Development of Instrumental ORAM System for Radiation Dosimetry

B. M. Cullum[1]; J. Mobley[1]; J. S. Bogard[1]; M. Moscovitch[2]; and T. Vo-Dinh[1*]

[1]Oak Ridge National Laboratory; P.O. Box 2008; Oak Ridge, TN 37831-6101

[2]Georgetown University; Medical Center; Washington, D. C.

ABSTRACT

The development of an optical-based dosimeter for neutrons and heavy charged particles is described. It is based on the use of three dimensional (3-D) optical memory materials, used in optical computing applications, and multiphoton fluorescence of photochromic dyes. Development and characterization of various types of dosimeter materials are described as well as the optical readout system. In addition, various excitation geometries for "reading" and "writing" to the optical memories are also discussed.

Keywords: 3D-ORAM, optical memories, radiation dosimeter, multiphoton fluorescence, photochromic dyes, ICCD

I. Introduction

There is a great need for the development of a small, light-weight radiation dosimeter that can be rapidly monitored and reused. Presently, most radiation dosimeters measure only the radiation dosage the person or object to which the dosimeter is attached was exposed too. By developing a 3-D dosimeter, it may be possible to not only determine the amount of radiation that was present during exposure, but the type of radiation as well. The ability to measure these various parameters quickly and simultaneously would provide an excellent means of monitoring radiation events such as those in space. Most large charged particle and neutron radiation from space is reflected off of or absorbed by the Earth's atmosphere. However, in outer space as well as on some planets (i.e. mars) or satellites (i.e. the moon) there is either an atmosphere much smaller than Earth's or none at all. Due to this reduced atmosphere and man's quest to explore the universe, measurements of the amount and type of impinging radiation are very important.

The development of 3-D optical random access memory (3-D ORAM) dosimeters is based on the evolving technology of 3-D ORAM materials for optical computing purposes. These 3-D ORAM materials are composed of a simple polymer matrix in which is contained a photochromic dye. This photochromic dye is generally fluorescent in one of the two or more stable conformations and non-fluorescent in the other configuration(s). Conversion of the molecule from one state to a different state is achieved by the absorption of a specific amount of energy. This energy is typically provided by a photon event. For optical memory materials, when the dye is in the fluorescent state it said to be in the "written" form. The non-fluorescent state is termed the "unwritten" state. The promise of 3D-ORAM materials for the optical computing and dosimetry lies in the idea that unlike conventional computer memory materials, the entire volume of the material can be "written" to instead of only the surface as in conventional media. This would increase the storage capacity of a computer tremendously. For dosimetry applications, the use of the entire volume of the material can provide information on the direction of travel of the radiation as well as its type.

To monitor the individual memory elements, or "bits", in the 3-D ORAM material, a multiphoton excitation process is applied for both the "writing" and "reading" steps. This multiphoton excitation is achieved via a crossed beam configuration. Many different crossed beam configurations can be applied (see Figure 1) depending on the type of excitation or readout desired and the spatial resolution of the desired measurement. In one case, one of the two crossed beams can take the form of a plane of light that is focused via a cylindrical lens, while the other beam is focused to a point. Since only

* author to whom correspondence should be sent

Configuration # 1

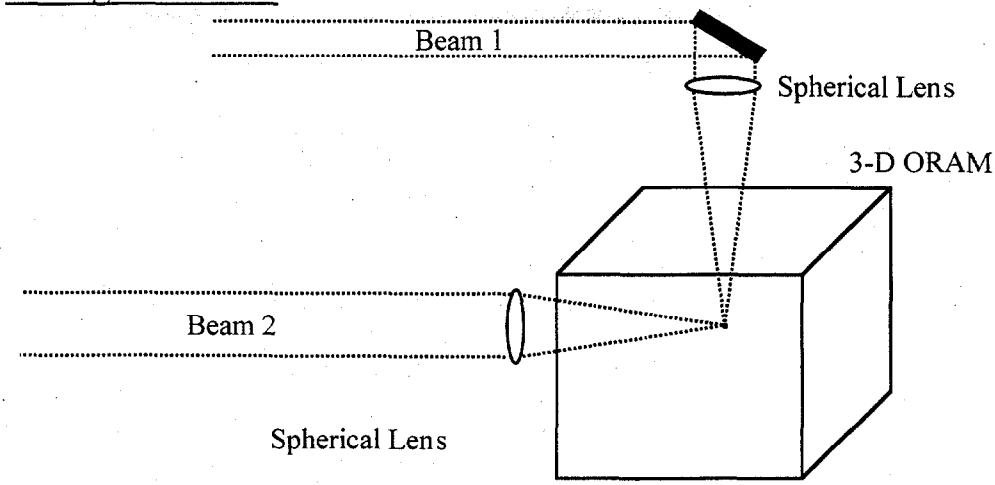

Figure 1a: Point by point addressing system using two spherical lenses.

Configuration # 2

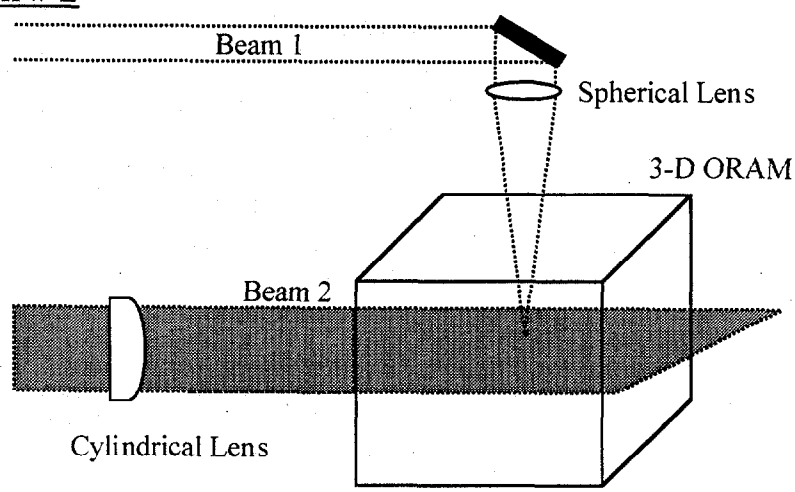

Figure 1b: Point by point addressing system using one spherical lens and one cylindrical lens.

Configuration # 3

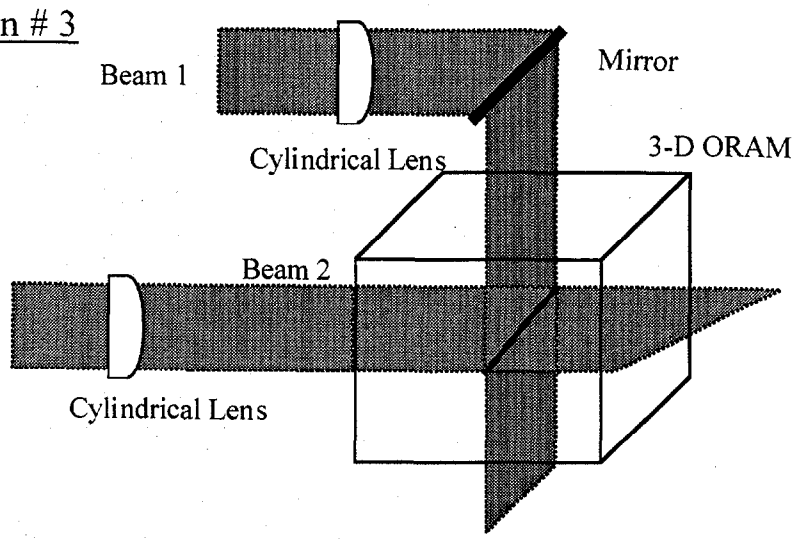

Figure 1c: Linear addressing system using two cylindrical lenses.

molecules that can simultaneously absorb photons from both of the different beams can be excited, or converted, excitation of only a single point is achieved. A second possibility for excitation is the crossing of two beams that have been focused to a point, once again achieving only excitation of a single bit. Therefore, the 3-D ORAM material can be "written" to or "read" from in a point by point fashion. In addition, once the material is written too, it can also be excited via a single photon absorption and read out in a planar format, however, a greater resolution should be capable using a two photon process.[1]

3-D ORAM materials can be used as radiation dosimeters by simply converting the entire material to the written form and exposing it to radiation. As radiation of various energy strikes the 3-D ORAM material, the written form of the dye molecule is converted back to the unwritten form.[2] Therefore by monitoring the decrease in fluorescence, of the optical memory material, the dose of radiation can be calculated. In addition, by reading out the fluorescence point by point in the 3-D ORAM material, a high-resolution image of the non-fluorescent tracks in the material can be obtained. Based on the path of the track, the direction of the impinging radiation can be determined and based on the depth of penetration and size of the track, the type of radiation that the 3-D ORAM dosimeter was exposed to should also be able to be determined.[3] Preliminary studies using computer optical memories as dosimeters to 2-MeV alpha particles have confirmed their ability to monitor charged particles while being transparent to gamma ray and x-ray photons. Several different photochromic dyes have been investigated for use in optical memory materials[4-6], however, one or more of the different conformations is typically unstable thus making it unsuitable a radiation dosimeter. This paper will discuss the development and characterization of two different optical memory materials as well as the optical readout system and excitation parameters necessary for detection of radiation tracks.

II. 3-D ORAM Fabrication

Fabrication and characterization of an optical memory material is one of the primary steps in the development of a 3-D ORAM for radiation dosimetry. Construction of a 3-D ORAM material depends on the fluorescent properties of the specific photochromic dye chosen. An optimal dye for optical memory storage is one that: 1) has two stable conformations that can be converted from one to the other through a two photon absorption process using an easily accessible light source 2) is stable in both conformations and 3) is capable of being placed in a polymer matrix. We have investigated the use of two such photochromic dyes for use in our optical memory materials. These are a spirobenzopyran (5'-chloro-6-nitro-1', 3', 3'-tri-methyl-spiro-[2H-1-benzopyran-2,2'-indoline) (Chroma Chemicals; Yellow Springs, OH) and anthracene (Aldrich Chemical; Milwaukee, WI).

Spirobenzopyran is one of the most well characterized photochromic dyes. It has been studied extensively for use in 3-D ORAM materials for optical computing. The two different conformers of the dye and the energy necessary for conversion of one form to the other shown in Figure 2a.

The left side of this figure shows the dye in its non-fluorescent form. However, upon absorption of a photon of 355 nm light, the molecule is converted to its fluorescent conformation shown on the right. In addition to conversion via a single photon of 355 nm light, the simultaneous absorption of two photons having the equivalent energy can also cause conversion. Such a two photon scheme could include the absorption of one photon of 532 nm light and an additional photon of 1064 nm light as depicted in Figure 2b. Since all of these three wavelengths are easily achievable via an Nd:YAG laser and its harmonics, an excitation source of sufficient energy is simple to obtain. In addition to the two excitation schemes for "writing" to the polymer described previously, absorption of two photon of 532nm light followed by relaxation of the S_2 to the S_1 state can also provide a means of conversion (see Figure 2b). Once in the written state, the spirobenzopyran can be read via fluorescence. Excitation of the fluorescent conformation can be achieved via a single photon of 532 nm light or two photons of 1064 nm light and the resulting fluorescence at approximately 640 nm can then be monitored.

In addition to spirobenzopyran, we have investigated anthracene as a possible photochromic dye for use in 3-D ORAM dosimeter materials. When anthracene molecules are located close to each other, an anthracene dimer can be easily formed. This dimer/monomer conversion and its reverse have been reported to be possible via absorption of light.[6] In addition to optical conversion of one form to the other, it has been shown that the dimeric form of the anthracene complex is non-fluorescent while anthracene monomer is highly fluorescent. Conversion of the dimer to the monomer and its reverse is depicted in Figure 3a. The "unwritten" dimeric form of the anthracene complex can be converted to the written monomer form via the absorption of 266 nm light. This conversion can also be performed by the simultaneous absorption of two photons of 532 nm light as shown in Figure 3b. Once the dimer has been split into its two monomeric components, it is in the " written form." The excitation of this "written", fluorescent, form is then achieved via the absorption of a single photon

Spirobenzopyran

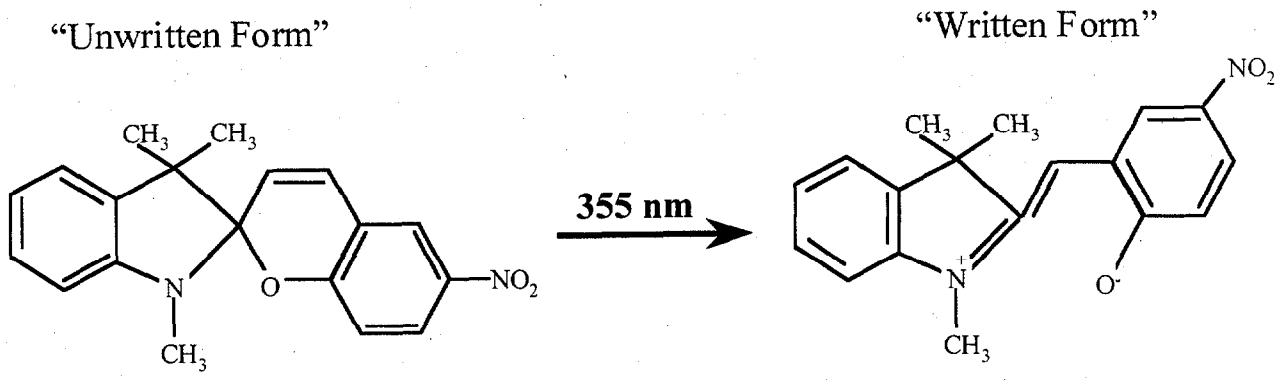

Figure 2a: Two photo-induced conformations of spirobenzopyran.

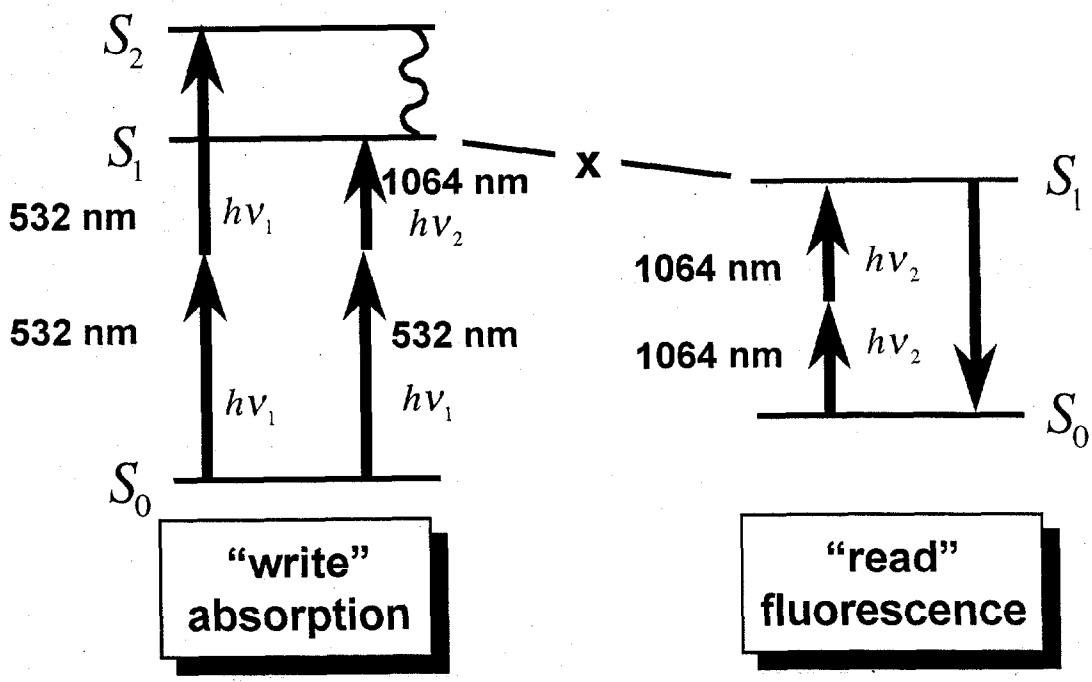

Figure 2b: Two photon conversion and excitation schemes of spirobenzopyran.

Anthracene/Anthracene Dimer

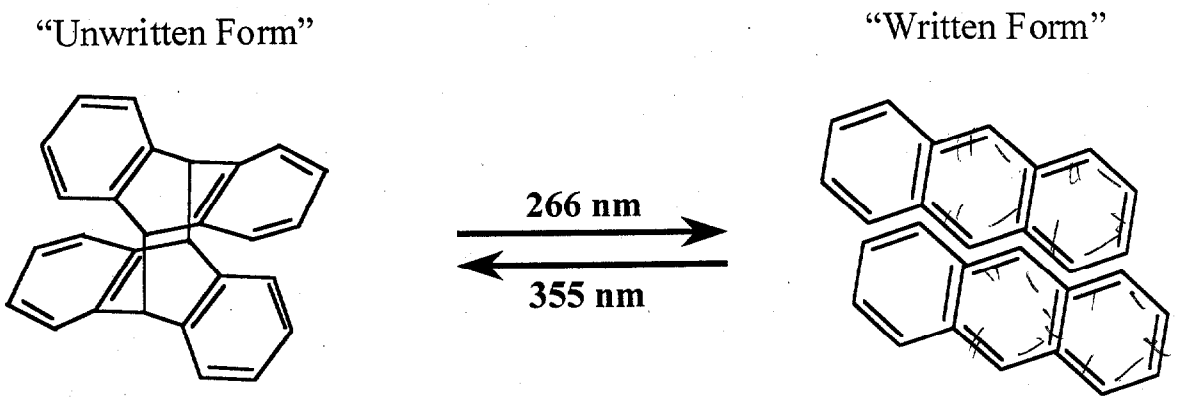

Figure 3a: Two photo-induced conformations of anthracene.

rearrange double bond

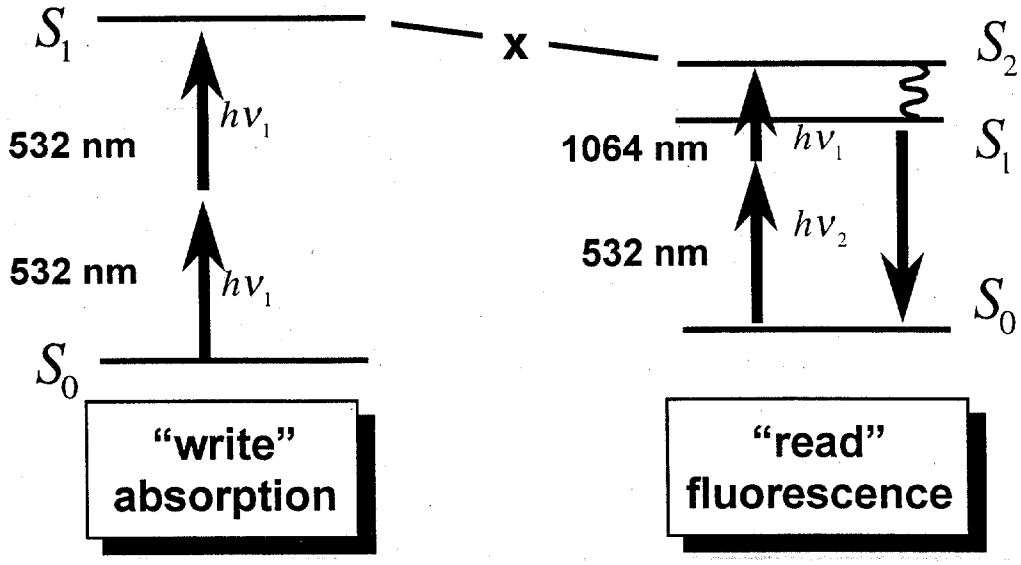

Figure 3b: Two photon conversion and excitation schemes of anthracene.

of 355 nm light or one photon 532 nm light and one photon of 1064 nm light. The resulting fluorescence is then monitored at 410 nm. Following emission of a photon, the "written" monomer form is then converted back to the dimer.

Both dyes are polymerized into polymethylmethacrylate (PMMA) matrices, which acts as structural supports and constraints, fixing the dye molecules into place. Optimization of the polymerization process was achieved by varying the temperature of the initiating reaction and initiator concentration, with the following procedure producing the most consistent and homogeneous optical memory materials. First, the dye is dissolved into a methyl methacrylate (Aldrich Chemical; Milwaukee, WI) solution at concentrations ranging between 0.1 to 1% (wt/wt). Three milliliters of dye/methyl methacrylate solution is then placed into a small glass vial. Once in the vial 0.5% (wt/wt) of benzoyl peroxide (Aldrich Chemical; Milwaukee, WI) is added to each vial as an initiator to the polymerization of the methyl methacrylate. The vials are then capped and shaken until all of the benzoyl peroxide has dissolved. Once dissolved, the caps are removed from the vials and they are placed in a hot water bath, where they were submerged to a point where the solution inside the vial was below the water level of the bath. The hot water bath is maintained at a temperature of approximately 85-90 °C for approximately 15 minutes. At this time the polymerization has begun and the solution is noticeably more viscous. This viscous solution is then placed into a second water bath that is maintained at a temperature of 55 °C. The vials are left in the 55 °C water for 12 hours at which time the entire solution has polymerized and the vial is broken releasing the polymer.

Prior to the fabrication of spirobenzopyran doped 3D-ORAM materials, the spirobenzopyran was purified by recrystallization from methanol to remove any impurities which may reduce its quantum yield. Upon polymerization of spirobenzopyran into the PMMA matrix, a yellowish orange polymer is formed. The polymers containing the higher weight percents of dye are more orange than the polymers with the lower concentration of dye. Initial tests reveal that upon exposure to ultraviolet light, the polymer is converted to the "written" form which is a much darker reddish purple color than the original orange "unwritten state." However, this excited state (red color) then thermally relaxes to the ground state within 20 minutes under ambient conditions. To overcome this problem, we have investigated the use of low temperature conditions for long term storage. For this evaluation, samples were placed in a freezer at –10 °C, and the fluorescence of the samples was visually monitored periodically over a three month period. Based on these observations, the conversion of the "written" state to the "unwritten" state still occurs to a significant extent even at reduced temperatures. However, this reduced temperature does prevent the spirobenzopyran material from significant conversion over the period of several days to a couple of weeks, but the transformation still occurs making this material unsuitable for most applications.

Anthracene doped polymers were also created using the same polymerization technique, and the resulting polymers had a slight yellowish color. The polymers with the higher weight percent of anthracene exhibited the most yellowish color. As with the spirobenzopyran doped polymers, several different polymers were made at various weight percents of anthracene, to determine the minimum amount of dopent necessary for a significant signal. The anthracene and anthracene dimer reaction was chosen as a primary candidate for investigation due to the stability of the complex. It has been reported in the literature that the anthracene and anthracene dimer do not exhibit any noticeable conversion at room temperature to different conformations, allowing for a much more stable and reliable sample matrix. Long term stability tests were performed on the anthracene doped polymers. Initial investigation of this material revealed that it was much more stable than the spirobenzopyran while not sacrificing significantly in the area of fluorescence efficiency (quantum yield). These materials have been stored at both room temperature and in a freezer at – 10 °C. The fluorescent state, the "written form," of the dye was then regularly monitored visually over the same three month time period as the spirobenzopyran doped polymers. Over this three month time period, no noticeable change in fluorescence intensity was visible for either the frozen or the room temperature samples. The unwritten form of these anthracene based polymers was also investigated, and it was found that over a three month time period, there appeared to be a slight conversion of the "unwritten" form to the "written," fluorescent, form for the samples kept at room temperature. However, even with this slight conversion, it appears that the reaction kinetics for this process are very slow and that this material is more than suitable for exposure periods of a couple of months or less.

In addition to the spirobenzopyran and anthracene 3-D ORAM materials, we have begun to investigate other possible photochromic dyes. These include 9-methylanthracene, fulgides, and diarylalkenes. It has been reported in the literature that these compounds have the possibility of being good candidates for optical data storage devices due to their photochromic behavior and stability of their different states. Along with testing other photochromic materials, we have also begun to investigate other means of immobilization of dye molecules into polymer matrices, such as dissolution and evaporation of the solvent.

III. Irradiation of Samples

To test the effectiveness of these 3-D ORAM materials for the detection of ionizing radiation, irradiation of the two different materials, spirobenzopyran and anthracene, is being performed. The samples have been placed in front of a sealed source of Cf-252 with a fluence rate of approximately 3×10^3 neutrons/cm^2•s. Following exposure, these samples will be placed in the reading device to determine if there is any noticeable difference in fluorescence intensity between the exposed sample and an unexposed control sample. Using the optical readout system, the relative decrease in fluorescence between the two samples as well as the tracks left in the irradiated sample will be measured.

IV. Optical Readout System

Figure 4 shows the optical readout system that has been constructed for analysis of the 3-D ORAM materials. Based on the initial two photochromic dyes chosen for testing, a Nd:YAG laser (Spectron Laser Systems; Warwickshire, U.K.) has been selected as the excitation source. This laser is capable of producing wavelengths at the fundamental, 1064 nm, the second harmonic, 532 nm, and the third harmonic, 355 nm, for excitation. Depending on the specific dye, and the operation to be performed, "writing" or "reading," the appropriate wavelengths are split into two beam paths that are focused into the sample at right angles to each other. The dye molecules located at the overlap of the two beams can then either be "written" to or "read" from quickly. By changing the focusing lens on the two different light paths, various types of addressing can be performed. A point by point addressing of the cube can be performed by either using two spherical lens or one spherical lens and one cylindrical lens. In the case of the spherical and cylindrical lens combination, addressing of an entire plane of the sample can be performed simply by varying the location at which light passed through the spherical lens is focused. By overlapping beams that have been focused by two cylindrical lens, lines of data locations can be addressed. Because these addressing techniques are based on the two photon absorption from crossed laser beams, the Gaussian intensity profile of the intersecting beams will provide an excellent means spatial resolution[1]. Therefore, by knowing the exact location of the two beams and their overlap region, highly resolved track information should be able to be obtained. For rapid readout, when track information is not required, or the rapid "writing" to of the 3-D ORAM material prior to irradiation, a single photon excitation scheme employing a cylindrical lens will allow for addressing of an entire plane of the polymer matrix.

For initial studies, the sample is placed on an x-y-z translational stage that is used to position the 3-D ORAM materials for addressing. However, for more precise measurements of particle tracks, the two light paths will be varied independently of one another by computer controlled mirror mounts, allowing slight angular changes to be made very precisely. To provide a simple and reliable means of switching between the "reading" and "writing" configurations, key optical components such as mirrors and beam splitters have been placed on kinematic bases. The final key component of the system is the detector. Due to the pulsed nature of the excitation step, and the need for planar readout (imaging) an intensified charge coupled device (ICCD) (Princeton Instruments; Trenton, NJ) was chosen. This ICCD offers a minimum gate width of 5 ns which is much shorter than the fluorescence signal generated from anthracene and spirobenzopyran based optical memories.

V. Conclusions

We have fabricated two different types of 3-D ORAM materials, spirobenzopyran doped PMMA polymers and anthracene doped PMMA polymers. These polymers have been characterized based on their fluorescence efficiency, ability to be copolymerized and their stability over both long and short term exposures to ambient and freezing temperatures. From this characterization it was found that the anthracene doped polymers are both very fluorescent after immobilization into a polymer matrix and still retain their ability to convert between monomer and dimer at the concentrations studied. In addition, both states of the complex exhibit long term stability at both ambient and freezing temperatures. Spirobenzopyran based 3-D ORAM materials however, failed to exhibit stability of the "written" state at either ambient or reduced temperatures, making it unsuitable for most dosimetry applications.

An optical readout device for the 3-D ORAM material has been constructed, that should be capable of monitoring individual tracks left in the polymer by ionizing radiation sources. This system consists of two orthogonal light paths that intersect in the 3-D ORAM material producing a two photon absorption for either "writing" or "reading" purposes. Initial tests demonstrated the usefulness of this system for the addressing and reading of specific "bits" in the polymer matrices.

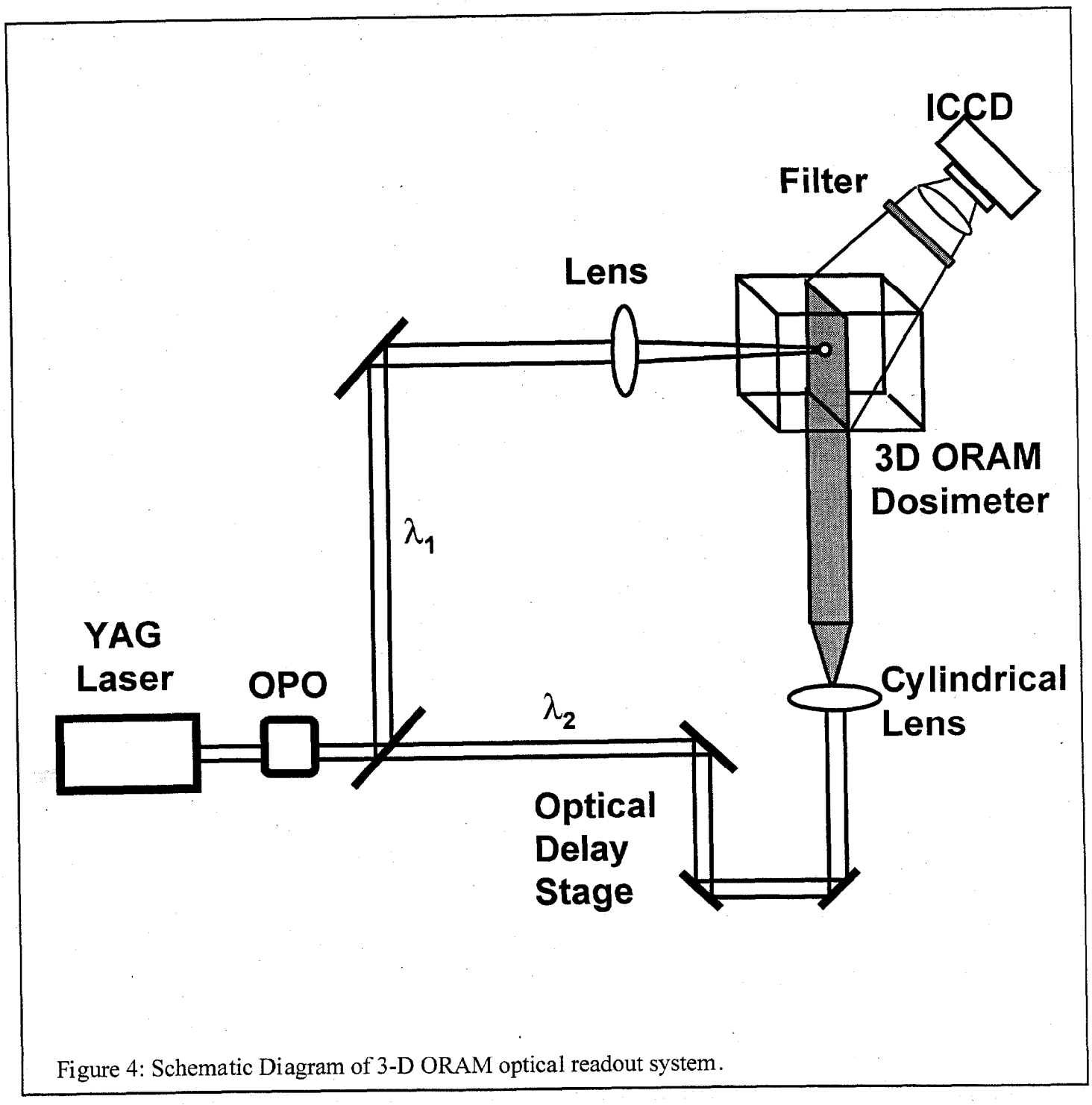

Figure 4: Schematic Diagram of 3-D ORAM optical readout system.

VI. Acknowledgements

This research is sponsored by the U.S. Department of Energy under contract DE-AC05-960R22464 (NN-20 Program) with Lockheed Martin Energy Research Corp. B. M. Cullum and J. Mobley are also supported by an appointment to the Oak Ridge National Laboratory Postdoctoral Research Program administered jointly by the Oak Ridge Institute for Science and Education and Oak Ridge National Laboratory.

VII. References

1. J. Mobley, J. S. Bogard, M. Moscovitch and T. Vo-Dinh, "Signal Expressions and Initial Design for a 3-D ORAM Radiation Dosimeter Reader," SPIE Proceedings 3534, (1999).

2. M. Moscovitch and D. Emfietzoglou, "Simulation of Radiation Effects on Three-Dimensional Computer Optical Memories," J. Appl. Phys. 81, 169-178 (1997).

3. G. W. Phillips, A. K. Readshaw, G. O. Brown, R. G. Weiss, N. A. Guardala, J. L. Price, S. C. Mueller and M. Moscovitch, "Observation of Radiation Effects on Three-Dimensional Optical-Random-Access-Memory Materials for Use in Radiation Dosimetery," submitted for publication in Int. J. of Applied Radiation and Isotopes.

4. M. M Wang, S. C. Esener, F. B. McCormick, I. Cokgor, A. S. Dvornikov and P. M. Rentzepis, "Experimental Characterization of a Two-Photon Memory," Opt. Lett. 22(8), 558-560 (1997).

5. A. S. Dvornikov, S. C. Esener and P. M. Rentzepis, "Three-Dimensional Optical Storage Memory by Means of Two-Photon Interaction," Optical Computing Hardware, J. Jahns and S. H. Lee (Eds), Academic Press Inc. (Boston) 287-325 (1994).

6. A. S. Dvornikov and P. M. Rentzepis, "Anthracene Monomer-Dimer Photochemistry: High Density 3D Optical Storage Memory," Res. Chem. Intermed. 22(2), 115-128 (1996).