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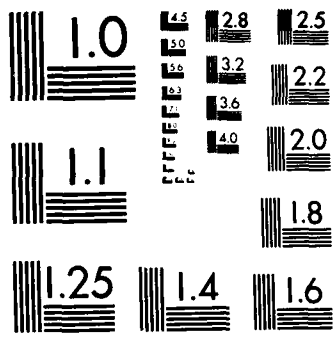

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Fast Burning of Persistent Spectral Holes in Small Laser Spots Using Photon-Gated Materials

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FAST BURNING OF PERSISTENT SPECTRAL HOLES IN SMALL LASER SPOTS USING PHOTON-GATED MATERIALS

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ABSTRACT: We report extremely fast (30 ns) burning of detectable persistent spectral holes in 200 μm diameter laser spots using a new photon-gated donor-acceptor material: a derivative of zinc-tetrabenzoporphyrin as a donor with chloroform acceptors in a poly(methyl methacrylate) thin film. The fast burning pulse near 630 nm was accompanied by a 200 ms gating pulse at 488 nm to produce the $\simeq$ 1 % deep spectral holes in transmission. This result illustrates one crucial advantage of photon-gated materials over single-photon materials: greatly increased reading fluences can be tolerated, allowing fast burning in small laser spots to be easily detected.

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nsburn

Persistent spectral hole-burning (PHB) in inhomogeneously broadened transitions in solids has been proposed as the foundation for a frequency domain optical storage (FDOS) system [1] [2] in which the presence or absence of a spectral hole at a particular laser frequency is utilized to encode as many as 1000 or more bits in the frequency domain within a single focused laser spot. The future success of the FDOS concept will rely on progress in several technological and engineering areas [3] ; however, the most critical research problems at present concern the storage material itself [4].

Most previously studied PHB materials have utilized linear, single-photon (or one-color) mechanisms. Modeling studies indicate that such mechanisms have serious limitations for FDOS applications [5] due to destructive readout. Destructive reading occurs because holes written with burning times in the 10-100 ns range in focused laser spots are usually quite shallow, and reading intensities large enough to give useful detected signal-to-noise can wash away the written information by burning of the entire frequency range scanned by the laser. In one crucial experimental study of a single-photon material [6], a sophisticated form of laser FM spectroscopy had to be utilized in order to detect holes written in 100 ns; further, the laser spot size had to be kept large (7 mm in diameter) in order to maintain the reading intensity at a tolerable level.

One way to achieve nondestructive reading would be to utilize photon-gated (or two-color) mechanisms, where hole formation occurs only in the presence of an additional gating light source [7]. In photon-gating, the first photon at λ_1 produces frequency-selective excitation within the inhomogeneously broadened absorption line to a long-lived intermediate state; the absorption of a second photon at λ_2 by the intermediate state results in a photoreaction (such as electron transfer) and thus a decrease in absorption (a spectral hole) at λ_1. After a search for such effects, several inorganic [8] [9] and organic [10] [11] materials were found that undergo photon-gating, although none has shown fast burning in small spots to date. A practical material for FDOS would probably have to produce detectable holes with 10 μm diameter laser spots in 100 μm thick films with burning (and reading) times in the 10-100 ns range [5] [12] .

Recently, we reported the observation of photon-gating by a new mechanism: donor-acceptor electron transfer from an excited donor chromophore to an acceptor molecule whose concentration can be modified [13]. The specific material consists of a tetrabenzoporphyrin derivative, meso-tetra(p-tolyl)-Zn-tetrabenzoporphyrin (TZT) in a thin poly(methylmethacrylate) (PMMA) host matrix, in the presence of chloroform ($CHCl_3$) acceptor molecules. The lowest $S_1 \leftarrow S_0$ transition near $\lambda_1 = 630$ nm has fairly high oscillator strength (0.17). From S_1, intersystem crossing to the lowest triplet T_1 occurs with high yield (0.8); this together with the fairly long triplet lifetime of 40 ms allows a large population of triplets to be formed [14]. If gating radiation near $\lambda_2 \simeq 500$ nm is present, $T_n \leftarrow T_1$ transitions occur and the excited electron transfers to the acceptor, forming a spectral hole. If λ_2 is not present, weak one-color holes are formed. The gating ratio, roughly defined as the ratio of the two-color hole depth to the one-color depth for equal burning times, is in the range 30-100. The high oscillator strength and photon-gated PHB allow fast burning experiments using thin films and focused laser spots, respectively, to be attempted for the first time.

This paper reports the observation of fast burning in small laser spots using the new thin-film TZT/PMMA/$CHCl_3$ material, a property that has not been achieved in any single-photon (or photon-gated) material to date. Using a pulsed dye laser and a 1 cm diameter spot, detectable holes were burned with a <u>single</u> 8 ns pulse at λ_1 together with a 200 ms gating pulse at λ_2. Moreover, using a cw dye laser and a 200 μm diameter laser spot, detectable holes were burned with λ_1 pulses as short as 30 ns, limited by the opening time of the acousto-optic

(AO) light modulator. Due to the high efficiency of this material, the holes were ≃ 1 % deep; thus the holes could be observed using simple transmission detection. These results underscore the crucial importance of high-efficiency photon-gated mechanisms in achieving practical frequency domain optical storage.

The samples routinely had an optical density at 630 nm in the range 0.5-1.0, thickness 50-100 μm, and a TZT concentration of 2 - 9 x 10^{17} molecules/cm^3. Details of the sample preparation and PHB mechanism may be found in Refs. [13] and [15] . A Ronchi ruling with 25 μ line widths was pressed against the sample and the number of light and dark regions in the transmitted beam was used to measure the laser spot size. The holes were burned either with a Molectron DL-14 pulsed DCM dye laser (8 ns nominal pulse width) pumped by a pulsed N_2 laser, or with a continuous-wave Ar^+-ion-pumped 3 Mhz linewidth DCM dye laser pulse produced by an acousto-optic modulator. The gating radiation was provided by a 17-20 mW beam from the Ar^+ ion laser at 488 nm. The holes were detected in transmission using only the cw dye laser and either a low-noise photodiode-preamplifier combination or an RCA 8852 phototube. The laser power variations during the 0.25 s laser scan were removed using a reference detector and a precision ratiometer (10 ms time constant); the ratiometer signal was offset and the result of 32-128 laser scans were averaged on a digital oscilloscope to yield a detection sensitivity of ≃ 0.1 % of the sample transmission. All measurements were performed at 1.4 K with the samples immersed in superfluid helium.

Figure 1 illustrates gated PHB using the pulsed dye laser for λ_1 in a 1 cm diameter spot. Part (a) of the figure shows the baseline optical density before burning. Particular care was taken to never stop the scanning so that no spectral features could be attributed to the cw reading dye laser. Figure 1(b) shows the result of one-color irradiation with a single 8 ns, 90 μJ pulse of light at λ_1 = 632 nm (0 GHz in the figure); no hole is observed.

Figure 1(c) shows that if an 8 ns λ_1 pulse is followed immediately by a 200 ms gating pulse at λ_2, a detectable spectral hole is easily formed. To the authors' knowledge, this is the fastest single-pulse hole-burning measured to date for any material. The temporal shape of the dye laser was measured to be a single pulse with no detectable long-time, low-intensity tail. The 4.1 GHz full-width at half-maximum (FWHM) for this hole was limited by the linewidth of the pulsed laser. The relative transmission change, 0.6%, was deep enough to be observed by simple transmission detection, which attests to the high sensitivity of this PHB material. The effective quantum efficiency, η_e, (defined in Ref. [12]) would be 0.5% for these conditions. This high efficiency results from the high TZT oscillator strength at λ_1, the high triplet yield, the long triplet lifetime, and the intrinsic efficiency of the electron transfer from the high-lying triplet levels. When the triplet yield is high, the bottlenecking effect of the triplet state is reduced compared to the situation with low triplet yield [6]. Figure 1(d) shows that a second two-color burn sequence produces a deeper hole.

The λ_1 burning fluence required in Figure 1(c) was only 120 $\mu J/cm^2$. This fluence can easily be reached using focused spots from a cw dye laser of modest power. However in this case, detection becomes more difficult because all of the λ_1 reading light must propagate through the same small focused laser spot. This is precisely why photon-gating is important for FDOS applications: in the limit of infinite gating ratio, reading intensities up to the saturation intensity (and perhaps higher) can be used without destruction of the written data. Fast burning in small spots then becomes an ultimate test of the gating ratio of the PHB material within the context of a particular detection technique.

Figure 2 shows a series of holes burned by the cw dye laser using 200 μm diameter spots in conjunction with the 200 ms gating pulse. Considering first the upper part of the figure, the λ_1 light of 1.5 mW power was controlled by an 80 MHz acousto-optic modulator with contrast ratio greater than 2000:1. To reduce hole-burning by the leakage through the AO modulator, a mechanical shutter of 1.9 ms duration bracketed the opening time of the modulator. It should be emphasized that the 19 mW gating beam was not focused tightly - a 0.5 cm diameter spot was sufficient. Figure 2(a) shows the baseline before burning; the curvature in this and in the other spectra in Figures 2 and 3 is repeatable and due to weak Fabry-Perot resonances in the optical system. Traces 2(b), 2(c), and 2(d) show the resulting spectrum for 100 μs, 10 μs, and 1μs λ_1 burn times, respectively. Trace 2(e) shows the shallow hole burned by the AO leakage light alone during the opening time of the 1.9 ms mechanical shutter. As the burning energy is decreased, the holes become first narrower and then shallower which is reasonable when the λ_1 burn time is much less than the triplet lifetime.

To study shorter burning times, higher burning power and less AO leakage light was required. (Smaller spots were also utilized and holes were detected, but mechanical vibrations of the optical cryostat prevented careful measurements under these conditions.) The lower half of Figure 2 displays the resulting spectra for 10 mW power at λ_1 using a 200 MHz AO modulator with 10,000:1 contrast ratio to produce the fast pulse. To prevent burning from the leakage light in this case, a second AO modulator with 10 μs opening time was used to bracket the opening time in addition to the mechanical shutter. Traces 2(f), 2(g), 2(h), and 2(i) show the detected holes for 300 ns, 100 ns, 50 ns, and 30 ns burn times, respectively. Again as one might expect, the hole first narrows and then becomes shallower as the burn energy is reduced. Trace 2(j) shows the very weak artifact hole burned if only the bracketing 10 μs AO and the mechanical shutter are opened.

The holes in Figure 2 were detected with a reading fluence of 1.0 mJ/cm^2, even though the 30 ns hole required only 960 nJ/cm^2 at λ_1 to form. In smaller spots the reading fluence would necessarily increase, thus it would be useful to know how much hole depth one sacrifices at higher reading fluences due to the weak one-color burning. Figure 3 shows the hole depth remaining after various irradiation fluences. To acquire these data, a hole was burned in 10 μs using two-color irradiation and a λ_1 fluence of 38 $\mu J/cm^2$ and then scanned with the minimum total fluence necessary for good signal-to-noise, 0.61 mJ/cm^2 (12 nW cw incident on the sample). It should be emphasized that the reading fluence was spread over a 30 GHz range, while the hole full-width at half-maximum was $\simeq$ 3.5 GHz. The first two points show that at this fluence the detected hole depth remains essentially constant. Then this same hole was irradiated (with the laser still scanning) with a higher intensity for 16 s and then rescanned with 0.61 mJ/cm^2 to detect the remaining depth. The data show the impressive result that large scanning fluences are required before 50 % of the hole depth is lost. This is a direct reflection of the photon-gated nature of this material; further, the relevant "gating ratio" under scanning irradiation conditions seems to be more like 10^3 - 10^4, depending upon how much loss of hole depth can be tolerated.

The role of power broadening during reading and writing is not easy to determine, because the observed hole widths in Figures 1 and 2 and for larger spots and longer burn times in Ref. [13] are much wider than the lifetime-limited width of 49 MHz. The extra width may be due to two-level-system dephasing processes that normally occur in polymer hosts, but a more probable mechanism could be inhomogeneous Stark broadening induced by the products of the electron-transfer process. Whatever the source of the extra width, it is clear from the lower half of Figure 2 (burning intensity 32 W/cm^2) that this material can tolerate burning intensities far greater than the estimated two-level saturation intensity of 0.2 W/cm^2 without further broadening. Moreover, the results presented here show that to achieve fast hole production in small laser spots, one need only saturate the singlet-singlet transition strongly; the subsequent irradiation at λ_2 acts efficiently to produce spectral holes $\simeq$ 1 % deep. An important question that should be addressed in future studies would be whether or not high-speed reading in small laser spots would produce excessive broadening of the detected holes.

In conclusion, we have observed gated hole production with 30 ns pulses in 200 μm spots, and with a single 8 ns pulse in 1 cm diameter spots in a new thin-film photon-gated material. The gating light pulse of 200 ms acts as a "developer" for centers that were placed in the lowest triplet state by the site-selecting λ_1 pulse. If many bits were to be written in the frequency domain in this material, one would simply inject short pulses at all the λ_1 wavelengths desired and then irradiate with the long λ_2 pulse. These results illustrate the superiority of photon-gated over single-photon mechanisms for FDOS applications.

ACKNOWLEDGEMENT

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FIGURE CAPTIONS

Figure 1. Photon-gated PHB in 1 cm diameter laser spot using using a pulsed dye laser for λ_1. (a) spectrum before burning using a 10 nW cw dye laser for detection, (b) spectrum after irradiation by a single 8 ns λ_1 pulse at 0 GHz (632 nm) with no gating pulse, (c) spectrum after one λ_1 pulse in conjunction with a 200 ms gating pulse at λ_2 = 488 nm, (d) spectrum after a second two-color irradiation at the same λ_1. The vertical scale applies to trace (a); the other traces have been offset vertically.

Figure 2. Fast photon-gated PHB in a 200 μm diameter laser spot using an acousto-optically switched cw dye laser for λ_1. The relative absorption change is defined by $\Delta\alpha/\alpha_i = (\alpha_f - \alpha_i)/\alpha_i$ where the subscripts i and f refer to initial and final, respectively. Upper half: 1.5 mW λ_1 burning power, single AO. (a) typical baseline before burning, (b) 100 μs λ_1 burn time, (c) 10 μs, (d) 1 μs, and (e) hole produced by the AO modulator leakage. Lower half: 10 mW λ_1 burning power, dual AO. (f) 300 ns λ_1 burn time, (g) 100 ns, (h) 50 ns, (i) 30 ns, and (j) hole produced by the leakage light through the fast AO modulator. The λ_2 beam at 488 nm was 0.5 cm in diameter and 200 ms long, and a fresh spectral region was used for each spectrum. The vertical scale is exact for traces (a) and (f); the other traces have been offset vertically.

Figure 3. Fractional hole depth remaining after scanning irradiation over 30 GHz at various total (cumulative) fluences. The reading beam was 200 μm in diameter, and the irradiation time for each point was 16 s.

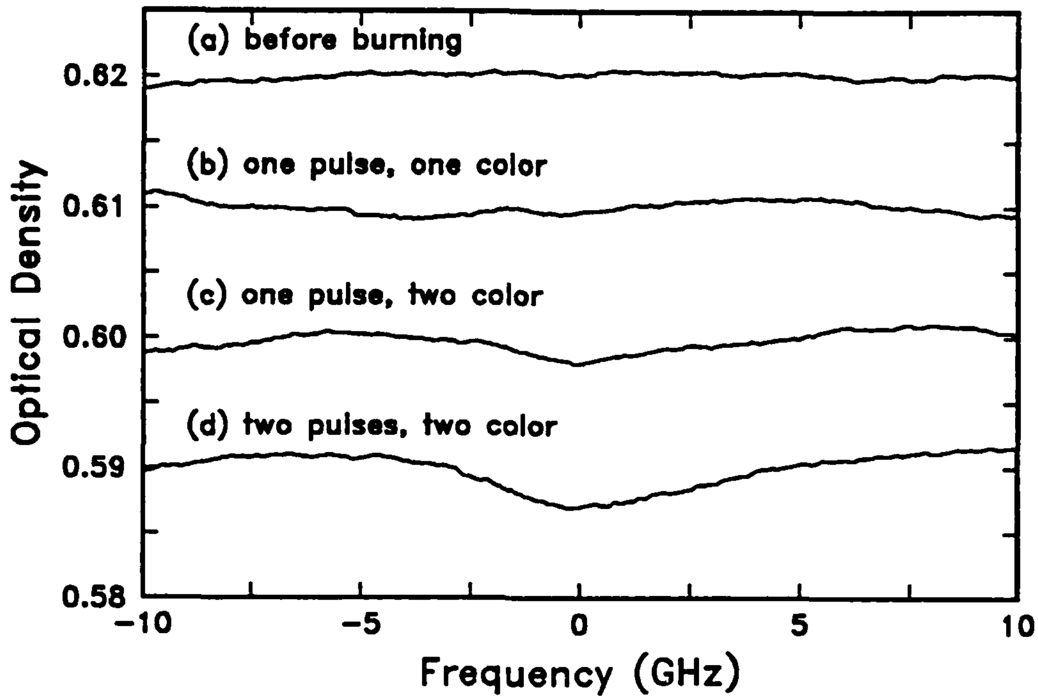
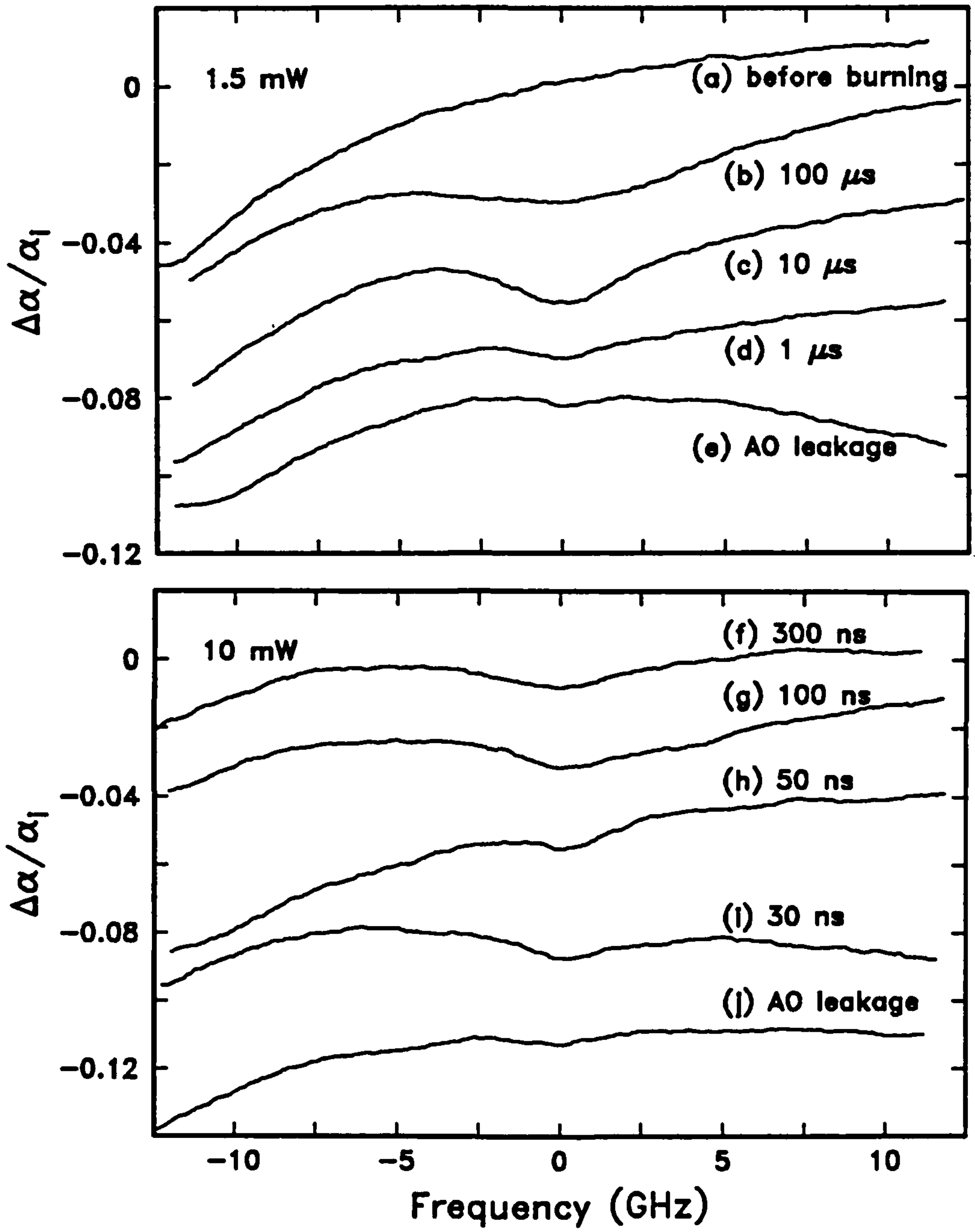

(a) before burning
(b) one pulse, one color
(c) one pulse, two color
(d) two pulses, two color
Optical Density
0.62
0.61
0.60
0.59
0.58
−10
−5
0
5
10
Frequency (GHz)

Fig. 1



1.5 mW
(a) before burning
(b) 100 μs
(c) 10 μs
(d) 1 μs
(e) AO leakage
0
−0.04
−0.08
−0.12
Δα/α₁
10 mW
(f) 300 ns
(g) 100 ns
(h) 50 ns
(i) 30 ns
(j) AO leakage
0
−0.04
−0.08
−0.12
Δα/α₁
−10
−5
0
5
10
Frequency (GHz)

Fig. 2

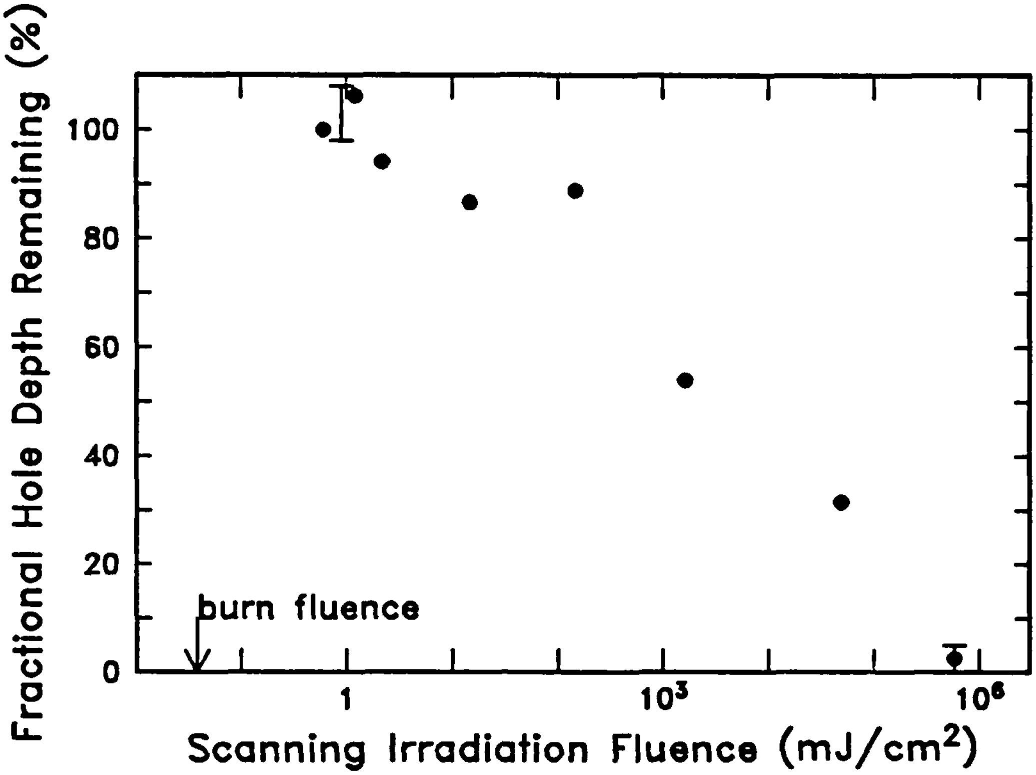

Fractional Hole Depth Remaining (%)
100
80
60
40
20
0
burn fluence
1
10^3
10^6
Scanning Irradiation Fluence (mJ/cm^2)

Fig. 3

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