Submillisecond response of a photorefractive polymer under single nanosecond pulse exposure

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Individual nanosecond pulses at 532 nm are applied to record gratings in photorefractive composite. At 4 mJ/cm^2 illumination, maximum diffraction efficiencies of 56% have been reached with a build-up time of only 300 μs (t_1) demonstrating one order of magnitude faster recording compared to writing with continuous wave beams. This fast response enables applications in optical processing requiring frame rates of 100 Hz or more. Due to the short duration of the writing pulses, the recording is insensitive to vibrations. © *2006 American Institute of Physics*.
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Organic photorefractive (PR) materials offer the advantages of low-cost, ease of fabrication, tunability over the properties as well as large optical nonlinearity compared to their inorganic counterparts.[1,2] The thin film devices of these polymer composites have shown 100% diffraction efficiencies,[3] millisecond response times,[4,5] and sensitivity in the infrared spectrum.[6–8] Organic photorefractives have the potential to become prominent materials for many applications in real-time holography and optical processing.[2,9] Even though some applications necessitate fast recording speeds, the fastest organic photorefractive materials reported so far show response times in the millisecond range.[4,5,10] The origin of this limit can be attributed to charge-carrier generation and transport and the reorientation of the nonlinear-optical chromophores.[2] Selecting transport matrices with drift mobilities more than two orders of magnitude higher than poly(*n*-vinylcarbazole) improved the response time by only several times.[10] Depending on the type of composite, the orientation of chromophores can have some or no limitation at all on reducing the speed.[2] A complementary approach such as light-induced filling of traps[11,12] has also been used to improve the speed. One can also speed up the charge-carrier generation through writing with a single-shot pulse, similar to the case in holographic time of flight (HTOF) experiments.[13] In this work, we report that a single nanosecond pulse can create sufficient charge carriers in a short time which can significantly improve the response time while showing a large diffraction efficiency.

We have carefully selected the functional elements of this composite for the purpose of fast writing and decay. The hole-transport polymer poly(acrylic tetraphenyldiaminobiphenyl) (PATPD) was chosen, because it has a relatively large mobility and the ionization potential (I_P) for this polymer is lower than the other components added into it.[14] In this way, the deep trap density was kept to be minimal to achieve larger drift mobility. The existing shallow traps are believed to be due to conformational disorder. In addition to the transport polymer, a rapidly orienting nonlinear-optical chromophore 4-homopiperidinobenzylidenemalononitrile (7-DCST) is selected due to its fast orientation in several hundreds of microseconds. The system also includes the plasticizer *N*-ethyl carbazole (ECZ) and an efficient sensitizer C_{60}. A similar type of composite has been reported in our earlier work.[14] In the present case, the chromophore concentration is reduced for better transparency at the recording wavelength of 532 nm. The composite consisted of PATPD:7-DCST:ECZ:C_{60} (54.5:25:20:0.5 wt %). The material was sandwiched in between two pieces of indium tin oxide coated glasses and the thickness of the film was 105 μm. The absorption coefficients of the composite were measured to be 104 cm^{-1} at 532 nm and 30 cm^{-1} at 633 nm.

To characterize the PR properties of the samples, both degenerate (D) and nondegenerate (ND) four-wave mixing (FWM) experiments were performed in the standard tilted-sample geometry. Two interfering *s*-polarized beams (532 nm) with a total pulse fluence of 4 mJ/cm^2 and 1 ns pulse width created the grating. A counterpropagating *p*-polarized cw beam (532 nm, DFWM) or a slightly deviated cw beam (633 nm, NDFWM) probed the efficiency of the grating (Fig. 1). The writing beams were incident on the sample with an interbeam angle of 20° in air and the sample normal was tilted 60° relative to the writing beam bisector resulting in a grating period of 2.6 μm. When readout at 633 nm, the probe beam was deviated from the counterpropagating angle to satisfy the Bragg condition. Reading with the red beam is preferred, due to lower absorption of the film at longer wavelengths.

Under steady-state continuous wave (cw) 532 nm writing conditions, the peak of the diffraction efficiency (overmodulation) is reached at larger fields for the red reading

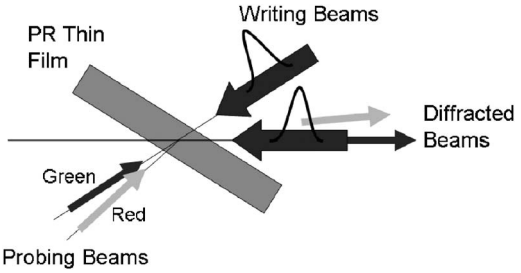

FIG. 1. Tilted transmission geometry used in the writing process. Note that the Bragg-matched reading angles are different for green and red readings.

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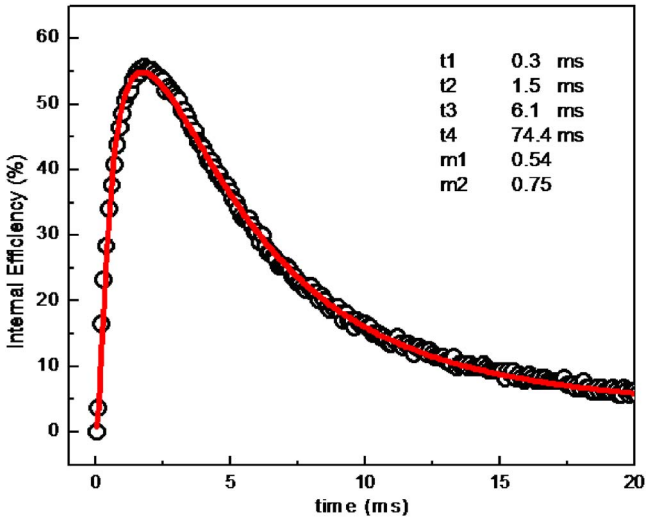

FIG. 2. (Color online) Fast rise and decay of diffraction efficiency of PATPD:7-DCST:ECZ:C_{60} (54.5:25:20:0.5 wt %) when exposed to two interfering single pulses of 1 ns pulse width with a total of 4 mJ/cm^2 fluence. The bias field was kept at 95 V/μm and the reading beam wavelength was at 633 nm. The internal efficiency reached a maximum of 56% (or 35% efficiency after all losses) in only 1.8 ms time. The fast time constant for the rise section of the curve is 300 μs. The line is an exponential fit function with four time constants (two for the rise and two for the decay).

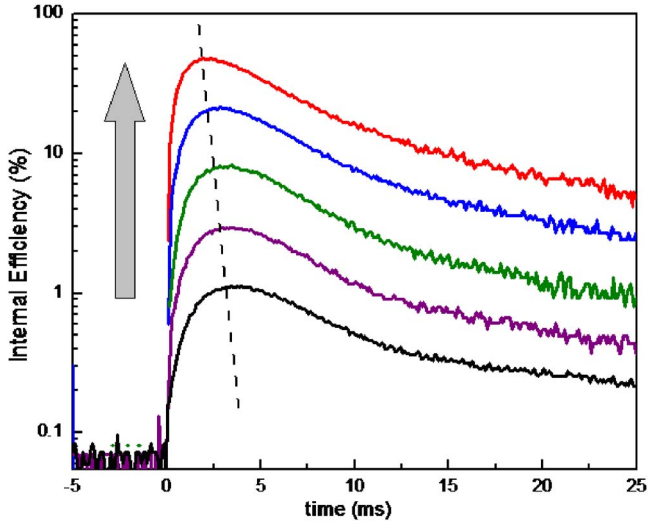

FIG. 3. (Color online) Single pulse diffraction efficiency when the total pulse energies are varied as 0.2, 0.38, 0.75, 1.5, and 3.0 mJ/cm^2. The maximum diffraction efficiency increases linearly with the pulse energy for the most part.

case compared to the green reading case. This difference can simply be attributed to the wavelength factor in the formula for diffraction efficiency in thick holograms derived by Kogelnik:[15]

$$\eta \propto \sin^2\left[\frac{\pi \Delta n d}{\lambda \sqrt{\cos\alpha_i \cos\alpha_d}} \hat{e}_i \cdot \hat{e}_d\right], \tag{1}$$

where Δn is the index modulation, d the thickness of the film, λ the probe wavelength, α_i and α_d the angles for the incident and diffracted beams in the material, and $\hat{e}_i$ and $\hat{e}_d$ the polarization vectors. For red reading, in addition to different wavelengths, the incident and diffracted angles are slightly smaller than in the green reading case. Therefore, for red reading the index modulation has to be larger (more field required) to reach the peak efficiency. For cw recording, large internal diffraction efficiencies of 85%–95% can be obtained for both red and green readings and the time constant of the fast transient response was ~4 ms at 1.2 W/cm^2 (or ~4.8 mJ/cm^2) irradiance.

In the case of single pulse exposure, the two writing beams create a light grating for the duration of the pulse width which is ~1 ns, in our case. The recording is almost instantaneous and eliminates the unwanted effects of mechanical vibration in the system. The maximum diffraction efficiency, on the other hand, is reached after ~1–2 ms due to the slow hopping charge transport mechanism that takes place in polymers as well as chromophore orientation. A maximum of 56% internal or 35% external (after all losses) diffraction efficiency is observed. Rise and decay of the diffracted signal are depicted in Fig. 2. The readout wavelength was 633 nm and the bias field was at 95 V/μm. The temporal characteristics of the space-charge field as well as the index modulation can be extracted by fitting the data to an exponential function with four different time constants (two for rise and two for decay):

$$\Delta n \propto [1 - m_1 \exp(-t/t_1) - (1 - m_1)\exp(-t/t_2)] \times [m_2 \exp(-t/t_3) + (1 - m_2)\exp(-t/t_4)], \tag{2}$$

$$\eta \propto \sin^2[B\Delta n]. \tag{3}$$

Here, m_1,m_2 are weighing factors, t_1, t_2 and t_3, t_4 time constants for rise and decay, respectively, and B a constant. From the fitted curve we find the fast rise time constant (t_1) to be 300 μs with a weighting factor (m_1) of 0.54, which is one order of magnitude less than the shortest time constants reported earlier.[4,5,10] In HTOF experiment, a shorter response time has been observed; however, the observed efficiency was very low.[13] When the rise and decay portions of the data are separated and fitted to the commonly used biexponential function,[5] we still obtain very similar values for the time constants.

The pulse energy defines the number of carriers that can be generated in the material. Note that since charge generation is through linear absorption process, the peak power of the pulse does not contribute to the photorefractive effect, but the pulse energy does. Nanosecond pulses with different pulse widths will show the same photorefractive response if their pulse energies are the same. An irradiance of 4 mJ/cm^2 in 105-μm-thick film corresponds to 10^{18} photons/cm^3, more than half of which are being absorbed. The quantum efficiency, trapping, and recombination rate will reduce the total density of trapped charges. For pulse energies of 0.4–3 mJ/cm^2 the maximum diffraction efficiency is linearly related to the pulse fluence (Fig. 3). Varying the pulse energy improves the recording time only very slightly. This can be attributed to the fact that speed is limited by mobility and possibly chromophore orientation, not charge-carrier generation. The decay of the grating is also insensitive to writing fluence.

Operation of this PR device at 100 Hz or higher frame rates requires the decay time to be short too, so that the information from the next frame will not overlap with that from the previous frame. The decay of a grating can be accelerated by uniform illumination. One can use a gated cw illumination at 532 nm, a short time after the writing pulse

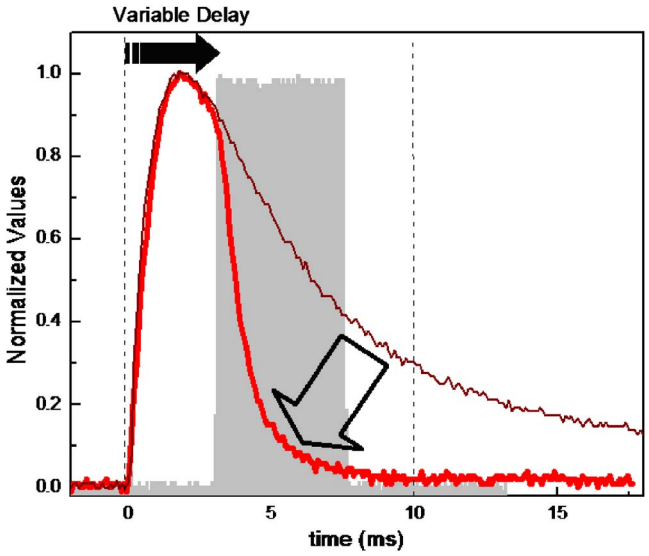

FIG. 4. (Color online) Decay of the grating diffraction efficiency is accelerated through a separate, uniform cw illumination at 532 nm. The gated illumination lasted only 5 ms (gray window) with an exposure of 6 mJ/cm^2. The grating is totally erased 10 ms after the pulse arrived. This fast rise and decay proves that we can operate this device at 100 Hz (write and erase) frame rates using single pulse writing and gated erasure.

ceases, to help erase the grating. As shown in Fig. 4, with a gated exposure of only 6 mJ/cm^2, we were able to erase the grating in a 10 ms window. The delay between the writing pulse and uniform gated exposure can be further adjusted for the best signal-to-noise ratio. In another possible experimental configuration, a pulsed laser can be employed for both writing (nonuniform illumination) and erasing (uniform illumination). The pulses can be sent at 200 Hz, and a fast acousto-optic modulator can switch the polarization between *s* (writing) and *p* (erasing) at 200 Hz.

In summary, one can use single-shot pulsed illumination to further improve the dynamic response of photorefractive polymers. The single pulse creates the necessary charge carriers in a very short time; therefore the speed is limited by the material's drift mobility and chromophore orientation. We have achieved a response time of 300 μs through single pulse writing. Single-shot writing has the further advantage that the recording of gratings is insensitive to vibrations.

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[1]B. Kippelen and N. Peyghambarian, *Polymers for Photonic Applications II*, Advances in Polymer Science (Springer, Berlin, 2003), Vol. 161, p. 87.
[2]O. Ostroverkhova and W. E. Moerner, Chem. Rev. (Washington, D.C.) **104**, 3267 (2004).
[3]K. Meerholz, B. L. Volodin, Sandalphon, B. Kippelen, and N. Peyghambarian, Nature (London) **371**, 497 (1994).
[4]D. Wright, M. A. Diaz-Garcia, J. D. Casperson, M. DeClue, W. E. Moerner, and R. J. Twieg, Appl. Phys. Lett. **73**, 1490 (1998).
[5]J. A. Herlocker, K. B. Ferrio, E. Hendrickx, B. D. Guenther, S. Mery, B. Kippelen, and N. Peyghambarian, Appl. Phys. Lett. **74**, 2253 (1999).
[6]M. Eralp, J. Thomas, S. Tay, G. Li, G. Meredith, A. Schülzgen, G. A. Walker, S. Barlow, S. R. Marder, and N. Peyghambarian, Appl. Phys. Lett. **85**, 1095 (2004).
[7]S. Tay, J. Thomas, M. Eralp, G. Li, S. Marder, G. A. Walker, S. Barlow, M. Yamamoto, R. Norwood, A. Schülzgen, and N. Peyghambarian, Appl. Phys. Lett. **87**, 171105 (2005).
[8]J. G. Winiarz, L. Zhang, J. Park, and P. N. Prasad, J. Phys. Chem. B **106**, 967 (2002).
[9]G. Li, M. Eralp, J. Thomas, S. Tay, A. Schülzgen, R. A. Norwood, and N. Peyghambarian, Appl. Phys. Lett. **86**, 161103 (2005).
[10]U. Hofmann, A. Schreiber, D. Haarer, S. J. Zilker, A. Bacher, D. D. C. Bradley, M. Redecker, M. Inbasekaran, W. W. Wu, and E. P. Woo, Chem. Phys. Lett. **311**, 41 (1999).
[11]E. Mecher, F. Gallego-Gomez, H. Tillmann, H. H. Horhold, J. C. Hummelen, and K. Meerholz, Nature (London) **418**, 959 (2002).
[12]J. Wolff, S. Schloter, U. Hofmann, D. Haarer, and S. J. Zilker, J. Opt. Soc. Am. B **16**, 1080 (1999).
[13]S. J. Zilker, M. Grasruck, J. Wolff, S. Schloter, A. Leopold, M. A. Kol'chenko, U. Hofmann, A. Schreiber, P. Strohriegl, C. Hohle, and D. Haarer, Chem. Phys. Lett. **306**, 285 (1999).
[14]J. Thomas, C. Fuentes-Hernandez, M. Yamamoto, K. Cammack, K. Matsumoto, G. Walker, S. Barlow, G. Meredith, B. Kippelen, S. R. Marder, and N. Peyghambarian, Adv. Mater. (Weinheim, Ger.) **16**, 2032 (2004).
[15]H. Kogelnik, Bell Syst. Tech. J. **48**, 2909 (1969).