Three-dimensional optical data storage in a fluorescent dye-doped photopolymer

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We propose a new, to our knowledge, monolithic multilayer optical storage medium in which data may be stored through the diffusional redistribution of fluorescent molecules within a polymer host. The active portion of the medium consists of a photopolymer doped with a fluorescent dye that is polymerized at the focal point of a high-numerical-aperture lens. We believe that as fluorescent molecules bond to the polymer matrix they become more highly concentrated in the polymerized regions, resulting in the modulated data pattern. Since data readout is based on detection of fluorescence rather than index modulation as in other photopolymer-based memories, the problems of media shrinkage and optical scatter are of less concern. An intensity threshold observed in the recording response of this material due to the presence of inhibitor molecules in the photopolymer allows for the three-dimensional confinement of recorded bits and therefore multilayer recording. The nonlinear recording characteristics of this material were investigated through a simple model of photopolymerization and diffusion and verified experimentally. Both single-layer and multilayer recordings were demonstrated. © 2000 Optical Society of America


1. Introduction

Because of its high storage capacity and relatively inexpensive media, optical storage has proven to be a convenient means for the physical distribution of large quantities of information. However, despite the current search for shorter-wavelength lasers and more-efficient coding techniques, standard planar optical storage technologies may not be able to keep up with the ever-increasing demand for faster-data-rate, higher-capacity media. As a result, various new alternative optical technologies are currently being investigated including multilayer reflective media,1,2 near-field recording,3,4 volume holography,5,6 two-photon storage,7-9 bit-oriented index modulation,10,11 and others. With the exception of near-field recording all these technologies benefit from the increase in capacity that can be gained by the expansion of data storage into the third dimension of a thick medium.

In this paper we investigate what we believe is a new monolithic, multilayer optical medium that may have advantages over other new storage technologies in terms of ease of recording and readout while sharing the same characteristics of high density, fast access time, and parallel readout capability. The active portion of the medium is a photopolymer—similar to that used for other volume optical media—which has in addition been doped with a fluorescent organic dye. Recording occurs during photopolymerization when the distributions of dye become more highly concentrated in the polymerized regions, therefore producing a modulated fluorescence readout pattern. In this architecture recordings are bit oriented and are performed in a two-dimensional parallel fashion. The readout, which is based on excitation of fluorescence, is nondestructive and is also detected in two-dimensional parallel. Since index modulation, or changes in the material density, is not necessary for readout in this medium, some of the problems commonly associated with photopolymer memories such as shrinkage and optical scatter are less of a concern.12 This material is nonerasable; therefore, given its ease of production and low-cost materials, this medium is best suited for mass-distribution ROM applications.

In Sections 2–4 we investigate the properties of this new medium. In Section 2 we describe the material composition and the optical setups used for image recording. The fluorescence modulation pro-
cess, which is based on the diffusion of dye within the material, is described and shown experimentally. In Section 3 we then examine the nonlinear recording characteristics that were observed for this material. Specifically, a threshold in the recording intensity response is demonstrated that indicates that this material is suitable for multilayer data storage. The origin of this threshold is investigated with a simple model and verified through a series of recordings. Finally, in Section 4 we present the results of a four-layer recording and readout demonstration and discuss the limitations of this medium.

2. Materials and Recording

The medium consists of an inert polymer host in which both a fluorescent dye and a complete photopolymer system are suspended. The photopolymer used here polymerizes in a standard free-radical reaction and consists of the monomer dipentaerythritol pentaacrylate, the crosslinker 1-vinyl-2-pyrrolidinone, the initiator N-phenyl glycine, and the photosensitizer camphor quinone. The recording wavelength of this material is determined by the photosensitizer, which in this case has an absorption peak close to the blue 488-nm line of an argon-ion laser. In these results we chose Rhodamine B as the fluorescent dye, which absorbs well at the 543.5-nm wavelength of a green helium neon laser and has an orange fluorescence band from 560 to 640 nm. We also tried a number of other dyes with similar success including Bodipy Red, which has an absorption peak at 650 nm and fluorescence at 665 nm, thus allowing compact red diode lasers to be used for readout. All these active components are suspended in a binder of cellulose acetate propionate and dissolved in acetone.

The prepolymer mixture must be kept in a semiviscous state for the active components to have a sufficiently high diffusion rate; therefore samples are prepared in sealed square cuvets. After polymerization the material becomes solid and inert. Difficulties may arise from having a prepolymerized material that is not solid, since layers within the volume are potentially free to drift within the viscous medium unless the recorded layers are anchored to the bottom or all of the layers are recorded rapidly in a simultaneous manner. For these experiments we used the former approach to avoid movement of the data; however, for this material to be useful as a mass distribution ROM media an appropriate optical data stamping technique should be developed so that information can be duplicated in the media in a rapid, inexpensive fashion. Implementing massively parallel recording may be one approach to rapid optical data stamping.

The mechanism of recording in this material is shown in Fig. 1. Before recording, the fluorescent dye molecules are evenly distributed throughout the medium; however, during the recording process a modulation of the fluorescence intensity according to the recorded pattern is developed. We believe that this modulation results from a binding of dye molecules to the polymer matrix, since it has been observed that Rhodamine B can itself act as a photoinitiator for this monomer without any other additional dopants. Two processes are therefore initiated by exposure to blue light: polymerization and dye fixing. In the exposed areas the monomer undergoes a polymerization process that solidifies the matrix while, simultaneously, photoexcited dye molecules bind to both monomer and polymer molecules. Dye molecules that are incorporated in the polymer matrix will become fixed in their location, resulting in a concentration gradient of free dye molecules in the material. This concentration gradient causes more dye to diffuse into the dark regions thereby increasing the total fluorescence level observed in the exposed areas and reducing that in the unexposed areas. Once the material has been fully polymerized and all the free dye molecules have been bonded, the fluorescence modulation is fixed and recorded im-

![Fig. 1. Mechanism of recording.](image-url)
ages are permanent. Materials that operate on a principle similar to that described here have also recently been developed for holographic memories with the goal of maximizing index modulation rather than fluorescence modulation.14

Figure 2 shows the optical setup used for both recording and read out of data. An argon laser illuminates a mask that is imaged through a 4-f system to a certain depth within the recording media. The rotating diffuser immediately before the mask is necessary to reduce interlayer cross talk by means of breaking up the spatial coherence of the source and randomizing the diffraction image of the beam along its propagation path except when it is in focus. An Olympus 40×/0.6 N.A. microscope objective that can variably compensate the spherical aberrations of up to 2.5 mm of plastic or glass is used to focus into the medium. The position of the microscope objective is stepped axially to image to different depths within the medium for multilayer recordings. Images are recorded in exposures typically ranging from 2 to 20 s with the argon laser focused down to recording intensities between 1 and 10 W/cm².

Readout is performed by means of blocking the recording beam and illuminating the recorded layer orthogonally with 350 μW from the green He–Ne laser. The green beam is cylindrically focused into a thin sheet of light approximately 15 μm thick to select just one layer out of the volume. The fluorescent dye absorbs the green light and then emits an orange fluorescence that is collected and imaged onto the CCD detector. The orthogonal nature of the readout scheme permits two-dimensional parallel detection of data, which in a high-speed readout system may allow for extremely high data transfer rates.

A typical single-plane recording of a U.S. Air Force resolution target is shown in Fig. 3. The average contrast ratio of this image is less than 2:1. The smallest resolvable line pair group is group 5/6, which after demagnification corresponds to 1.28 μm/line pair, or a 0.64-μm minimum feature size. The material therefore exhibits submicrometer resolution, which is a necessary requirement for a high-density optical storage medium. In this picture the green illumination beam is entering from the right-hand side. On the left-hand side of the image it is possible to see some nonuniformities in the readout beam that look like shadows. These shadows are a result of the small index changes that occur when the material polymerizes causing scatter and focusing in the beam. No attempt was made in this study to minimize the index-of-refraction modulations; however, further optimization of the material composition would be desirable for reducing these effects and improving the optical quality of the medium. Recorded samples that were stored in the dark for several months also showed a slight degradation in image quality, most likely from evaporation of the solvent due to leaks in the cuvet seal. A more stable solvent would be preferred to improve the shelf life of the material.

We can observe the diffusion process of the dye during recording by exposing a large region in the material. Figure 4 shows four images in which the left half of the sample has been exposed to light. Immediately after exposure an edge enhancement of the boundary between the exposed and the unexposed regions may be observed as dye diffuses into the exposed region [see Fig. 4(a)]. Dye concentration builds up most quickly closest to the edges, leaving a dye-depleted region immediately outside the exposed area. Over a period of minutes the entire exposed region will slowly rise to a uniform fluorescence level [see Fig. 4(b)]. The edge-enhanced recording observed in 4(a) can be fixed, however, by immediate application of a second exposure that uniformly illuminates the entire image and bonds all the dye in the sample. Figures 4(c) and 4(d) show a fixed
image 30 s and 5 min, respectively, after the second exposure. It can be seen that the characteristic edge-enhanced structure is still evident even several minutes after the exposure.

Because the fluorescent signal strength of a recorded data image is dependent on diffusion of dye from neighboring unexposed regions, it can be seen that the recorded fluorescence intensity may vary depending on the size of the recorded bit and the number of neighboring bits that have been recorded. For recording of digital data modulation codes such as a biphase (or Manchester) code may be necessary to ensure uniform signal strength of recorded bits.
3. Nonlinear Polymerization

A. Modeling

For any particular medium to be viable as a three-dimensional optical medium it must be possible to selectively record layers within the volume without adversely affecting the information stored at other layers. This material exhibits an intensity threshold in its recording curve that results from the presence of the inhibitor oxygen. Oxygen is dissolved in air. In most cases the presence of oxygen in photopolymers exhibits itself as an exposure time threshold; however, in this material an intensity threshold may also be observed that is due to the material’s high diffusion rate. The existence of this threshold is independent of the presence of the fluorescent dye and can be demonstrated through intensity threshold measurements. The existence of this threshold may also be observed that is due to the material’s high diffusion rate. The existence of this intensity threshold is independent of the presence of the fluorescent dye and can be demonstrated through a simple model of the polymerization process of a photopolymer.

The processes considered in this model are free-radical generation by light, chain initiation (the creation of a radical site on a monomer or polymer), chain propagation (the addition of monomers to a polymer chain), chain termination (the neutralization of a polymer radical site), radical annihilation (the neutralization of free radicals with one another), inhibition (the neutralization of radicals by oxygen), and diffusion. We wish to write down the rate equations for the following components of the photopolymer: the monomer (M), the polymer (P), the inhibitor (H), the free-radical initiators (R), the radical sites on the polymer chain (P), and the neutral components such as the solvent or binder (N). For some arbitrary input light intensity I(x, y, z, t) the rate equations are given as

\[
\frac{\partial [R]}{\partial t} = \left( \frac{\sigma \eta}{k_\omega} \right) I(x, y, z, t) [R] + \alpha_R \nabla^2 [R] - k_i [R] [M] + [P] - k_a [R]^2 - k_{ap} [R] [P] - k_{ap} [R] [H],
\]

(1)

\[
\frac{\partial [H]}{\partial t} = \alpha_H \nabla^2 [H] - k_i [H] [R] + [P],
\]

(2)

\[
\frac{\partial [M]}{\partial t} = \alpha_M \nabla \cdot ([N] \nabla [M] - [M] \nabla [N]) - k_p [M] [R] + [P],
\]

(3)

\[
\frac{\partial [P]}{\partial t} = k_i [R] [M] + [P] - k_{ap} [R] [P] - k_{ap} [R] [H],
\]

(4)

\[
\frac{\partial [P]}{\partial t} = k_p [M] [R] + [P],
\]

(5)

where the k’s correspond to the rate coefficients for the polymerization processes of chain initiation (k_i), chain propagation (k_p), chain termination (k_i), radical annihilation (k_a), and inhibition (k_{ap}); the α’s correspond to the diffusion constants for free radicals (\alpha_R), inhibitors (\alpha_{R}), and monomers and neutral components (\alpha_{M}); \sigma is the absorption cross section at the given wavelength; and \eta is the conversion efficiency of the initiator into free radicals. We assume that the number of free radicals generated is small compared with the total concentration of initiators (R). The various constants in these equations have either been measured from the material or taken as typical values from the literature.

Polymer and radical sites on the polymer are assumed not to diffuse. The remaining components must interdiffuse as a multicomponent system. To simplify this problem we may observe that the concentration of free radicals and inhibitors is much smaller than that of monomers, polymers, and neutral components and therefore may be approximated to diffuse freely. We are left then with diffusion in a bicomponent system (between monomers and neutral components) which—if we assume that the densities of these components are similar—may be approximated as shown in Eq. (3) subject to the conservation of mass equation,

\[
[M] + [P] + [N] = \text{constant}.
\]

(6)

As polymerization occurs, the monomer concentration will drop, leading to diffusion of monomers into the exposed areas and expulsion of the neutral component. Polymerization will cease when the neutral component has been completely expelled from the irradiated region and all of the monomer has been converted to polymer.

As a measure of the degree of both the polymerization and diffusion in the material we define a modulation ratio that is directly proportional to the polymer plus the monomer content,

\[
\text{modulation ratio} = \frac{[M](0, t) + [P](0, t)}{[M](2a, t) + [P](2a, t)},
\]

(7)

where the modulation is compared between the center of the exposed region and a point one diameter away. A high modulation ratio will indicate a high degree of polymerization and diffusion of the monomer.

We wish to simulate the recording of a single bit in the media. To reduce the complexity of the computation, a spherically symmetric intensity distribution was chosen.

\[
I(r) = \begin{cases} I_0 & \text{for } r \leq a \\ 0 & \text{for } r > a \end{cases},
\]

(8)

allowing the solution to be solved in terms of \( r \) and \( t \) only.

The rate equations are solved numerically for a given set of parameters. Figures 5 and 6 show the component concentrations at \( r = 0 \) during an exposure for two different intensity levels. We can see that, for a low recording intensity, \( I_0 = 0.41 \text{ W/cm}^2 \) (see Fig. 5), the rate of radical generation and inhibitor consumption is slower than the diffusional rate of the inhibitor, and therefore the inhibitor concentra-
tion never reaches a zero level but instead plateaus into a quasi-equilibrium state. Polymerization in the exposed region is therefore negligible even for long exposure times. However, for a higher recording intensity, $I_0 = 0.65 \text{ W/cm}^2$ (see Fig. 6), the inhibitor consumption rate is higher than the diffusional rate and the inhibitor concentration falls to a low enough level for polymerization to occur. It can be seen that after a short induction time monomers begin to be converted into polymer while more monomer flows into the exposed region, resulting in an increasing modulation ratio.

Somewhere between the two intensities shown in these two figures there will exist a certain crossover threshold when the inhibitor consumption rate surpasses the compensating diffusion rate. In Fig. 7 modulation ratio is plotted as a function of recording intensity for three different exposure energies. The exposure time is compensated in each according to the recording intensity to maintain a constant exposure energy. As expected, in each curve there is a distinct intensity threshold followed by a rapid increase in the degree of polymerization. For much higher intensities (and shorter exposure times) the modulation ratio begins to fall off again, since there is less time for monomer components to diffuse. Radical annihilation—which is proportional to the square of the radical concentration if we assume that annihilation occurs as the recombination of two free-radicals—will also become a greater factor at higher intensities and also reduce the polymerization rate.

In designing a material for a three-dimensional medium the sharp threshold observed here is the desired characteristic. For a beam sharply focused into the material, recording will occur only at the most highly focused spot where the intensity reaches above the recording threshold. Elsewhere, the medium will not be affected. Sharpening the threshold—making the ratio between the threshold and saturation intensities closer to 1—will have the desirable effect of increasing the number of layers that may be recorded in a single medium. We can modify the position of the threshold level by adjusting the balance between inhibitor consumption and diffusion either by increasing the initial concentration of inhibitors through the addition of another inhibitor besides oxygen or by increasing the diffusion rate in the material through changes in the chemical composition or by heating of the material. The position of the saturation level is determined by the polymerization rate, which can also be modified by a number of different parameters. Using the model, we are able to choose intelligent directions for optimization of the
medium that maximize the threshold/saturation ratio.

It should be noted that this model excludes many higher-order polymerization effects. For example, in the model we did not take into account the expected reduction in diffusion rate that will occur as the exposed regions reach higher levels of polymerization. Known as the gel effect,\(^{17}\) this reduction in diffusion would be expected to increase the rate of polymerization (as the rate of chain termination is slowed) while decreasing the flow of monomer into the exposed regions. Differences in our model and our experimental results may be accounted for by the gel effect as well as other thermal and optical photopolymerization effects that have not been included.

**B. Experiment**

In the model described above we have examined only the polymerization process of a standard photopolymer and have not included the fixing and diffusion of the fluorescent dye included in the fluorescent photopolymer medium. We now experimentally investigate the fluorescence contrast ratio that results during recording in this medium, which includes the nonlinear processes of both the polymerization and the dye diffusion. Although polymerization modulation ratio and fluorescence contrast ratio are not equivalent measurements, we can use the more easily observable fluorescence contrast ratio as some indication of the degree of polymerization, since fluorescence modulation will not occur unless the dye position has become fixed.

We experimentally investigated the recording characteristics of this material through a series of recordings under different exposure conditions while measuring the observed fluorescence contrast ratio for 4-μm-wide bars. Figure 8 shows the resulting contrast ratio of recordings for varying exposure energies at three different recording intensities. The two higher intensities show a short induction period followed by polymerization; however, for the lowest recording intensity (0.42 W/cm\(^2\)) no image was formed regardless of the exposure energy. The apparent recording intensity threshold may be observed more clearly in Fig. 9 where contrast ratio is plotted over a range of different intensities. In all recordings the exposure time was adjusted to produce a constant total exposure energy. It can be seen that below a recording intensity of approximately 0.6 W/cm\(^2\) no image is formed. The contrast ratio increases rapidly for intensities higher than the threshold and then plateaus at different levels depending on the total exposure energy. Experimentally we observe the same intensity threshold effect predicted by the polymerization model. This threshold now allows us to perform multilayer recording.

**4. Multilayer Recording**

To demonstrate the multilayer capability of this medium four images at varying depths were recorded (see Fig. 10). Images were recorded in order from deepest to shallowest with a 70-μm spacing between layers. It can be seen that the deeper images are somewhat brighter than the images closer to the surface. We determined from experiment that this is not a result of the recording order but more likely a difference in the material component concentrations in the thin layer closest to the surface of the media. Evaporation of the solvent during sample preparation may result in reduced dye mobility and therefore a reduced image contrast. A small degree of interlayer cross talk is also visible between the images. Because the illumination beam for the mask was not completely uniform, the recording intensity had to be increased to record the outer edges of each image. The higher intensity in the center of each image exceeds the intensity threshold condition.
at neighboring planes, resulting in cross talk. This difficulty highlights the importance of having a uniform illumination beam maintained at just above the threshold recording intensity.

The minimum acceptable spacing between layers is determined by the effective numerical aperture (N.A.) of the recording optics as well as the degree of nonlinearity in the recording process. The depth over which an image is recorded will be determined by the rate at which the focused image expands and falls below the recording intensity threshold. The focal depth of a lens is inversely proportional to the square of the N.A. In these recordings the N.A. of the recording optics is only moderately high; moreover the features sizes in the images are large. When the feature sizes are reduced, diffraction out of the focal plane will more quickly blur the image data and produce a uniform, low-intensity background that will not be recorded on preceding or subsequent layers. It should also be noted that when high-N.A. optics are used it becomes necessary to compensate for the spherical aberrations induced by imaging through a thick medium. This can be done either through the use of aberration-corrected optics—as was used here—or fluid immersion lenses, which have the added advantage of allowing for even higher N.A.’s although typically shorter working distances.

In addition to the layer spacing, the total usable thickness of the material will determine the maximum number of layers recordable in a single medium. As we have mentioned, the maximum thickness of the media can be limited by optical clarity concerns. Optimizations of the material composition that minimize index-of-refraction modulations and density changes of the material during recording will allow for the use of thicker and therefore higher-capacity media.

5. Conclusion

We have demonstrated what we believe to be a new optical recording medium that records information through the redistribution of a fluorescent dye within a polymer host. This material exhibits an intensity threshold response that is due to the diffusional nature of the recording process, allowing for the three-dimensional confinement of recorded bits. Our conceptual description of the recording process has been verified by a simple model of photopolymerization and diffusion, and recordings in this material have been shown to exhibit both high resolution and the capability for multiple layers. Four layers have been recorded on 70-μm-layer spacings with only a minimal amount of interlayer cross talk visible. The recording and readout architectures of this memory both permit parallel optical transfer of data, which eventually may provide extremely high data transfer rates, whereas the multilayer capability of this medium indicates that
high capacities may be achieved while still allowing for fast access times. Improvements must still be made in the material composition, particularly in terms of material stability, nonlinearity, and optical quality. Provided that a suitable optical data stamping technique can be developed, the high recording sensitivity and ease of manufacture demonstrated here indicate that this material may have potential as a high-capacity, low-cost medium for information storage and distribution.

References