Three-Dimensional Optical Random Access Memory Materials for Use as Radiation Dosimeters

Brian M. Cullum,[†] Joel Mobley,[†] James S. Bogard,[†] Marko Moscovitch,[‡] Gary W. Phillips,[§] and Tuan Vo-Dinh*,[†]

Oak Ridge National Laboratory, Bethel Valley Road, MS-6101, P.O. Box 2008, Oak Ridge, Tennessee 37831-6101, Georgetown University Medical Center, 3970 Reservoir Rd NW, Washington DC 20007, and U.S. Naval Research Laboratory, 4555 Overlook Avenue SW, Washington D.C. 20375

This article describes the development of the first three-dimensional optical random access memory (3D-ORAM) material and readout system for monitoring energetic neutrons. Two different photochromic dyes, 5′-chloro-6-nitro-1′,3′,3′-trimethylspiro-[2H-1-benzopyran-2,2′-indoline] (spirobenzopyran) and anthracene, have been investigated for use in these 3-D ORAM dosimeter materials. These dyes were immobilized in a poly(methyl methacrylate) support, and the resulting dosimeter materials were irradiated with neutrons from a Cf-252 source. Fluorescence measurements from the dosimeter show a dramatic decrease in the overall fluorescence intensity of the 3D-ORAM dosimeter exposed to the Cf-252, relative to a nonirradiated dosimeter. In addition, a two-photon excitation readout system has been developed for determining characteristics of the radiation that are necessary for estimating dose.

The monitoring of ionizing radiation, such as energetic neutrons, is of great importance in both terrestrial environments such as a nuclear facilities and extraterrestrial environments such as the space station or other planets like Mars. At nuclear plants, there is a strong need for practical radiation dosimeters to monitor personnel neutron exposures. In environments outside the confines of the Earth's atmosphere, astronauts could be subjected to a great deal more radiation than persons on Earth. Over the years, several different methods have been developed for neutron dosimetry. The most common personnel dosimeters for the monitoring of neutrons are thermoluminescent dosimeters.[1] However, the thermoluminescence effect typically depends on the availability of thermal neutrons. To provide sensitivity to energetic neutrons, these dosimeters are placed on individuals and the albedo effect, neutron moderation by the wearer's body to thermal energies and reflection back to the dosimeter, is utilized.[1] The albedo effect, however, has a very strong dependence on the energy of the incident neutrons, and therefore the neutron energy must be known for an accurate dose estimate. Without a precise neutron energy spectrum, errors as great as 10−100% are possible.[2] For application in situations where the neutron energies are well known (e.g., nuclear facilities), these dosimeters work well. However, in nuclear waste sites or in space explorations, where the energy spectrum is less well known, it is important to have a dosimeter that is capable of measuring neutron dose accurately without foreknowledge of neutron energy.

Moscovitch and Emfietzoglou, at Georgetown University, have recently modeled the effect of heavy charged particles (protons, α-particles, and $^{12}C^{3+}$) on three-dimensional (3D) optical memory materials that are being developed for computer data storage.[3] The function of these 3D memory materials or 3D-ORAMs (three-dimensional optical random access memories) is based on the fluorescence of a photochromic dye that has been immobilized in a polymer matrix. These materials have previously been used for optical data storage.[4–9] Photochromic dyes used in these memory materials must exist in at least two different isomeric forms, which can be interconverted from one form to another by the absorption of light. One of the two isomeric forms is typically fluorescent, while the other is not fluorescent. Therefore, by converting the dye to the fluorescent isomeric form, a single bit of digital data can be recorded in the polymer cube. This bit of data, can then be excited and read out based on its fluorescence, with a "1" represented by a fluorescent area and a "0" represented by a nonfluorescent area. To erase the data, a different wavelength of light is used to convert the fluorescent, "written," form back to the nonfluorescent, "unwritten," form. By using two-photon

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* Corresponding author: (e-mail) vodinht@ornl.gov.
† Oak Ridge National Laboratory.
‡ Georgetown University Medical Center.
§ U.S. Naval Research Laboratory.

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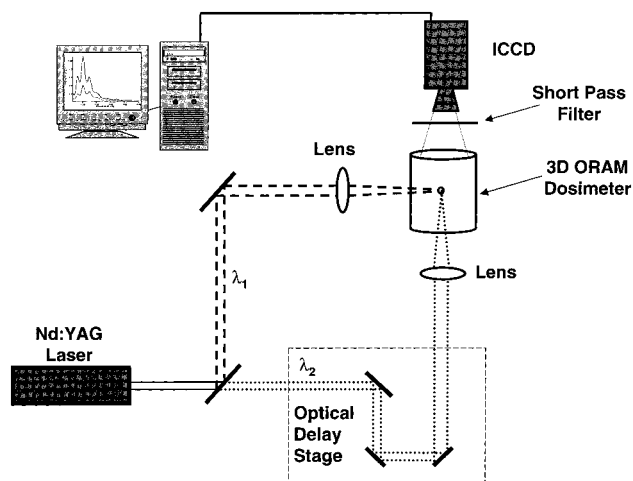
Figure 1. Schematic diagram of a two-photon crossed beam excitation scheme for reading or writing to the 3D-ORAM material.

excitation of these 3D-ORAMs, in a crossed beam configuration for the writing process, it is possible to address a single point within the cube.[4,9] The volume of this single point is defined by the overlap of the focal volumes of the two overlapping beams. To read out the data that has been "written" to the 3D-ORAM material, either a two-photon crossed beam excitation scheme (see Figure 1) or a single-photon excitation using a planar beam can be employed. The crossed beam configuration will allow reading of a single bit at a time (serial readout), while fluorescence from the single planar excitation beam can be imaged onto a two-dimensional detector such as a charge-coupled device (CCD) allowing for simultaneous readout of multiple bits (parallel readout).

Due to the nature of the excitation mechanism and to the data storage format, these 3D-ORAM materials are subject to data alteration by ionizing radiation, much the same as conventional semiconductor-based memories are today.[3] While this is a problem that has to be addressed and overcome by the optical data storage community, it promises to be useful as a new method for detecting ionizing radiation consisting of neutrons or heavy charged particles (HCP), offering significant advantages over current methods. As a result of the energy deposited in the 3D-ORAM along the path of an incident HCP or neutron, photochromic dye molecules are converted from one isomeric form to other, thereby causing a change in the overall fluorescence of the polymer cube. This overall change in fluorescence can then be measured and correlated with radiation dose, much the same as in a thermoluminescence dosimeter. However, unlike with thermoluminescence dosimeters, a two-photon crossed beam readout system should be able to determine the spatial characteristics of individual particle tracks left behind in the 3D-ORAM dosimeter by the ionizing radiation. One should be able to derive the energy spectrum of incident neutron or HCP radiation from particle track characteristics such as penetration depth and the density of the fluorescence changes.[10] The effect of various charged particles (protons, α-particles, and $^{12}C^{3+}$) on thin films of poly(methyl methacrylate) (PMMA) doped with spirobenzopyran was demonstrated previously by Phillips et al.,[2] who used confocal laser

microscopy to show that radiation of various energies, ranging from 0.6 to 2.5 MeV, could be distinguished by the width of the depth profile and the fluorescence intensity. It has been shown, however, that the fluorescent form of spirobenzopyran, merocyanine, is unstable at ambient temperatures.[11] This makes it necessary to perform measurements on the dosimeter material immediately after exposure.

In this paper, we describe the development of the first 3D-ORAM dosimeters (based on anthracene- and spirobenzopyran-doped PMMA polymers) for the measurement of energetic neutrons, the effect of neutron radiation on these polymers, and the development of a crossed beam readout system that can be used for spatially resolved fluorescence imaging of the 3D-ORAMs. The signal readout system for these 3D-ORAM materials has been developed based on theoretical calculations[12] describing the configuration of the two beams that provides the optimum signal-to-background ratio.

Chemicals. The two photochromic dyes used in this work were 5′-chloro-6-nitro-1′,3′,3′-trimethylspiro-[2H-1-benzopyran-2,2′-indoline] (Chroma Chemicals; Yellow Springs, OH) and anthracene (Aldrich Chemical Co.; Milwaukee, WI). These dyes were immobilized in a PMMA matrix, for structural support, using a thermally initiated polymerization process. Prior to immobilization, the spirobenzopyran was purified by recrystallization from methanol. The anthracene was used without any further purification. Methyl methacrylate and benzoyl peroxide were also purchased from Aldrich Chemical and required no further purification.

3D-ORAM Fabrication. 3D-ORAM dosimeter materials were created through a three-step polymerization process. First, 3 g of methyl methacrylate was pipetted into a small vial, along with various weight percents of the dye to be immobilized. Concentrations of dye that were tested ranged from 0.1 to 1.0% (w/w). Concentrations higher than 1.0% were not investigated due to the insolubility of these dyes in the methyl methacrylate at higher concentrations. Once the dye was mixed with the methyl methacrylate, it was allowed to dissolve completely prior to the addition of the initiator, 0.5% (w/w) benzoyl peroxide. Following dissolution of the benzoyl peroxide, the vials were placed in a water bath that was maintained at a temperature of 90 °C for ∼15 min, thus initiating the polymerization process. After 15 min, the solution begins to become viscous and the temperature of the water bath is reduced to 50 °C, to prevent bubble formation in the partially polymerized matrix. The samples are then kept in the 50 °C water bath for 12 h, allowing the methyl methacrylate to fully polymerize. Once the polymerization is complete, the vials surrounding the samples are broken in order to extract the polymer cylinder, which is then cut and polished with lapping paper. Lapping paper with grains ranging from 32 to 0.5 μm was used to create the optically flat surfaces of the polymer material.

3D-ORAM Irradiation. Irradiation of the 3D-ORAM materials was performed by placing them 0.5 m from an unmoderated sealed source of Cf-252 in a low-scatter configuration. Total neutron fluence at the location of the 3D-ORAM sample was (6.70 ± 0.34)

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$\times~10^{10}~cm^{-2}$. The mean neutron fluence rate at this location was $\sim 3 \times 10^3~cm^{-2}~s^{-1}$.

Optical Readout System. The optical readout system used in this work is primarily composed of the following: (1) a Q-switched, frequency-doubled Nd:YAG laser (Spectron Laser Systems, Warwickshire, U.K.), (2) dielectric mirrors, (3) an $x-y-z$ translational stage for sample placement, (4) a short-pass filter to reject the excitation source, and (5) an intensified charge-coupled device (ICCD; Andor Technologies, South Windsor, CT). A schematic diagram of the optical readout system is shown in Figure 1. The laser beam is split into two parts upon exiting the housing, and the two different beams are steered to the sample by dielectric mirrors. In the shorter of the two beam paths, a variable optical delay was constructed (see dashed rectangle in Figure 1). This optical delay stage is constructed using multiple dielectric mirrors that can be translated together, thus allowing both of the excitation beams to strike their focal point at the same time. Both of the orthogonal beams are then focused down to the same point inside the polymer using 1-in.-diameter biconvex lenses, each having a focal length of 2 in. This crossed beam excitation allows the dye molecules, at the intersection of the two beams, to simultaneously absorb the energy of one photon from each beam, thereby providing an excitation equivalent to the sum of the two individual photons. The resulting fluorescence, which occurs at shorter wavelengths than either of the two individual excitation beams, is then imaged on an ICCD after passing through a 500-nm short-pass filter. The ICCD was triggered using the Q-switch sync output of the laser. To optimize the signal-to-noise ratio of the resulting image, the optical gate width of the ICCD was kept at 300 ns. This time was determined based on the pulse-to-pulse jitter of the Nd:YAG laser. Images collected on the camera were then downloaded to a computer for further analysis.

RESULTS AND DISCUSSION

Dye Comparison. Two different photochromic dyes, spirobenzopyran and anthracene, were tested for use in 3D-ORAM dosimeters. PMMA is an excellent support matrix for these dyes since plastics are radiometrically similar to human tissue. The excitation schemes for these two different dyes are shown in parts a and b of Figure 2, respectively. When polymerized, the spirobenzopyran remains in its nonfluorescent state. However, upon the absorption of 355-nm light (or the equivalent absorption of one photon of 532-nm light and one photon of 1064-nm light), the spirobenzopyran is converted to the merocyanine form, which can be made to fluoresce following excitation with 532-nm light (or the simultaneous absorption of two 1064-nm photons).

Prior to irradiation of the sample, stability tests of the spirobenzopyran samples were performed. These experiments consisted of converting the spirobenzopyran into the merocyanine form and monitoring the overall fluorescence of the 3D-ORAM polymer over time with a fiber-optic-coupled fluorometer (Perkin-Elmer; Norwalk, CT). From these experiments, it was found that, by leaving the polymer in ambient conditions, greater than 50% of the fluorescent (merocyanine) form of the dye was converted back into the nonfluorescent form within 1 h of the original conversion. The use of spirobenzopyran for radiation dosimetry, therefore, would be complicated by this rapid inherent interconversion, unless analysis occurred immediately after exposure or
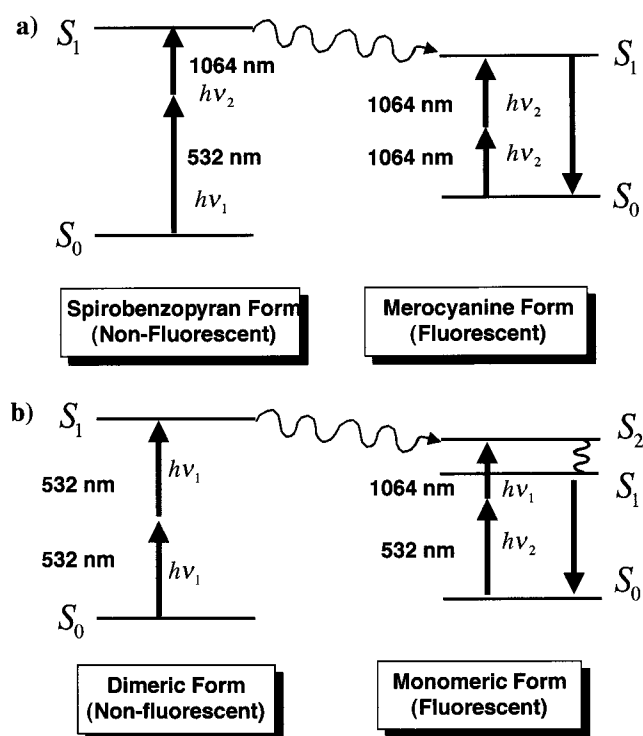
Figure 2. Conversion and excitation schemes for the photochromic dyes (a) spirobenzopyran and (b) anthracene.

the interconversion rate were significantly reduced. To reduce the rate of conversion of the fluorescent form of the dye to the nonfluorescent form, the samples were converted to the fluorescent form and stored in a freezer at $-10~^{\circ}C$, while fluorescence measurements were taken over time. From these experiments, it was found that the lower temperature did reduce the interconversion; however, greater than 50% of the merocyanine form had been converted back to the nonfluorescent form within one month.

Figure 2b shows the excitation scheme for the anthracene-doped 3D-ORAM materials. Following polymerization of the anthracene-doped polymer, the anthracene molecules typically reside in a nonfluorescent dimeric form. However, upon absorption of 266-nm light or the simultaneous absorption of two photons of 532-nm light, the dimeric form is broken apart yielding monomeric anthracene. 3D-ORAM polymers based on this dye are yellowish in color in both the fluorescent and nonfluorescent states. In its monomeric form, the anthracene can be excited by either the absorption of a single photon of 355-nm light or the simultaneous absorption of a 1064-nm photon and a 532-nm photon. Once excited, the anthracene molecules fluoresce.

The stability of the two different states of the anthracene-doped 3D-ORAM materials was investigated by monitoring the fluorescence of the polymer matrix with the same fiber-optic-coupled fluorometer setup used for the spirobenzopyran monitoring. Both the fluorescent (monomeric) form and the nonfluorescent (dimeric) form showed less than 1% interconversion, at room temperature, over the three-month period in which they were examined. These results indicate that anthracene-based 3D-ORAM materials are much more photostable than spirobenzopyran materials.

Effect of Irradiation on the 3D-ORAM Samples. To verify the effect of radiation on anthracene-doped 3D-ORAM samples, two polymers containing 1% (w/w) anthracene were placed on
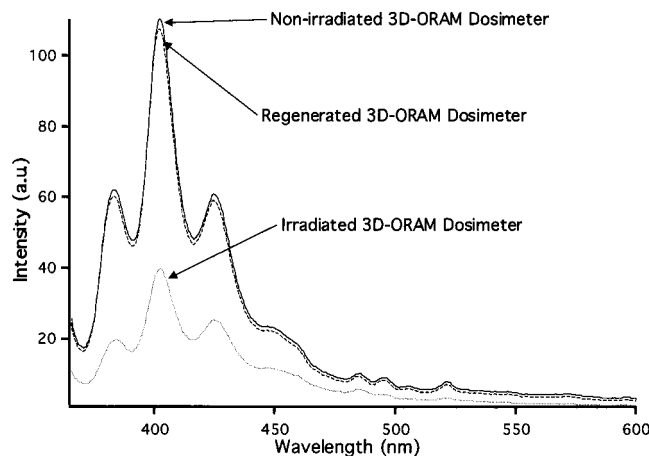
Figure 3. Fluorescence emission spectra of anthracene-doped 3D-ORAM dosimeter matrix prior to (solid line) and after irradiation by Cf-252 (dotted line) as well as regenerated by UV light (dashed line).

Figure 4. Average fluorescence intensity of 3D-ORAM dosimeters at the fluorescence maximums of the spectra. (A) represents the fluorescence intensity of a nonirradiated sample prepared in the same batch as the irradiated sample and the control. (B) represents the fluorescence intensity of the of the nonirradiated control sample. (C) represents the fluorescence intensity of the irradiated sample prior to irradiation. (D) represents the fluorescence intensity of the irradiated sample. (E) represents the fluorescence intensity of the irradiated sample after exposure to UV light. Error bars represent the standard deviation of the three measurements obtained for each sample.

an ultraviolet ("black") light source to convert the anthracene dimer into its fluorescent (monomeric) form. Following conversion, one sample was exposed to neutrons from Cf-252 while another was stored in a radiation-free environment under the same environmental conditions. After exposure to $(6.70 \pm 0.34) \times 10^{10}$ neutrons/cm^2, the sample was examined using a fiber-optic probe coupled to a fluorometer. The excitation wavelength of the fluorometer was set to 355 nm, which is absorbed by the S_1 band of anthracene. The resulting fluorescence emission spectra of the irradiated and nonirradiated 3D-ORAM samples are shown in Figure 3. From these spectra, the characteristic vibronic bands of anthracene between 370 and 470 nm are apparent. It is also apparent from this figure that the fluorescence intensity of the nonirradiated sample is much greater than the intensity of the irradiated sample. This suggests that the energetic neutrons passing through the sample cause the monomeric form of the anthracene to be readily converted back into the dimeric form. While the exact mechanism of this process is still under investigation, it most likely occurs as the result of localized heating along the paths of protons scattered in collisions with the incident neutrons. The dotted line in Figure 3 shows the fluorescence emission spectrum of an anthracene-doped 3D-ORAM polymer that has been irradiated with neutrons from Cf-252. From this spectrum and the spectrum of the nonirradiated sample (solid line), it is apparent that the fluorescence intensity of the irradiated sample is only ~35% of that of the nonirradiated sample (at the fluorescence maxima). Also shown in Figure 3 is the fluorescence spectrum of the irradiated sample following exposure to a black light (UV) source for 1 h (dashed line). From this spectrum, it is apparent that the sample has regained greater than 98% of its original fluorescence intensity. This result suggests that the majority of the anthracene monomer is not destroyed, but converted back to the dimeric form upon exposure to energetic neutrons. This will allow for repeated use of a 3D-ORAM dosimeter, possibly leading to a near-real-time readout and regenerable system.

Quantitative analyses of the variability in the 3D-ORAM fabrication process, and in the irradiation and regeneration processes are shown in Figure 4. Average fluorescence intensities of three measurements performed on individual 3D-ORAM
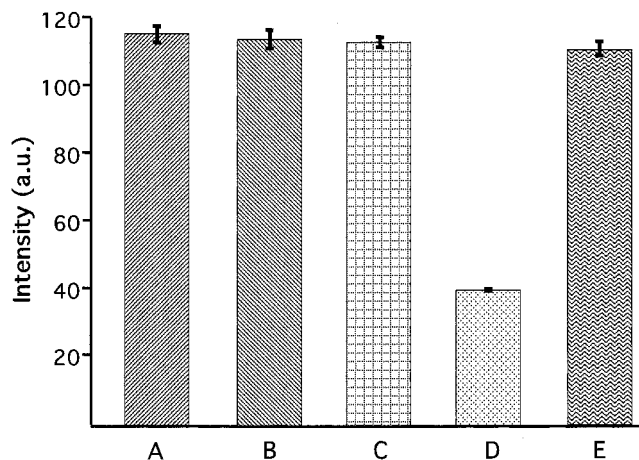
dosimeters under various conditions are shown in Figure 4, with the error bars corresponding to the standard deviations of those measurements. To quantify the differences between 3D-ORAM dosimeters produced from the same batch, the fluorescence intensity of three identical polymers was measured. The values of these intensity measurements are 115 ± 2.4, 114 ± 2.6 and 112 ± 1.6, corresponding to samples A, B, and C, respectively, with a mean and standard deviation of 113.7 ± 3.9. The individual fluorescence intensities are not different from the mean within the 95% confidence interval. Measurements from samples A and B represent the fluorescence intensities of the controls. Sample C represents the fluorescence intensity of the irradiated sample prior to neutron irradiation. Sample D represents the fluorescence intensity of the same dosimeter in sample C following irradiation with 6.7×10^{10} neutrons/cm^2 from a Cf-252 source. The average value and standard deviation of three fluorescence intensity measurements taken on sample C is 39.6 ± 0.3. This corresponds to a reduction in fluorescence intensity of ~65% following irradiation. Also shown in Figure 4, sample E, is the fluorescence intensity of the irradiated sample following regeneration by exposure to a black-light source for 1 h. The average fluorescence intensity of this sample and its associated standard deviation was found to be 110 ± 2.2, which is the same as the mean of the nonirradiated samples, within the 95% confidence interval. This shows that there is no significant difference in the fluorescence intensity before irradiation and after regeneration of the 3D-ORAM with UV light.

Crossed Beam Optical Readout System. In addition to the development and testing of 3D-ORAM neutron dosimeter materials that are both stable at room temperature and possess dimensions large enough to record neutron tracks left behind by scattered protons, we have also constructed a simple optical readout system for monitoring these tracks. The system we have developed (see Figure 1) is based on the same design used for
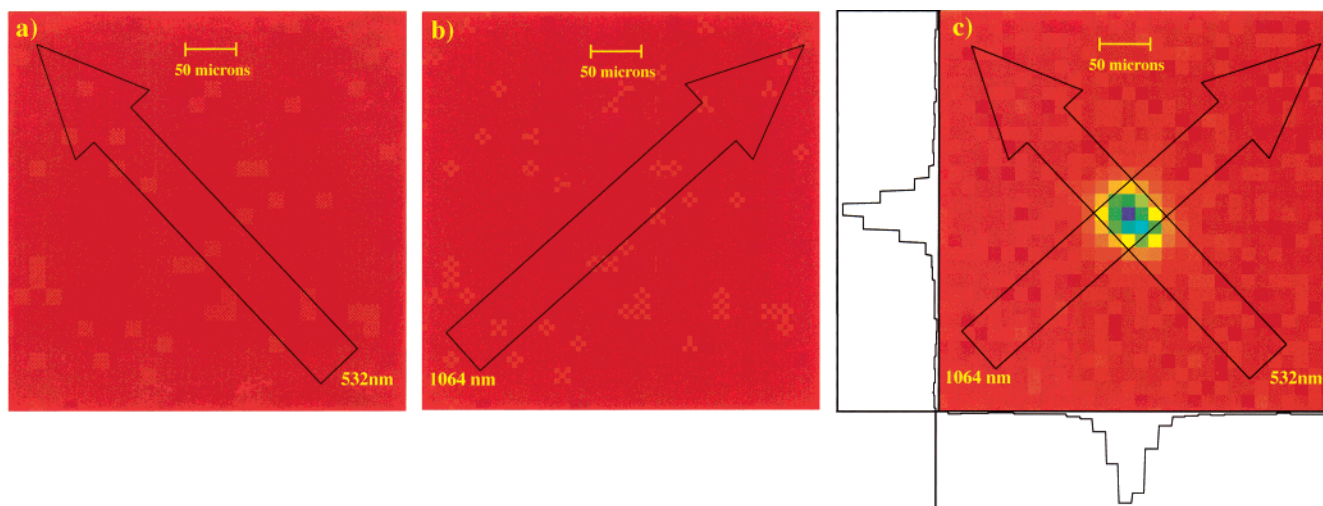
Figure 5. Fluorescence image of an anthracene-doped 3D-ORAM dosimeter using the crossed beam optical readout system. (a) and (b) show the image of the sample with only the 532-nm beam and 1064-nm beam passing through the sample, respectively. (c) shows the resulting fluorescence image obtained when both beams are present.

writing to 3D optical memory devices for optical computing purposes. As described earlier, the system consists of two laser beams that enter the 3D-ORAM dosimeter sample orthogonal to each other and are focused to the same point. For the anthracene fluorescence excitation, one of the beams was the first harmonic of the Nd:YAG laser (1064 nm) and the other was the second harmonic (532 nm). By placing an anthracene-doped 3D-ORAM dosimeter on the $x-y-z$ translation stage, located at the focus of the two lasers, fluorescence images can be obtained at specific locations within the sample. The sample can then be translated very precisely using the $x-y-z$ translational stage to monitor different regions in the dosimeter. Panels a and b of Figure 5 show two images of the anthracene-doped 3D-ORAM dosimeter upon excitation with 532- and 1064-nm laser light, respectively. Each arrow in these figures represents the major axis and direction of propagation of the different wavelength beams through the sample. There is no apparent fluorescence from the anthracene in either of these images. However, when both beams are allowed to pass through the dosimeter at the same time, as shown in Figure 5c, a region of fluorescence is observed at the overlap of the two beams. This fluorescent region is ~90 μm in diameter and has a maximum intensity in the center of the overlapping beams. This maximum occurs in the center of the two beams since this is the location where the power density of the two lasers is the greatest. This observation is in agreement with previous theoretical calculations of the crossed beam laser excitation process.[12] Histograms of the fluorescence intensity of the image in both the x and y planes are displayed on the sides of the image, revealing the sharp decrease in the fluorescence intensity on all sides of the fluorescent spot. This is expected since the power density of each of the overlapping excitation beams decreases rapidly with distance from the focal point. The 90-μm diameter of these fluorescence spots is believed to be a result of "pitting" of the sample by the 1064-nm laser beam. This diameter is much larger than the diffraction-limited size of the focused laser beams, suggesting that the beams are being scattered somewhat at the focal point. In addition, upon visual examination of the 3D-ORAM dosimeters, a small imperfection in the polymer is noticed following excitation. This imperfection occurs only as a result of

focusing the 1064-nm beam to a point and not the 532-nm beam. This is believed to be due to the increased absorption of 1064-nm photons (over 532-nm photons) by the PMMA, resulting in a localized heating of the polymer which generates a small fracture. This small fracture then causes light at the focus of the two laser beams to be scattered, creating a larger excitation area than is expected from optical diffraction theory. However, since this small fracture only occurs at the focus of the 1064-nm laser, it should be possible to prevent fractures by varying the laser powers of the two beams. This will in turn permit us to obtain much more localized images. These images could then be used to monitor the tracks left behind by protons scattered from individual neutrons. Information from the tracks, such as path length and the density of the fluorescence changes along the track, can then be used to determine dosimetrically important quantities such as particle energy and linear energy transfer.

CONCLUSIONS

We have demonstrated, for the first time, the feasibility of using 3D-ORAM materials as radiation dosimeters for monitoring energetic neutrons. Of these 3D-ORAM materials, anthracene-doped PMMA polymers offer a much more stable dosimeter that does not interconvert between the different states at room temperature for periods of less than three months. Due to the compactness and light weight of these 3D-ORAM dosimeters, they would provide an excellent radiation capture device for applications as diverse as radiation monitoring of hazardous waste sites and future space exploration. The use of these materials in manned space exploration is particularly intriguing, since it is important to measure the amount and type of radiation that would be expected to affect personnel and equipment. Measuring neutron radiation is expected to be particularly important in the human exploration of Mars, for instance. The flux of neutrons reaching the Martian surface is expected to be much greater than that experienced on Earth because of the thinner Martian atmosphere. By placing 3D-ORAM polymers on a Martian lander, and returning them to Earth for examination, it should be possible to determine the fluence and energy spectrum of the incident radiation