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PHOTOCHEMISTRY OF NITRO-NAPHTHALDEHYDE BASED 3D MEMORY MATERIALS

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Abstract We describe the characteristics of novel optical memory materials which we have developed for computer storage applications . Their optical and spectroscopic properties are briefly presented and the utilization of these materials in 3D optical storage devices, by means of two-photon absorption, is demonstrated.

INTRODUCTION

The capabilities of computers from the point of view of capacity, speed of input and output of information, power consumption and physical space are becoming continuously more restrictive as the amount of data to be processed keeps growing exponentially. The major component which is expected to determine the practical limits of high speed computing, will most probably be the memory. In addition, because of the huge data storage requirements, the need for the parallel execution of tasks and necessity of a compact, very high capacity low cost memory is becoming a practical necessity.[1]

For optical memories, the density of stored information depends upon the reciprocal of the wavelength raised to the power of the dimensions used to store information. For example, the information density which can be stored in a one-dimensional space, i.e., tape, is proportional to $1/\lambda$. This relationship also suggests that the information storage density is much higher for UV rather than IR light. For a two dimensional memory, the maximum theoretical storage density for a 2D storage device which uses light at 200 nm is 2.5×10^9 bits/cm^2. In the case of a 3D storage memory which utilizes the same wavelength of light, the maximum density which can be stored per cm^3 is 1.2×10^{14} bits/cm^3, an increase of 10^5 bits/cm^3.

Three-dimensional memories (3DM), because they extend the storage into three dimensions, make possible the achievement of higher capacities and foreseeably shorter access times. The optical method for storing and accessing information in 3D, currently used in our laboratory, is based on two photon processes.[2-5] This method relies on the

simultaneous interaction of two photons with a non-linear materials for storing the information in any 3D area within the bulk of the memory device.

In this paper we describe the formation and relevant properties of our new stable memory material which we have used for writing and accessing information inside the volume of a 3D memory device. We will also present the results of storing and accessing the information imprinted within the 3D volume of the memory by means of two photon absorption in this material dispersed in solid polymer hosts.

EXPERIMENTAL

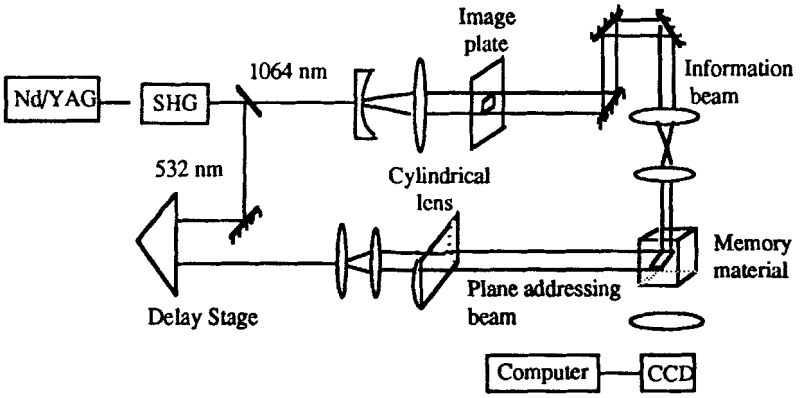


FIGURE 1 Experimental system for writing and reading information in 3D.

The experimental system for storing and accessing 3D information by means of two-photon absorption is shown in Figure 1. A "Quantel" Nd:YAG laser which emits 1064 nm 30 ps pulses at a repetition rate of 20 Hz was used for writing and accessing information from the 3D-memory device. KDP crystals were used to convert the fundamental to the SHG, THG and FHG frequencies.

The static absorption and fluorescence spectra were collected by a double beam Shimadzu UV160U spectrophotometer and a Shimadzu RF5000U spectrofluorophotometer respectively.

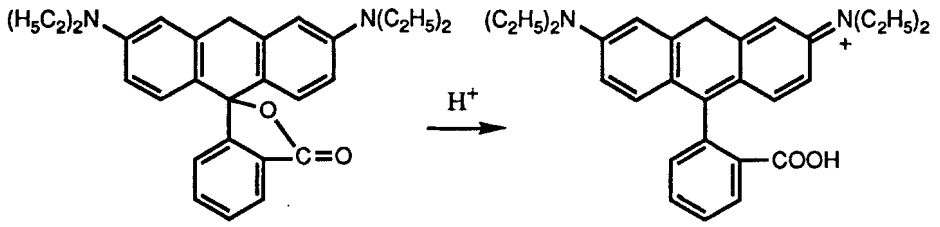
1-nitro-2-naphthaldehyde (NNA) was synthesized according to the method described in reference [6]. All other chemicals were purchased from Aldrich.

MEMORY MATERIALS

In the case of organic photochromic memory materials the binary codes, 0 and 1, are formed by the photo-chemical changes which lead to two distinct molecular forms with different structures. The write form of the memory material is usually colorless and

absorbs light in the UV region. The light absorbed by the molecules of this form, induces a photochemical reaction which leads to the formation of the written, colored form with its absorption spectrum shifted to the visible region. In the case of the 3D-two-photon optical memory method, described here, accessing of information is based on the detection of fluorescence, emitted by the written bits. The emitted light is detected by a photodiode or Charge Coupled Device (CCD) and is processed as 1 in the binary code. The proper selection of materials which provide widely separated spectra for the write and read forms is extremely important because it assures that only the "written" molecules emit light and only from the area of the written memory that is being. This wide spectra separation is responsible to the absence of crosstolk.

In our experiments on writing information in 3D format we have utilized different photochromic materials such as spiropyrans, naphthacenequinones, dimer-monomer systems and others[3,4,7]. The new memory material discussed in this paper was designed for 3D-memory ROM devices, where the information should be written once, stored indefinitely, but may be retrieved an unlimited number of times. It is composed of an organic dye which has different structures when dispersed in acidic or basic host media. It is known, that some organic dyes, such as Rhodamine B, may exist in two forms, depending on acidity and polarity of the matrix or solvent. One of these forms, Rhodamine B base, is colorless and shows complete absence of fluorescence. However, in the presence of acid, this colorless form undergoes transformation into a colored, strongly fluorescing dye, Rhodamine B, which is well known as a stable and efficient laser dye:



Rhodamine B base Rhodamine B

Using molecules which have these properties we have developed new optical storage materials which are composed of two components:

1) a molecule, which when excited to its first allowed electronic state is converted into an acid (referred to in this paper as acid generator); 2) the second component is an organic dye precursor, which reacts with the photogenerated acid to form a room temperature stable, strongly fluorescing dye. The write form of this memory material is

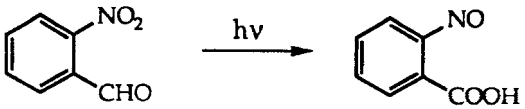
the mixture of the acid generator and the dye precursor. The written form is the fluorescing dye material which is the product of the chemical reaction that takes place after photoactivation.

A variety of dye precursors and acid generators [8-11] exist, however to be suitable for use with two-photon 3D memory devices, these molecules must posses the following characteristics:

1) the photoprocesses which generates the acid must have a high quantum efficiency; 2) both the write and read forms of the 3D material should have a long term, years, stability at room temperature; 3) the written form should be a light stable, strongly fluorescing dye 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 355 nm region or another easily accessible two photon wavelength. For example, the 1064 and 532 nm (SHG) pulses from Nd:YAG laser, which are the wavelengths that we currently employ for 3D volume writing.

The new ROM material, which we describe here, possesses all of the above properties and therefore we have been able to utilize it successfully in 3D-memory devices.

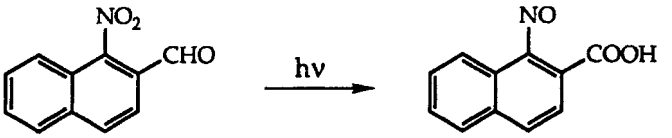
In earlier experiments we have used o-nitro-benzaldehyde (NBA) as the acid generator, which upon excitation with UV light [12] undergoes phototransformation into the corresponding nitroso acid:



Rhodamine B base was the dye precursor, which we found to react with the photogenerated nitroso-acid to form the colored Rhodamine B dye. Figure 2 shows the absorption spectra of o-nitro-benzaldehyde and Rhodamine B base and their maxima which are located below 400 nm. After excitation with 355 nm light, the solution develops a deep pink color and a bright red fluorescence was emitted from this form when the solution was illuminated with 532 nm light. An identical color change and fluorescence were observed after 355 nm irradiation, when these same two components were dispersed in solid PMMA matrices. In the case of solid matrices, both the unexposed and colored areas, unwritten and written areas, of the polymer film or block when stored in the dark did not show any spectral changes or degradation at room temperature.

Because the o-nitro-benzaldehyde has a very weak absorption band at 355 nm, see Figure 2, two-photon writing with 1064 and 532 nm beams has a very low efficiency. To increase the efficiency of the writing process we designed a new memory material where 1-nitro-2-naphthaldehyde (NNA) was utilized as the acid generator component instead of o-nitro-benzaldehyde. Unlike o-nitro-benzaldehyde, the properties of NNA are very little known, which induced us to investigate the photochemical behavior of this compound. Our studies on the detailed mechanism and kinetics of the photochemical reactions of NNA will be published elsewhere, here we describe briefly only the steps which are important for the operation of the memory device.

We found, that when NNA was excited with UV light it experienced the same photochemical rearrangement to nitroso-acid as o-nitro-benzaldehyde:



The quantum efficiency of this photoreaction was measured to be 50% and we found that it did not depend on either excitation wavelength or polarity of the host medium.

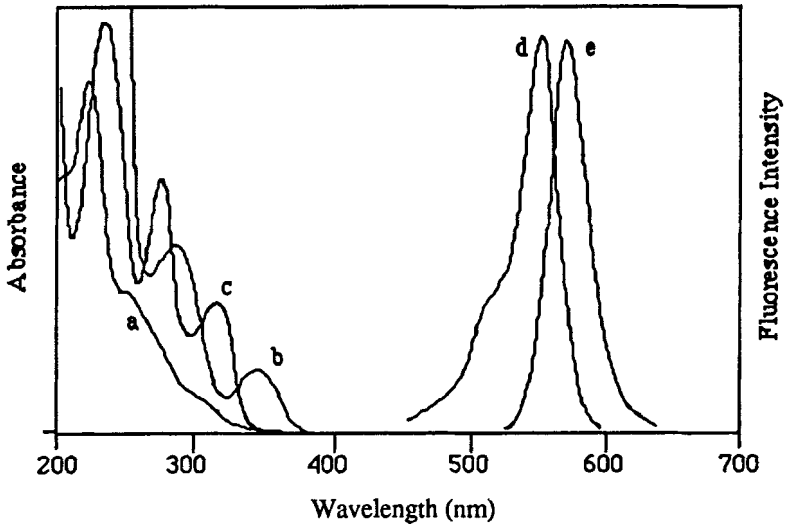


FIGURE 2 Absorption spectra of a) NBA, b) NNA, c) Rhodamine B base, d) Rhodamine B and e) fluorescence spectrum of Rhodamine B.

The absorption spectrum of NNA is shown in Figure 2. Because of the additional benzene ring in the molecular structure, the absorption spectrum of NNA is red shifted compared to the o-nitro-benzaldehyde spectrum and consequently the

absorption band at 355 nm is now very intense. The spectral characteristics of NNA in several solvents are listed in Table I.

TABLE I Spectroscopic properties of NNA.

Solvent	λ, nm (ε)
ethyl acetate	345 (2400); 282 (8000)
acetonitrile	345 (2400); 287 (7400); 245 (42100); 209 (26000)
cyclohexane	334,348 (2400); 268,278 (10200); 247,241(45400)
1,2-dichloroethane	347 (2300); 283 (7500); 248 (35000)

The nitroso-acid, after excitation of NNA with 355 nm light, reacts with Rhodamine B base transforming this colorless dye precursor into a deep colored fluorescing dye. The same process was observed when the same components were dispersed in a rigid PMMA matrix and excited with light of the same wavelength. This polymer based light sensitive molecular system we have successfully utilized as a ROM memory material, for our 3D optical memory system, to store many 2D planes inside the 3D volume of the memory.

STORE AND ACCESS OF INFORMATION IN 3D

The information storing method is shown schematically in Figure 1. To store information in a polymer block containing the memory material, we employ two photons at two different wavelengths. The photon energy of each beam was smaller than the energy gap between the ground state, S_0, and the first allowed excited electronic level, S_1. Each light beam therefore propagates though the medium without any observable absorption. When the two beams intersect at a preselected plane within the memory volume an absorption will occur if the energy gap is equal to or smaller than the sum of the two photon energies, which subsequently causes the writing reaction to take place. The induced change into the colored, written, form distinguishes this microvolume from any other area in the memory bulk where molecules have not been excited. The two molecular structures now present, i.e., the original and the one created by the two photon absorption, become the "write" and "read" forms, respectively, of the 3D optical storage memory. For the successful completion of this type of writing and reading operation, the light beams which perform either function must also be capable of traversing the medium unimpaired and be absorbed only at preselected areas within the memory volume where the two beams intersect.

The ROM material, described above, has the absorption band of its light sensitive component, the NNA molecule, at about 355 nm as shown in Figure 2. The excitation in this electronic state was achieved by the simultaneous absorption of 1064 and 532 nm, 30 psec light pulses. Each of these pulses, alone, propagates throughout the medium without being absorbed, because NNA does not have any allowed excited states at these wavelengths.

We were able to store many 2D megabit size disks, inside the volume of a 1 cm^3, by intersecting the 1064 nm information beam and the 532 nm addressing beam inside a 1 cm^3 memory device, which is composed of NNA and Rhodamine B base dispersed in PMMA. In the case where the information of an entire page is to be accessed simultaneously, rather than in a bit by bit mode, a single, low intensity 532 nm plane beam is used to illuminate the written 2D page and consequently induce fluorescence by one photon process, as shown in the schematic diagram of Figure 1 . The reading 532 nm beam has the dimensions of only the 2D plane to be read and as it propagates through the bulk of the memory device intersects and excites only molecules in this plane. These planes subsequently fluoresce, without accessing any information stored in neighboring 2D planes. One such 2D plane is shown in Figure 3. The fluorescence emitted by the bits being read is detected and recorded by a CCD which transmits the signal directly to the processor.

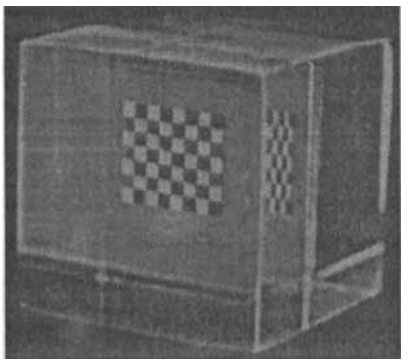


FIGURE 3 A "chessbord" 2D plane image stored inside the memory cube.

Another important property which the memory material must exhibit is reading light fatigue resistance. When the reading light is absorbed by a written bit it may introduce some undesirable photoreactions, such as decomposition of the written molecules which will lead to loss of stored information and the loss becomes unacceptable after a small number of reading cycles are performed. To estimate the fatigue resistance of our ROM material, we measured the change in fluorescence intensity emitted by the written bits as a function of reading cycles at various 532 nm

reading light energies. The results of these experiments show that if the reading light energies are less than 4 mJ/cm^2 no significant fatigue of the written form or loss of stored information was observed even after 10^6 reading cycles.

Our ROM material was also found to be stable at room temperature for long periods of time, years, and no reactions which may cause the erasure of the written information were observed at this temperature. The experimental data show that written images, which have been stored for over a year, at room temperature, do not show any noticeable difference between the initial fluorescence intensity and after a year.

SUMMARY

The optical and spectroscopic properties of a new organic ROM material have been measured and its utilization in 3D optical storage memory devices has been demonstrated.

We have, also, described the means which we have used to write, successfully, many 2D planes of information inside the volume of a 3D solid device which is composed of our new ROM material dispersed in a PMMA matrix. In addition we demonstrated that all the information in a 2D plane may be accessed simultaneously, thus making this memory device suitable for parallel processing.

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