Three-Dimensional Optical Storage Memory

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A novel three-dimensional (3-D) optical memory device is presented that allows fast random access of the information and extremely high bit densities. This device is based on two-photon writing, reading, and erasing of the information in a photochromic material embedded in a polymer matrix. Absorption and emission data show that two-photon writing and reading of information is feasible. The advantages and properties of such a 3-D optical memory are discussed.

SEMICONDUCTOR-BASED COMPUTER technology and architecture have improved to such an extent that shortly a critical point may be reached, where size and price will limit the use of high-performance computers. The major component that modulates these attributes of high-performance computers is the memory. Because of the huge data storage requirements of these instruments, a new, compact, low-cost, very high-capacity, high-speed memory device is needed to handle the high data volume afforded by parallel computing, which may be provided by a 3-D memory.

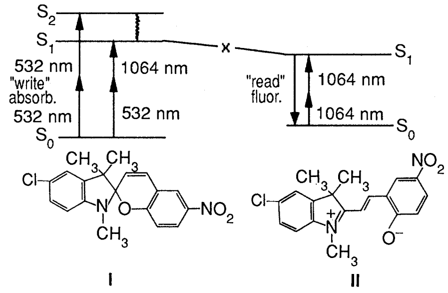
In a two-dimensional memory, the theoretical storage density (proportional to $1/\lambda^2$) is 3.5×10^8 bits/cm^2 for $\lambda = 532$ nm, whereas in a 3-D memory the maximum storage density is 6.5×10^{12} bits/cm^3. Although these values represent an upper limit to the storage capacity, the advantages of 3-D data storage versus the current information storage media become apparent. Volume information storage has been considered through holographic recording in phase-recording media (*1–3*).

Here we present the principles for a 3-D optical memory device (*4*) that may be used to construct a 3-D parallel optical memory system. Such a 3-D optical memory device is based on volume and erasable optical storage in an amplitude-recording medium (Fig. 1). This is achieved by two-photon excitation (*5, 6*) of the two forms of a spirobenzopyran (*7, 8*) embedded in a polymer matrix. This photochromic molecule, initially in the spiropyran form (I), absorbs only in the ultraviolet region of the optical spectrum, and on excitation yields the merocyanine form (II) via heterolytic cleavage (scheme 1). This merocyanine form absorbs in the green-red region of the visible spectrum and emits red-shifted fluorescence when excited with green light.

We emphasize that this method is based on a "virtual" two-photon process in which neither of the two photons can be absorbed individually: both must be absorbed simultaneously, which necessitates that the two beams overlap in time and space (*6*) within the 3-D medium. This is in contrast to a sequential biphotonic process (*9*), or photon-gated hole burning (*10*), in which each photon is absorbed independently via real levels. Since the two-photon absorption process occurs only at the place where the two beams overlap, within the volume of the memory, this process achieves true 3-D information storage (Fig. 1).

The advantages of such a 3-D memory are (i) immense information storage capacity (up to 10^{12} bits/cm^3), (ii) random access, (iii) parallel addressing, (iv) very fast optical writing and reading speed, nanoseconds and faster, (v) small size (that is, cubed centimeters) and low cost, (vi) absence of mechanical or moving parts, (vii) minimal cross-talk between adjacent bits, and (viii) high reading sensitivity.

The information storage process involves writing, reading, and erasing of information in a binary format provided by the two distinct photochemical forms of spirobenzopyran. An energy level diagram with the molecular structures of the "write" and "read" forms is displayed in scheme 1. The fundamental laser beam and its higher harmonics have been used as the excitation sources. For "writing," which requires excitation in the ultraviolet range, two-photon absorption of either a 1064-nm photon and a 532-nm photon (achieving 355-nm excitation), or two 532-nm photons (corresponding to 266-nm excitation) has been used. However, for two beams of equal wavelength, two-photon absorption induced by each beam separately may occur. This may be diminished by the use of a weak 532-nm and a strong 1064-nm beam.



Scheme 1.

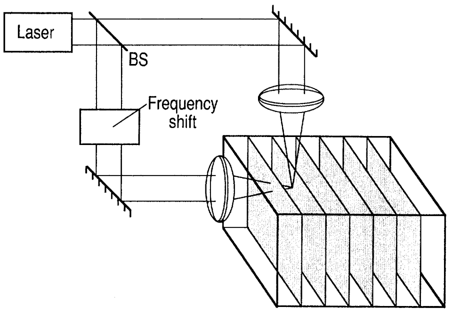


Fig. 1. Schematic diagram of a 3-D optical memory based on a two-photon process. Replacing lenses with holographic gratings allows parallel addressing. BS, beam splitter.

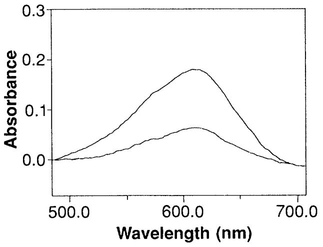


Fig. 2. Room temperature visible absorption spectrum of 1% SP in a PSt film. Upper curve: after irradiation for 5 s with 355 nm, the pulse fluence was 4 mJ/cm^2. Lower curve: after irradiation for 60 s with 532 nm and 1064 nm, the total pulse fluence was 20 mJ/cm^2.

In practice, by translating the beams along the axes of the sample, which may be in the form of a cube, the required spatial resolution is achieved in the form of colored spots throughout the cube and stored in a page format with several pages superimposed in the memory device. A complication may arise from the presence of fluorescence from the excited spiroform, which, if absorbed by adjacent molecules, would subsequently transform them to the written form and thus introduce cross-talk between adjacent bits. To avoid this, molecules that do not substantially fluoresce in the write form are chosen.

The read cycle operates similarly to the writing cycle except that the "reading" form absorbs at longer wavelengths than the write form, hence one or both laser beam wavelengths must be different than the ones used for writing. Since only molecules that have been written will absorb this long wavelength light, fluorescence will be emitted only from the written molecules (Fig. 2). Self-absorption of the fluorescence by spirobenzopyran molecules does not affect the reading process because most of the fluorescence is emitted at longer wavelengths than the absorption bands. Fluorescence absorbed by adjacent bits will yield signals that are either too weak to be detected or can be easily eliminated with electronic discrimina-

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Table 1. Lifetimes (τ_1 and τ_2) of SP fluorescence in solution and in polymer matrices monitored at 600 nm. Lifetime uncertainty (±SE) is ±10% as determined by the noise in our spectra.

Solvent or matrix	Amount	τ_1, amplitude (ps)	τ_2, amplitude (ps)
Methanol	$2.9 \times 10^{-5}M$	40, 0.75	300, 0.25
PMMA	1%	1300, 0.60	3300, 0.40
PEtG	1%	600, 0.62	2500, 0.38
PSt	1%	1800, 0.60	4000, 0.40

tors. Since reading is based on fluorescence, a zero background process, this method has the advantage of a high reading sensitivity. Erasing may be achieved by either temperature or light. When erasing by temperature the entire memory is erased, whereas erasing with light affects only the selected bits.

A passively/actively mode-locked Nd^{3+}: yttrium aluminum garnet (YAG) laser emitted 1064-nm, 20-ps pulses at 20 Hz. The 1064-nm, the 532-nm second harmonic, the 355-nm third harmonic, and the 266-nm fourth harmonic were used in the experiments described here. The one-photon– and two-photon–induced fluorescence spectra were dispersed with a 0.25-nm monochromator and detected by an intensified diode array coupled to a microcomputer. The time-resolved spectra were obtained with a streak camera. The molecule 5′-chloro-6-nitro-1′,3′,3′,-tri-methyl-spiro- [2H-1-benzopyran-2,2′-indoline] (SP) was purified by recrystallization from methanol and benzene. The polymer hosts polystyrene (PSt), polymethylmethacrylate (PMMA), and polyethyleneglycol (PEtG) were used as received. The solvents methanol chloroform and dichloroethane were high-performance liquid chromatography (HPLC) grade and were used without further purification.

Thin polymer films (100 μm) containing 1% SP by weight were prepared on a glass slide by solvent casting from a dichloroethane solution that contained 30% PSt by weight, or from a chloroform solution containing either 30% PMMA or 30% PEtG by weight. All films were placed in a vacuum for several hours before being used.

The molecule absorbs approximately two to three times less (*11*) at 355 nm than at 266 nm. The two-photon photochromism of SP in PSt is induced by spatially and temporally overlapping the 532-nm beam with the 1064-nm beam (Fig. 2). The sum of these energies of the two photons equals the energy of a one-photon transition at 355 nm. When the film is irradiated with only the 532-nm beam or the 1064-nm beam, no photochromism is observed. Since this process depends on the square of the laser peak power, picosecond pulses are preferable because of their inherent high peak power [for details on two-photon processes see (*5, 12*)]. Two-photon–induced photochromism of SP in PEtG was also observed. Since the PEtG host polymer does not absorb significantly at 266 nm and the absorption cross section of SP at 266 nm is higher than the absorption cross section at 355 nm, the two-photon absorption was readily observed in this system. When possible, lower power is used because it decreases the possibility of photochemical decomposition. The absorption spectrum of the merocyanine form of SP is blue-shifted in the PEtG matrix relative to the absorption spectrum in PSt. In addition we find that the absorption of the merocyanine form of SP in PEtG shifts at dry ice temperatures. The appearance of different colored forms at different temperatures has been attributed to equilibrium between various merocyanine isomers and aggregates (*7*). In the polymer matrix, aggregation is enhanced at low temperatures. In PMMA the absorption of the merocyanine form is also blue-shifted relative to PSt. However, when the PMMA films are placed in dry ice (−78°C), a color change is not observed. Formation of different types of aggregates leads to shifts in the absorption spectra of the merocyanines (*13*).

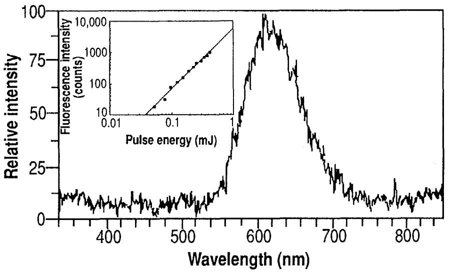

Fig. 3. Room-temperature two-photon–induced fluorescence spectra of the colored merocyanine form of 1% SP in PMMA. (**Inset**) Log-log plot of the fluorescence intensity versus excitation pulse energy. A slope ±SE of 1.94 ± 0.1 is measured.

The fluorescence of the merocyanine form of the spirobenzopyrans has been observed previously (*14–16*). We find that the fluorescence exhibits at least biexponential decays (Table 1). The cause for these multiexponential decays may be due to simultaneous conversion to spiroform and decay to merocyanine ground state. Previously single exponential lifetimes of a different spirobenzopyran molecule have been reported (*16*); because the molecules that we studied were of different concentrations, such discrepancies are to be expected.

The two-photon fluorescence of the merocyanine form of SP was observed in PMMA (Fig. 3) and PEtG and the spectra were found to be identical to the one-photon spectrum. The two-photon–induced fluorescence was the result of excitation by 1064-nm photons. The energy dependence of the two-photon–induced fluorescence intensity of SP in PMMA is shown as an insert in Fig. 3. As expected for a two-photon process, an essentially square dependence of the fluorescence intensity on excitation power is observed.

The colored merocyanine persists for several minutes at room temperature. A biexponential decay (fading) of the ground state–colored merocyanine form (written form) of SP in PMMA at room temperature was observed with a decay constant (k) of $k_1 = 0.00173\ s^{-1}$ and $k_2 = 0.00024\ s^{-1}$ and amplitudes 0.2365 for k_1 and 0.489 for k_2, in reasonable agreement with previous results (*13*). However, in PEtG and PSt the k's are one to two orders of magnitude larger than in PMMA. The fading is dependent on the concentration (*13*) and free volume distribution (*17*). Several films of SP in PMMA kept at −78°C maintained the violet color of the merocyanine (written) form of SP for several weeks.

The data presented here show the feasibility of a 3-D optical memory device based on two-photon processes. An obvious advantage of this new memory, in addition to the 3-D nature of the device, is the random access and parallel addressing of the information. Any bit plane can be accessed by focusing the beams on the appropriate plane. The speed limits for the memory are (i) the molecular transfer rate for writing and (ii) the fluorescence lifetime for reading. This does not take into account limitations imposed by the processor and other associated components. This new method allows also parallel bit addressing, resulting in high random-access rates. For parallel addressing, the dynamic focusing lenses may be replaced by holographic grating or other devices providing parallel write-read-erase capability. Cross-talk and scattering of the beams, which are common in holographic memories, do not present a problem in this case because the volume accessed by the overlapping beams is well defined and is, in principle, diffraction limited.

Fatigue, defined as the gradual loss of the ability to change color after repeated read and write cycles, is a very important draw back of any device. However, a judicious choice of the chemical medium may provide a material that would sustain a very large number of cycles. In addition, if the medium is kept at low temperatures (for example, in dry ice), side reactions are suppressed and fatigue may be minimized to a large extent; at low temperatures the persistence of the written form is extended considerably. Other molecules and matrices are possible candidates that could improve the speed, power consumption, and lifetime of the device.

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Orthogonal Self-Assembled Monolayers: Alkanethiols on Gold and Alkane Carboxylic Acids on Alumina

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This work demonstrates the practicality of forming two self-assembled monolayers (SAMs), independently but simultaneously, by adsorption of two different adsorbates from a common solution onto a substrate exposing two different materials at its surface. The experimental procedure and the degree of independence achieved in the resulting SAMs are illustrated by examination of monolayers obtained by adsorption of alkanethiols on gold and alkane carboxylic acids on alumina. This procedure provides a method for modifying the surface characteristics of microlithographically generated patterns and offers a versatile technique for controlling solid-vapor and solid-liquid interfacial properties in systems having patterns with dimensions of the order of 1 micrometer.

SELF-ASSEMBLED MONOLAYERS (SAMs) are highly ordered, quasi-two-dimensional structures formed by adsorption of appropriate precursors $X(CH_2)_nY$ from solution onto a solid substrate of metal or metal oxide (*1–5*). Techniques described to date for formation of SAMs offer very precise control over structure in the dimension perpendicular to the plane of the monolayer (*2*) but little control over structure or composition in the plane of the monolayer. For studies in wetting (*3*) and in microelectrochemistry (*6, 7*), we also wanted to be able to control structure and to form patterns in the plane of the monolayer. We describe a technique that combines the formation of SAMs with the microlithographic preparation of substrates for them having two or more materials exposed at their surface. This technique provides control over in-plane surface properties and structure at the scale of the dimensions reached by the microlithographically generated features.

We take advantage of systems of adsorbants (A_1, A_2, . . .) and substrates (S_1, S_2, . . .) that are "orthogonal" in formation of SAMs: that is, A_i adsorbs strongly on S_i but weakly on S_j; A_j adsorbs strongly on S_j but weakly on S_i. A number of orthogonal systems can be imagined based on different principles of surface coordination chemistry. In this report we illustrate the application of orthogonal systems to the formation of in-plane patterns using "hard" and "soft" acid-base interactions (*8*) to differentiate between areas in the plane: $S_1 = Al_2O_3$, $A_1 = RCO_2H$; and $S_2 = Au$, $A_2 = R'SH$.

To demonstrate orthogonality in SAMs formed on the different substrates, a number of preliminary experiments were conducted with areas large enough for contact angle and x-ray photoelectron spectroscopy (XPS) measurements. In these experiments, substrates were prepared by evaporation of aluminum (~500 Å) through a mask onto a gold substrate (*9*). On exposure of this patterned system to air, the surface of the aluminum oxidized spontaneously to aluminum oxide. Immersion of this substrate in an isooctane solution (*10*) containing an alkanethiol, $HS(CH_2)_mX$, and an alkane carboxylic acid, $HO_2C(CH_2)_nY$ (each ~1 m*M*), for 24 hours resulted in adsorption of the thiol preferentially on the gold (*4*) and the carboxylic acid preferentially on the aluminum oxide (Fig. 1) (*5*). The composition of the SAMs formed on the gold and alumina were examined by XPS (*11*) (Fig. 2) and wettability (Table 1). The important conclusion from the data in Table 1 is that, within the limits of detection of our experiments, pure monolayers of the two adsorbates—$HS(CH_2)_mX$ on gold and $HO_2C(CH_2)_nY$ on alumina—are formed independently on the two types of exposed interfaces by ad-

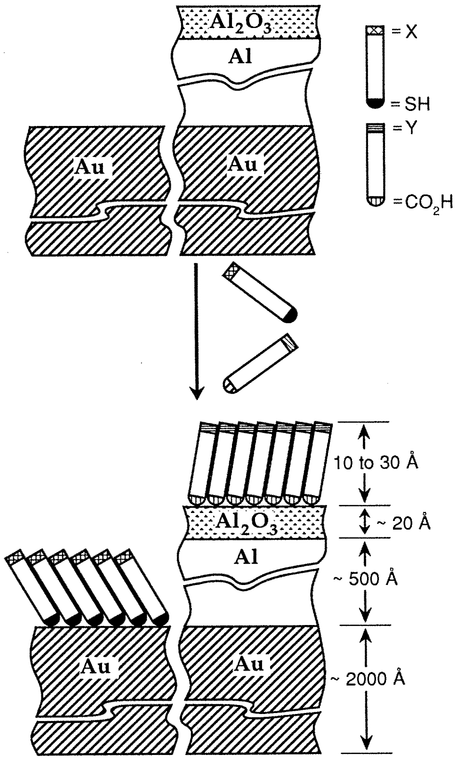

Fig. 1. Schematic illustration of the formation of orthogonal SAMs by adsorption of a mixture of alkanethiol [$HS(CH_2)_mX$] and alkyl carboxylic acid [$HO_2C(CH_2)_nY$] from a common solution onto a patterned gold–aluminum oxide surface.

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