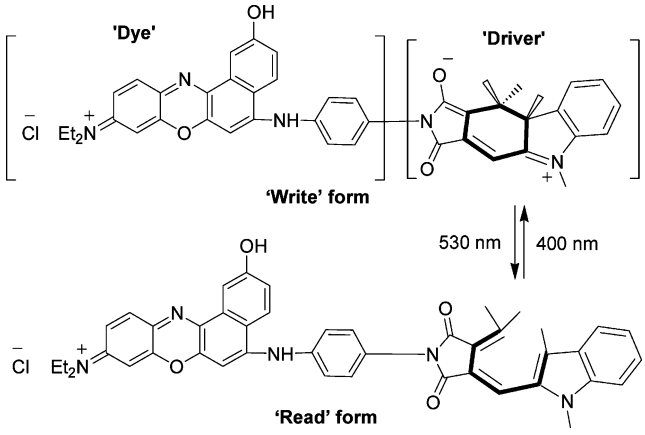


Figure 5. Schematic representation of the W/R/E processes with nondestructive readout.

SCHEME 5



transformed to the other isomeric form structure. Both photoisomeric forms of the "driver" are temperature stable and can be transformed from one to another only by excitation at their respective absorption bands, which are well separated from each other.

The second component, referred to as the "dye", is an intensely fluorescing molecule, whose emission quantum yield may be drastically altered by the structure of the attached "driver". The general concept of this molecule and its operation is shown schematically in Figure 5.

The "dye" component, which is chemically bonded to the "driver", has an intense absorption band at longer wavelengths than the "write" or "read" forms; therefore, no erasing occurs during the reading process. For this concept to work, the "dye" moiety must emit fluorescence only when the "driver" component is in either the polar or nonpolar form. Any of the stored data bits may be erased and revert to the original "write" form by illumination of the written form. The structure of the write and read no erase form designated, their photoreactions and the wavelengths used are shown in Scheme 5.

Figure 6 shows the absorption and fluorescence spectra of the "write" and "read" forms. The absorption spectrum of the molecule is a superposition of the "driver" and "dye" moieties absorption spectra. The photoreactions and spectral changes taking place in the "driver" are identical to those found in pure fulgimides. The 660 nm absorption band of the "dye" moiety remains unchanged; however, as mentioned previously, the fluorescence intensity depends strongly on the "driver" structure, reaching a quantum yield of 0.2 when the "driver" is in the open form and the molecule is uniformly dispersed in poly(methyl methacrylate) (PMMA).

This molecular memory was designed to have the fluorescence inducing wavelength, in the attached "dye" moiety, at a

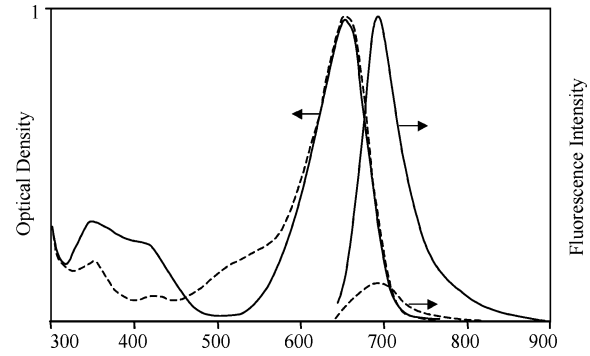


Figure 6. Absorption and fluorescence spectra of the composite molecule: solid line, "read"form; dashed line, "write" form.

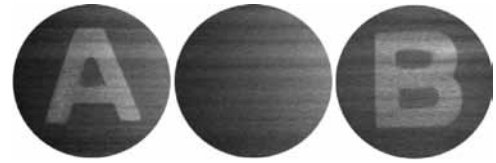


Figure 7. Written, erased, and rewritten images in composite molecule/PMMA disk.

wavelength longer than for the first excited electronic level of the "driver". This arrangement assures that no photochemical reaction occurs while reading, rendering the readout process completely nondestructive.

Figure 7 shows an image stored in this molecular memory. The stored image was read over 10^6 times by illumination with 660 nm light and no noticeable decrease in the intensity of the signal was observed. This provided unequivocal proof that the readout is indeed nondestructive. However, the stored information was easily erased by illumination with 400 nm light and subsequently new information could be stored in the erased molecules, bits, by excitation with 530 nm light. Temperature fatigue experiments and accelerated tests suggest that the information stored remains intact for very long periods of time, years, at room temperature.

4.6. WORM Materials. For archival applications where large amounts of data are to be stored and read, but not erased, WORM (Write Once Read Many) media, we have utilized a photoacid generator (PAG) and a dye precursor (DP).[37,38] Both are uniformly dispersed in a polymer host such as polymethyl methacrylate (PMMA) and a very small amount of plastisizers were added to improve the optical and write/read characteristics of the storage media. The PAGs used are light sensitive compounds that are thermally stable; however, 532 nm two-photon excitation initiates a photochemical reaction that generates acid. The photogenerated acid reacts with DP forming strongly fluorescing dye. These WORM materials are shown schematically in Figure 8.

The "write", zero form of the WORM material is composed of a colorless dye precursor and PAG molecules uniformly dispersed in a transparent polymer matrix such as PMAA and molded in the form of a 120 mm diameter × 2 mm thick disk. The PAG molecules absorb below 400 nm and the "write" form were formed to be thermally stable and can be stored in the dark for years without any change in their properties. Two-photon excitation of the "write" form generates colored spots (bits) of the "read" form, inside the volume of the disk where the laser beam was focused. The "read" form absorbs at the 630−650 nm region and emits intense fluorescence, when excited with 630−650 nm light. The "read" form is also thermally stable and may be stored for years without noticeable

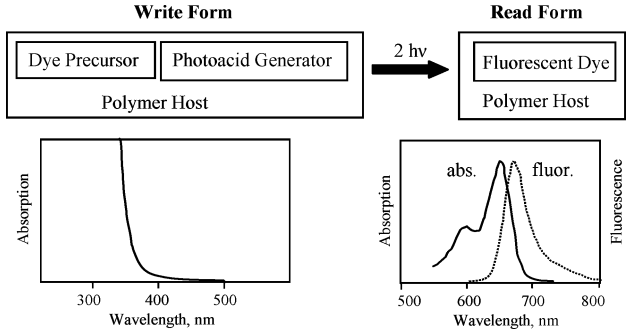


Figure 8. WORM materials composition and absorption and fluorescence spectra of "write" and "read" forms.

decay, or need for refreshing, as is the case for many tape storage devices. We determined that more than 10^6 times readout cycles could be performed without noticeable decrease in the fluorescence signal strength.

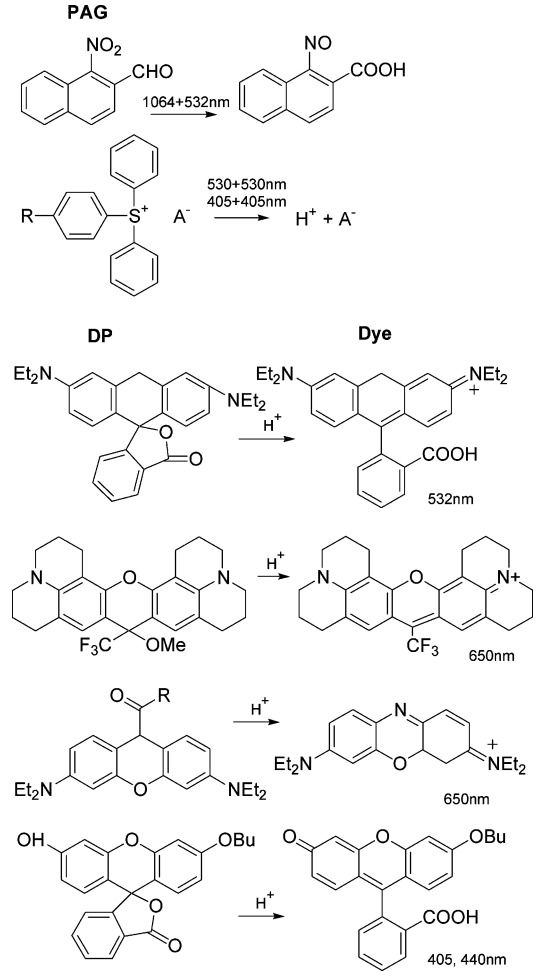
A variety of dye precursors and acid generators exist, however, to be suitable for as two-photon 3D memory media, the molecules must possess the following characteristics:

1. The photoproccesses that generates the acid must have a high quantum efficiency.
2. Both the write and read forms of the 3D media should have a long-term, years, stability at room temperature.
3. The written form should be a light stable, strongly fluorescing molecule that can sustain its fluorescence efficiency without degradation for at least 10^6 reading cycles.
4. The material should be highly soluble in monomers and the corresponding polymer hosts.
5. The absorption spectrum of the acid generator should have high absorption cross section in the accessible two photon wavelength, for example, 532 nm (SHG) pulses from Nd:YAG laser, which are the wavelengths that we employed for 3D volume writing.

We have used several photoacid generators, to assist in the writing process of WORM devices, including onium salts such as commercially available triarylsulfonium salts and others specially designed and synthesized in our laboratory. Several dye precursors that generate Rhodamine and Oxazine type fluorescent dyes have been also used by us and in addition we have developed new ones with practically optimum properties. The structures and spectroscopic characteristics of some PAGs and DPs molecules used as WORM media are shown in Scheme 6.

4.7. WORM Disk Fabrication. To fabricate the WORM disk in the laboratory, the PAG and DP molecules were dissolved in methyl methacrylate monomer and the solution was filtered through 0.02 mm filter to remove solid particles. The filtered solution was then placed into a specially designed polymerization cell, the dissolved oxygen was removed by bubbling argon or applying vacuum. The cell was thereafter sealed and placed in a thermal bath for polymerization at a temperature that yields a high quality polymer disk without bubbles or imperfections. After polymerization was completed, the polymer bulk that contained the storage media was shaped to a disk and polished to optical quality. Because polishing is very time-consuming and mass production requires a molding process, we have also designed special molds for compression molding to fabricate disk that do not require post fabricating polishing. We have made several disks that were utilized for two-photon 3D optical storage that vary in size from 25 to 120 mm diameter and 2 to 10 mm thickness. The disk fabrication compounds are shown in Figure 9.

SCHEME 6



5. Systems

5.1. Two-Beam Recording. The earlier experimental systems that we utilized for writing and reading information in 3D format implemented the orthogonal beam scheme where two laser beams intersected each inside the volume of the memory device.[39,40] The typical experimental system is shown in Figure 10. The recording was performed by two-photon absorption of 1064 and 532 nm beams to generate the equivalent of a 355 nm pulse that excites the spiropyran molecule to the first excited singlet state that subsequently decays to form the open, written form.

The procedure used to access the information that is written within the volume of the memory is similar to the write process, except that the excitation wavelength of the read form is longer than of the write form and after excitation the molecule fluoresces with a lifetime of ~5 ns. Because the fluorescence spectrum is located at longer wavelengths than the absorption

Figure 9. Polymerization cell, compression mold, and fabricated WORM disk.

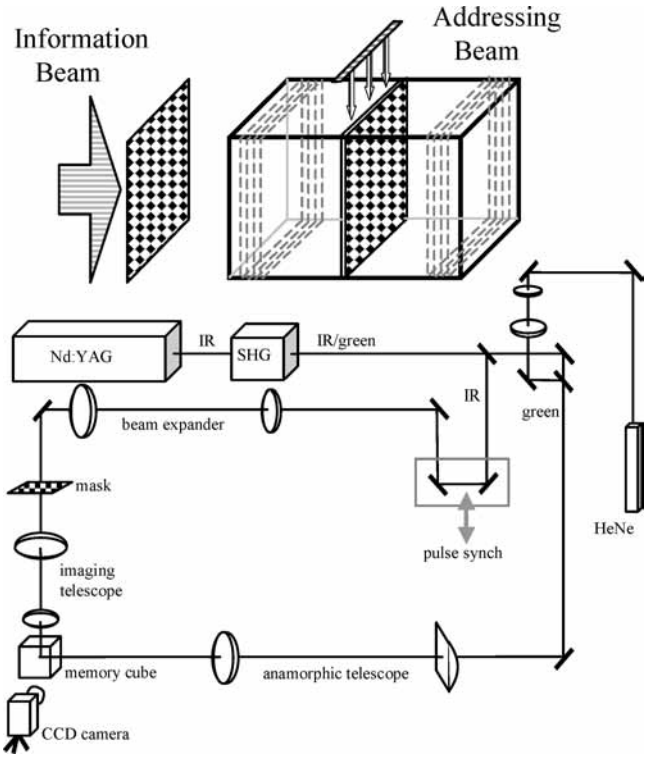


Figure 10. Two-beam recording system.

of either the write or read forms, the emission is not absorbed by the 3D media but is detected by an array of photodiodes or a charge coupled device (CCD) and processed as 1 in the binary code. Because the reading is based on fluorescence, a zero background process, this method has the advantage of a high reading sensitivity. Extremely low-level fluorescence measurements are possible by the use of photomultipliers or charge coupled devices, which are capable of single photon detection and very low background noise.

Figure 10 shows the optical system used to store two-dimensional plane inside the 3D cube storage device. The 1064 and 532 nm beams were emitted by a 35 ps, 20 Hz Nd:YAG laser. The 1064 nm was expanded and collimated to a 24 mm diameter beam and used as the information-carrying beam that passed through a spatial light modulator (SLM) that contained the information to be stored and be stored into a predetermined location within the volume of the memory device. The second harmonic 532 nm addressing beam was separated from the 1064 nm beam by a dichroic mirror, expanded by a negative cylindrical lens, and focused by a spherical lens onto the 1064 nm information carrying beam. The optical path lengths were adjusted to synchronize the arrival of both information and addressing beams at the same time at a preselected place within the memory cube.

The writing process was automated, and it was possible to store multiple data pages in the volume of the memory device. The memory, SLM, and imaging lens were mounted on motor driven linear stages, and custom software controlled the exposure time of the laser shutter, the position of the addressing beam inside the cube, and the imaging lens stage that adjusted automatically the focus at different planes within the memory.

A critical component of two-photon memories are the lasers that should emit high peak power pulsed beams for recording and low power CW beam for readout illumination. The readout laser represents less of a challenge, its requirements of moderate CW power, good mode and wavefront quality, low cost, and compact size are already met by small inexpensive laser diodes. The recording beams are more problematic, because of their stricter requirements:

1. High peak power, because the two-photon absorption probability is proportional to the square of the intensity. Short pulse laser systems, picosecond and femtosecond, provide the most efficient means for high power. The use of short pulses has a further advantage in that the optical damage intensity threshold increases approximately as the square root of the decrease in pulsewidth.

2. Their wavelengths must be matched to the storage media absorption. This generally implies that the sum of their photon energies be equal to or higher than the energy gap between the ground and the first allowed excited state.

In our experiments we, initially, used 35 ps, 20 Hz repetition-rate, mode-locked Nd:YAG laser systems. Recordings have also been demonstrated using a Ti:sapphire regenerative amplifier system providing 100 fs, 1 μJ pulses at a 76 MHz repetition-rate, and lately by a diode laser.

An important issue during recording and reading is the surface quality of the memory devices, disks, or cubes. Scratches and digs in the surface lead to scattering and "shadowing" of the addressing beam. These imperfections can also dramatically lower the effective optical damage threshold by causing local increases at the electric field distribution of the high intensity writing pulses. As mentioned previously, a high degree wavefront quality must be maintained to achieve high resolution imaging. For diffraction-limited imaging, the surface through which the data plane image and addressing beams enter must be flat to within a quarter wavelength. This is especially important in recording, since the first effect of aberration on the data plane image is a lowering of the peak intensity. Indeed, even a diffraction limited spot (e.g., an Airy disk with $\lambda/4$ aberration) has only 68% of the input beam's energy within its central disk. If the aberration is increased to $\lambda/2$, this number drops to 40%, and since the recording efficiency is proportional to the square of the intensity, it becomes evident that optical aberration has significant negative impact on the performance of the storage device.[40]

5.2. Single Beam Recording and Reading. Single beam two-photon recoding, which has been used to store 1 Terabyte in a DVD type of disk, also utilizes two-photon absorption, but from one focused beam.[38] This recording system resembles the 2D systems used by the storage industry, where two-photon absorption is achieved only at focal point, where the intensity is sufficiently high to induce a two-photon absorption process. Because this system uses only one beam and does not require spatial and temporal alignment of the short pulses, the optical alignment is relatively simple. Also the high repetition rate recording does not require use of large scale SLM for high-speed recording; however, it records one bit at a time, rather than a complete plane, disk. Parallel recording of several bits is achieved by splitting the recording beam into several parts and focusing them by an array of lenses.

When only one laser beam is used for two-photon recording, the recording location inside the media is controlled by the laser beam irradiance profile. The two-photon recording efficiency is scaled with the square of local laser irradiance (intensity). Because of this nonlinear response and sharp changing irradiance along a focusing beam, recording takes place only within a small volume around the focus of the laser beam. Figure 11 shows a schematic of our single-beam two-photon recording system. The system also includes a readout path and detector for evaluation of the recorded data.

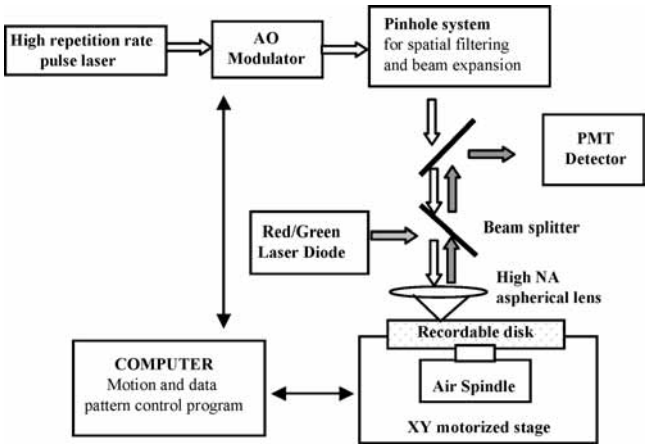


Figure 11. Single-beam two-photon recording system diagram.

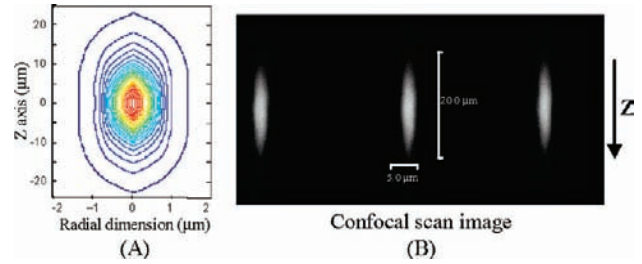


Figure 12. Estimated (A) and recorded (B) fluorescence bit shape along the recording depth (Z) by single-beam two-photon recording.

With a sharply focused beam, the two-photon absorption and consequently the recording efficiency drops very quickly along the depth from the center of the beam focus. The decreasing of the recording efficiency is closely scaled with the fourth order of the distance from the focus point and the shape of recorded fluorescence bit can be estimated by calculating the square of laser irradiance (intensity) distribution. Figure 12A shows a calculated irradiance (intensity) squared contour plot at the focus of the beam with 5% contour value step, based on a 0.32 NA (Numerical Aperture) and 710 nm TEM00 laser beam. Figure 12B shows a scanned fluorescence image of the bits recorded under the same conditions. The image is scanned along the recording depth (*Z*) using a confocal microscope. It appears that the fluorescent spots recorded with single-beam, two-photon process, have a long depth along the recording beam axis. This fluorescent spot depth is the dominant limiting factor for how close the layers can be recorded together without significant interlayer crosstalk. One means for shortening the depth of the fluorescent spots is to use higher NA (Numerical Aperture) optics in the recording system.

Typically, information is stored in our disks in data tracks that form a recorded data layer as on a conventional CD. However, in contrast to a CD, many data layers are closely packed together in our storage approach. Figure 13 shows typical confocal scanned images of data tracks within one layer and multiple layers along the depth. To resolve a written spot on a given track at a given layer, the readout optics and servo must be properly designed.

The recorded spots fluoresce when excited with the readout diode laser beam and, as expected, the fluorescence wavelength is Stoke's shifted from the read form absorption wavelength. We have designed synthesized and used several media whose absorption and emission can be tuned to match the wavelength of various lasers. The written spots can be excited by single or two-photon absorption; however, we use single photon because

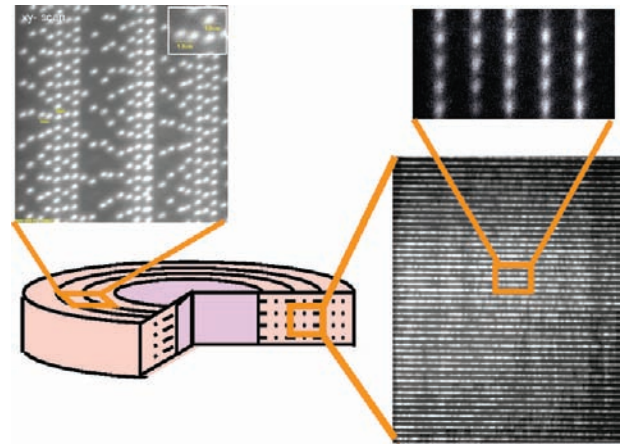


Figure 13. Multiple layers of data stored in the 3D memory disk.

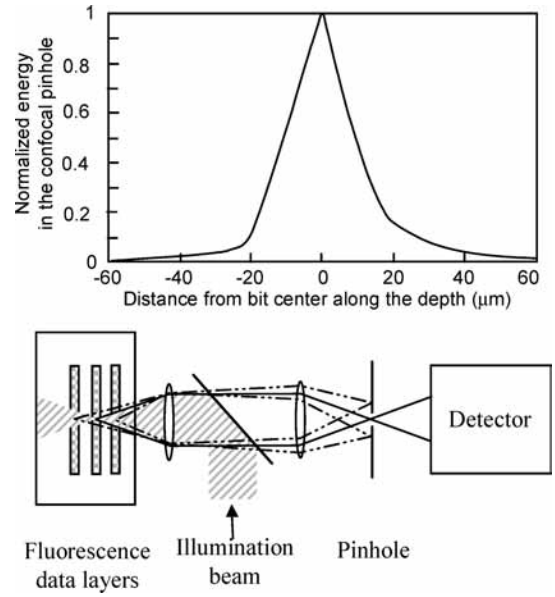


Figure 14. Confocal pinhole in the collinear readout system used to decrease layer crosstalk.

of its very high single photon absorption cross-section, low power, low cost, and the fact that compact diode lasers may be used for readout.

5.3. Signal Quality in Single Channel Collinear Readout. One simple approach to readout is the single channel collinear readout where the readout laser beam is focused into a data track and the fluorescent signal is collected by the same lens. By reading out single tone and random data patterns, we have experimentally measured over 40 dB CNR (Carrier to Noise Ratio) and better than 10^{-5} BER (Bit Error Rate) without ECC (Error Correction Coding).[41]

When we store many layers in one disk and access the fluorescence signal by the collinear readout method using a large detection window PMT, as shown in Figure 14, crosstalk between layers need to be considered as well. We find that the confocal architecture is an effective way to decrease this crosstalk. However, the pinhole used in our system might not be necessary for small aperture detectors, especially when the size of the detection window is close to the image size of the fluorescent spots. Figure 14 shows an estimated effect of the pinhole on decreasing interlayer crosstalk. The curve indicates that a 10 μm pinhole placed at a 1:2 image system could block over 90% of fluorescence coming from adjacent data layers, which are 30 μm away from the focus location of the

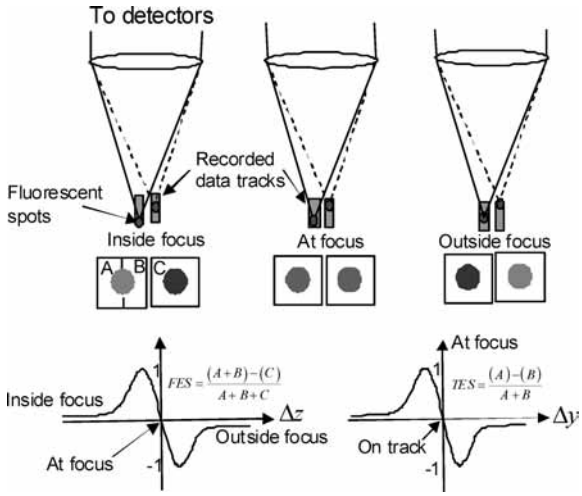


Figure 15. Schematic of focusing and error signal generation.

objective lens. In addition, this confocal architecture also prevents spurious background noise from impinging on the detector.

5.4. Tracking and Focusing Servo for Fluorescence Data Track. Nonreflective fluorescent media layers enable multilayer readout. This also brings a unique challenge for the servo control of the objective lens. The standard servo error signal generation techniques that use spot shape features and groove structures (i.e., astigmatic focus, and push−pull tracking[42]) are difficult to implement for this new type of fluorescent media. One solution is to servo the data tracks based on the readout signal strength variations in a push−pull focusing and a push−pull tracking structure shown in Figure 15.

The lateral (radial) dimension and longitudinal (depth direction) dimension of the recorded bit depend upon the recording optics. The fluorescent spot shape and power level changes more slowly in the focus direction due to the longitudinal dimension of the recorded mark. Two fluorescent spots are used to generate the FES (Focus Error Signal) and to drive the actuator countering the defocus. The two illumination spots (shown in Figure 15) are slightly defocused from each other, straddling the middle of the recorded tracks. The fluorescent light is collected into two detectors. When the objective lens is in focus, the same amount of fluorescent power is incident upon both detector #1 and detector #2. However, when the lens is "inside focus", the fluorescent power level on detector #1 is reduced relative to the fluorescent power level on detector #2. The situation is reversed when the lens is "outside focus". The FES is obtained by subtracting the two individual detector signals. The associated focus servo electronics control the current in the voice-coil actuator to maintain the power balance between the detectors. A similar approach is used to generate tracking error signal (TES), where the left and right halves of the bicell detector #1 are subtracted. When the lens is on track, the power levels on the two halves of detector #1 are equal, and the levels become unbalanced when the lens moves off track. The actuator drives the lens one way or the other based on the detector signal variation to maintain focusing and tracking.

5.5. Two-Dimensional Parallel Readout. One of the main advantages when using two-photon induced fluorescence media is that the readout could be performed in parallel not only from the same layer but also from multiple layers along the depth. This is because the recorded spots are not reflective for the readout beam and the media does not exhibit noticeable index change after recording. This prevents significant distortion of the readout laser beam phase front when traveling through the multiple recorded layers. Shaping and directing the readout beam differently make several optical system architectures possible for two-dimensional parallel readout. Those architectures include focusing the readout beam from the curve side or the top side of disk. In all the cases multiple fluorescing data bits can be imaged into a detector array for parallel readout thus considerably increasing readout data rate.

Two-dimensional readout, however, also brings challenges to the readout optics, detector array, data formatting, and data processing. It requires the optics for the readout laser beam to maintain a long depth of focus with a small beam waist at the focus, so that a large number of desired data bits can be illuminated simultaneously while only a small amount of crosstalk is generated from adjacent unwanted bits. Requirements for a uniform performance across different media depths and for a large field of view also complicate the imaging optical system design. However, parallel readout schemes when applied judiciously to two-photon recordable fluorescent multilayer disk media should considerably increase the data transfer rates and approach 1 Gbits/s.

5.6. 1 TB Recording. Figure 16 shows our single-beam two-photon recording and one-photon readout spin-stand system that enabled us to record 1 TB in DVD type disk.[38,41] The layout is a typical optical head arrangement that facilitates further evolution into a portable prototype of a TB class WORM data storage system. For the TB recording presented here we have use a HighQLaser system Picotrain series 532 nm Nd:vanadate laser, which emits pulses with 6.5 ps pulse width, ~7 nJ/pulse energy at a repetition rate of 75 MHz. An Isomet Acousto-Optic modulator was used for modulating the 532 nm recording laser while an automated computer program controls the tracking/layer addressing, objective lens movements, and motor speed control. The recording laser beam passes through a beam expander on its way to the objective lens assembly that focuses the recoding laser on the media inside the volume of the spinning disk where the data is recorded. To spin our storage disks at high and constant speeds, we used a Seagull high precision air-bearing spindle, Chiba motor and standard optical disk motor. After recording, to access the 1 TB data a 635 nm CW BlueSky circulaser diode operating at <0.5 mW is used to induce fluorescence, by a one-photon process, from the recorded data bits. The fluorescence is then picked up by the same objective lens and focused onto a detector such as a Hamamatsu R7400U PMT, with a 25 μm confocal pinhole that is used to decrease layer and tracking crosstalk from adjacent tracks and layers.

5.7. Liquid Immersion Lens. To store terabytes of information, we need to record hundreds of layers within the volume of the disk. The usual objective lenses could not perform this task adequately; therefore, we designed and utilized a novel type of objective lens that consist of a liquid immersion singlet (LIS) where the liquid is contained in a thin polyurethane membrane that is in contact with the lens on one side and with the spinning disk on the other, Figure 17. This lens has a numerical aperture NA = 1.0 at a working distance of 1.2 mm. The volume of the liquid is adjusted such that it allows access to inside layers of the disk volume without any change in spherical aberration. Using this 1.0 NA LIS lens integrated into an automated recording test stand, we were able to fully record 1 TB of test patterns in a 120 mm diameter, 1.2 mm thick disk having a track pitch of 0.8 μm and layer spacing of 5 μm. This is the first time, to our knowledge, that a two-photon 3D disk, or any other type of removable disk has been fully recorded and reported, especially at such high, TB, bit density.

The fully recorded 1 TB disk was achieved using 7 nJ/bit with the 1.0 NA objective lens. Note that each of the 200 layers in the 1 TB recording has the equivalent capacity of a 5 GB DVD.

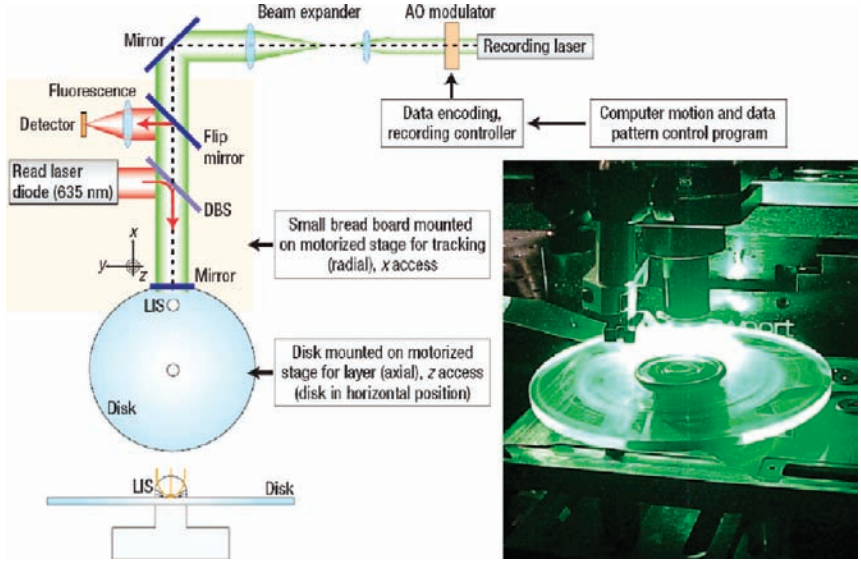


Figure 16. Experimental system used for recording 1 TB in a DVD size disk.

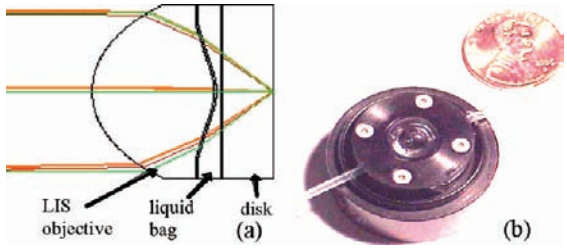


Figure 17. (a) Zemax layout of liquid immersion singlet (LIS) objective lens. (b) Assembled LIS in prototype opto-mechanical package.

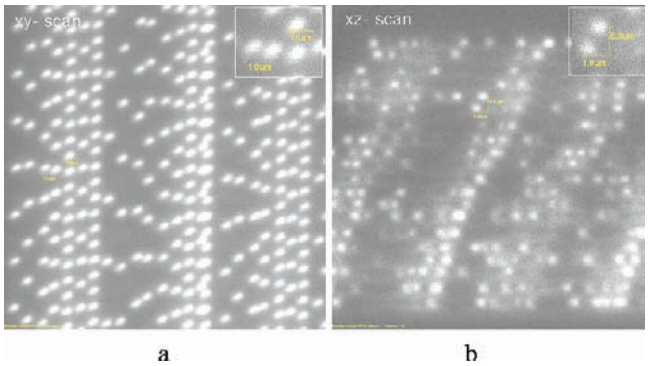


Figure 18. (a) Typical *xy* confocal microscope scan throughout different layers and (b) *xz* confocal microscope scan of ~30 layers. Track pitch of 0.8 μm and layer spacing of 5 μm recorded in the 120 mm diameter disk recorded at 7 nJ/bit from a single pulse of a 75 MHz repetition rate laser.

Typical *xy* confocal microscope scans of test tracks recorded in the 1TB 120 mm diameter 1.2 mm thick disk at a recording data rate of 5 Mbit/s are shown in Figure 18. The data recorded is a series of single tone pulse position modulated, ppm, test track patterns at a recording energy of 7 nJ/bit. Figure 18b shows a typical *xz* confocal microscope scan of ~20 layers separated by 5 μm. Higher single channel data rates of 25−100 Mbit/s are possible, which allows us to record data bits with a single pulse from the 75 MHz HighQLaser system.

The readout signal quality of the test patterns were found to have a CNR of 30−34 dB measured at 3 kHz. The readout signal quality is expected to be improved by constructing LIS lenses that are specially designed for the 635 nm diode laser rather than 532 nm.

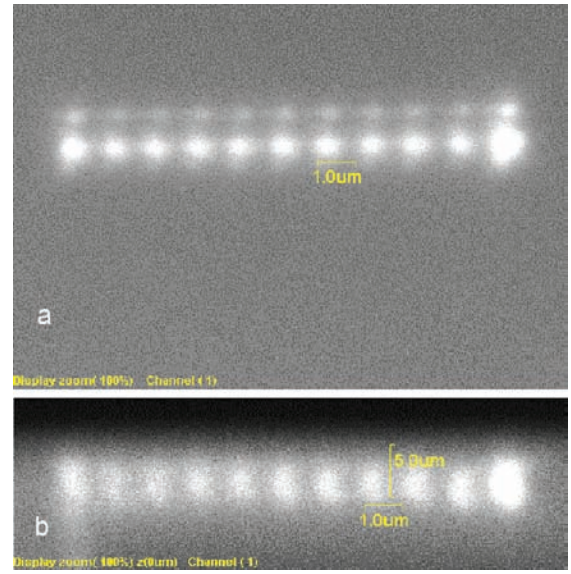


Figure 19. Confocal images of bits recorded with the 532 HighQ laser system with 20 mW of average power, the energy/bit is ~250 pJ, (a) *xy* scan and (b).

Figure 19 shows confocal images of bits recorded with the 532 HighQ laser system with 20 mW of average power; the energy/bit is ~250 pJ or a ~20× improvement from the 7 nJ full output pulse energy with 450 mW average power. This improvement in sensitivity opens the possibilities of testing at recording data rates beyond the repetition rate of this type of laser system; if an array type of modulator is employed, achievable data rates will increase from 75 MHz, 75 Mb/s to 1.5 GHz, 1.5 Gb/s. The bit dimensions will be the same as that obtained in the 1 TB recorded disk.

5.8. Two-Photon Recording with Diode Lasers. The ultimate aim of recording and accessing data with small, inexpensive laser diodes was implemented by utilizing Nichia 405 nm laser diodes to store information inside the volume of our two-photon disks.[38] A standard laser diode driver was used to modulate the 405 nm Nichia laser diode that is controlled by a standard LabView interface. To test recordings with the 405 nm Nichia laser diode, the experimental setup was adjusted by modifying slightly the divergence angle of collimation of the 405 nm laser beam incident on the LIS objective lens to compensate for the spherochromatism of the LIS, which is

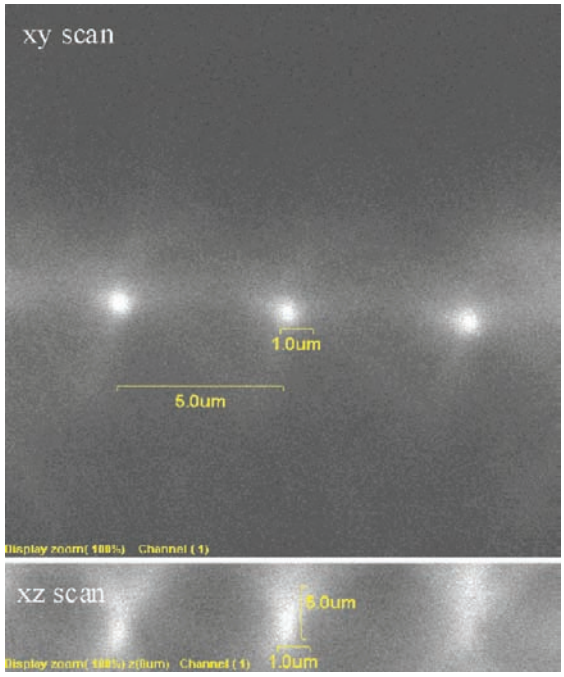


Figure 20. Confocal *xy* and *xz* scans of 405 nm laser diode recordings showing 0.5 μm lateral resolution.

designed for 532 nm. Figure 20 shows the confocal *xy* and *xz* scans of bits, recorded using a Nichia 405 nm laser diode, 12 mW of peak power at the lens, with 0.5 μm lateral resolution as expected from diffraction limit, $1.22\lambda/\mathrm{NA} = 0.494$ μm for 405 nm laser and NA = 1 lens. Using the 1TB system with the 405 nm Nichia laser diode instead of the 532 nm laser enables us to record at Blu-Ray layer densities rather than DVD layer densities that effectively increases the capacity of our disk to the 5 TB level.

6. Conclusion

We have presented the method, materials, and systems for 3D storage by means of two-photon absorption. Storage of entire GB disks in the form of planes inside the 3D volume of a cube was described. Also, the storage by two-photon absorption of hundreds of GB portable DVD size of disk using a focused beam was demonstrated and shown that we can access the information by single photon absorption of light emitted from a He/Ne or diode laser. Also, the very first full optical disk recording of 1 TB was shown to be accomplished by illuminating our novel two-photon 3-d optical data storage materials with 7 nJ/bit laser light. Further improvements in material sensitivities have shown that we can record a bit with 250 pJ. This feat enables us to use alternative recording laser formats that impact achievable recording data rates in the 1 Gb/s range. Recordings with 405 nm laser diodes that have a more desirable size, cost and power characteristics for commercial devices are now being used by us in two-photon high density recording experiments. With the capability of recording with 405 nm laser diodes these high-density optical data storage devices promised to become a reality.

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References and Notes

(1) Wilson, W. L.; Dhar, L.; Curtis, K. R. *Proc. SPIE* **2006**, 6335. 63350G/1.
(2) Matharu, A. S.; Jeeva, S.; Ramanujam, P. S. *Chem. Soc. Rev.* **2007**, *36*, 1868.
(3) Parthenopoulos, D. A.; Rentzepis, P. M. *Science* **1989**, *245*, 843.
(4) Walker, E.; Dvornikov, A. S.; Coblentz, K.; Rentzepis, P. M. *Appl. Opt.* **2008**, *47*, 4133.
(5) Strickler, J. H.; Webb, W. W. *Opt. Lett.* **1991**, *16*, 1780.
(6) Kawata, S.; Kawata, Y. *Chem. Rev.* **2000**, *100*, 1777.
(7) Irie, M. *Chem. Rev.* **2000**, *100*, 1685.
(8) Shen, Y.; Swiatkiewicz, J.; Jakubczyk, D.; Xu, F.; Prasad, P. N.; Vaia, R. A.; Reinhardt, B. A. *Appl. Opt.* **2001**, *40*, 938.
(9) Li, X.; Chon, J. W. M.; Evans, R. A.; Gu, M. *Appl. Phys. Lett.* **2008**, *92*, 063309.
(10) Goeppert-Mayer, M. *Ann. Phys.* **1931**, *9*, 273.
(11) Demtroder, W. In *Laser Spectroscopy*; Springer Verlag: New York, 1988.
(12) Corredor, C. C.; Huang, Z.; Belfield, K. D. *Adv. Mater.* **2006**, *18*, 2910.
(13) Cumpston, B. H.; Ananthavel, S. P.; Barlow, S.; Dyer, D. L.; Ehrlich, J. E.; Erskine, L. L.; Heikal, A. A.; Kuebler, S. M.; Lee, L. S.; McCord-Maughon, D.; Qin, J.; Röckel, H.; Rumi, M.; Wu, X.; Marder, S. R.; Perry, J. W. *Nature* **1999**, *398*, 51.
(14) Chung, S.; Kim, K.; Lin, T.; He, G. S.; Swiatkiewicz, J.; Prasad, P. N. *J. Phys. Chem. B* **1999**, *103*, 10741.
(15) Ogawa, K.; Kobuke, Y. *Org. Biomol. Chem* **2009**, *7*, 2241.
(16) Dvornikov, A. S.; Malkin, J.; Rentzepis, P. M. *J. Phys. Chem.* **1994**, *98*, 6746.
(17) Dvornikov, A. S.; Rentzepis, P. M. *Res. Chem. Intermed.* **1996**, *22*, 115.
(18) Heller, H. G. In *Handbook of Organic Photochemistry and Photobiology*; Horspool, W. M., Song, P., Eds.; CRC Press: Boca Raton, FL, 1995; p 173.
(19) Yokoyama, Y.; Tanka, T.; Yamane, T.; Kurita, Y. *Chem. Lett.* **1991**, 1125.
(20) Liang, Y. C.; Dvornikov, A. S.; Rentzepis, P. M. *Res. Chem. Intermed.* **1998**, *24*, 905.
(21) Liang, Y. C.; Dvornikov, A. S.; Rentzepis, P. M. *J. Mater. Chem.* **2000**, *10*, 2477.
(22) Matsushima, R.; Sakaguchi, H. *J. Photochem. Photobiol. A: Chem.* **1997**, *108*, 239.
(23) Willner, I.; Rubin, S.; Wonner, J.; Effenberger, F.; Bauerle, P. *J. Am. Chem. Soc.* **1992**, *114*, 3150.
(24) Cabrera, I.; Dittrich, A.; Ringsdorf, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 76.
(25) Deblauwe, V.; Smets, G. *Macromol. Chem.* **1988**, *189*, 2503.
(26) Liang, Y. C.; Dvornikov, A. S.; Rentzepis, P. M. *Macromolecules* **2002**, *35*, 9377–2002.
(27) Bouas-Laurent, H.; Durr, H. *Pure Appl. Chem.* **2001**, *73*, 639.
(28) Pudavar, H E.; Joshi, M. P.; Prasad, P. N.; Reinhardt, B. A. *Appl. Phys. Lett.* **1999**, *74*, 1338.
(29) Woike, T.; Kirchner, W.; Schetter, G.; Barthel, T.; Hyung-sang, K. S.; Haussuhl, S. *Opt. Commun.* **1994**, *106*, 6.
(30) Imlau, M.; Woike, T.; Schieder, R.; Rupp, R. A. *Phys. Rev. Lett.* **1999**, *82*, 2860.
(31) Kardinahl, T.; Franke, H. *Appl. Phys. A: Mater. Sci. Process.* **1995**, *61*, 23.
(32) Seibold, M.; Port, H. *Chem. Phys. Lett.* **1996**, *252*, 135.
(33) Yokoyama, Y.; Yamane, T.; Kurita, Y. *J. Chem. Soc., Chem. Commun.* **1991**, 1722.
(34) Matsui, F.; Taniguchi, H.; Yokoyama, Y.; Sugiyama, K.; Kurita, Y. *Chem. Lett.* **1994**, 1869.
(35) Norsten, T. B.; Branda, N. R. *J. Am. Chem. Soc.* **2001**, *123*, 1784.
(36) Norsten, T. B.; Branda, N. R. *Adv. Mater.* **2001**, *13*, 347.
(37) Dvornikov, A. S.; Rentzepis, P. M. *Opt. Commun.* **1997**, *136*, 1.
(38) Walker, E.; Dvornikov, A.; Coblentz, K.; Rentzepis, P. *Appl. Opt.* **2008**, *47*, 4133.
(39) Dvornikov, A. S.; Cokgor, I.; Wang, M.; McCormick, F. B.; Esener, S. E.; Rentzepis, P. M. *IEEE TCPMT - Part A* **1997**, *20*, 200.
(40) McCormick, F. B.; Cokgor, I.; Esener, S. C.; Dvornikov, A. S.; Rentzepis, P. M. *Proc. SPIE* **1996**, *2604*, 23.
(41) Walker, E.; Dvornikov, A.; Coblentz, K.; Esener, S.; Rentzepis, P. *Optics Express* **2007**, *15*, 12264.
(42) Zhang, H.; Walker, E. P.; Feng, W.; Zhang, Y.; Costa, J. M.; Dvornikov, A. S.; Esener, S.; Rentzepis. P. Proceedings of the First Eighteenth IEEE Symposium on Mass Storage Systems and Technologies (MSS'01), 2001, p 225.

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