High-performance photorefractive polymer operating at 1550 nm with near-video-rate response time

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The development of a high-performance photorefractive polymer composite operating at 1550 nm is reported. We show 40% internal diffraction efficiency with response time of 35 ms and a net gain of 20 cm^{-1} in four-wave mixing and two-beam coupling experiments, respectively. This is more than an order of magnitude improvement in the diffraction efficiency and net two beam coupling gain and two orders of magnitude in the response time than the previously reported photorefractive polymer operating at this technologically important wavelength. The improvement in photorefractive characteristics is accomplished by an enhanced orientation of the nonlinear optical chromophore in the present composite. © *2005 American Institute of Physics.*
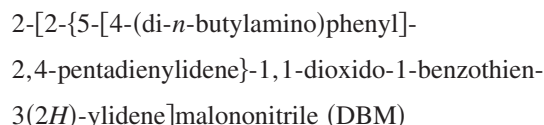[DOI: 10.1063/1.2117610]

The demand for holographic recording materials has been ever increasing for the past few decades. Photorefractive materials[1,2] have been studied extensively as candidate recording media. They offer large index modulations (dynamic range) and reversible recording that make them very attractive for applications, such as optical control of light,[3] all-optical beam clean-up,[4] optical coherence tomography,[5] and high-density optical data storage.[6,7] Recently, organic photorefractive materials[2,8,9] have drawn significant attention due to their high performance, compositional flexibility, and the low cost associated with their fabrication. Several photorefractive polymer composites operating at visible wavelengths with very high diffraction efficiencies and fast response times have been developed.[9–11] However, for a variety of holographic applications, such as optical communication and medical imaging, infrared (IR) sensitivity is required. The spectral window near 1550 nm exhibits minimal attenuation in various propagation media, such as optical fibers, the atmosphere, and human tissue, being the preferred wavelength for related technologies.

IR (800 to 1550 nm) sensitization of several photorefractive polymers was previously demonstrated.[12–14] For the polymer composite operating at the optical communication wavelength of 1550 nm,[14] the diffraction efficiency has been 3% with a comparably slow response (several seconds), preventing its feasible use in possible applications. In this letter, we report the development of a photorefractive polymer composite with significantly improved performance, showing an order of magnitude improvement in the diffraction efficiency (40%) at 1550 nm and two orders of magnitude improvement in the response time (35 ms). We also show a net two-beam coupling (TBC) gain of 20 cm^{-1} at 1550 nm in this polymer composite, clearly demonstrating the photorefractive nature of the gratings created. Steady-state ellipsometric measurements show that the orientational nonlinearity

(birefringence) of this material is more than an order of magnitude larger than of the previously reported two-photon photorefractive composite. As an inherent advantage of two-photon absorption (TPA) sensitization, the use of continuous-wave (cw) reading beams provides nondestructive readout in this polymer composite.[14,15] The optical quality of the films made of this polymer is excellent, and its shelf time was several months under standard laboratory conditions.

Primarily investigated in nonlinear optical (NLO) inorganic crystals, the photorefractive effect[1,2] uses photogenerated charges that drift and diffuse, creating a space-charge field to alter the refractive index of the medium through the electro-optic effect. By nonuniform illumination of the photorefractive material, phase information can be stored as index gratings that diffract incident light, allowing the retrieval of the recorded information. Photorefractive polymer composites use a number of functional components to achieve charge generation, transport, trapping, and electro-optic effects required to create refractive index gratings. We have developed composites utilizing a highly efficient hole transport matrix poly(acrylic tetraphenyldiaminobiphenyl) (PATPD) polymer,[16] a NLO chromophore with a high figure of merit, 4-homopiperidino benzylidine-malonitrile (7-DCST),[17] for orientational nonlinearity, and the plasticizer N-ethylcarbazole (ECZ) to reduce the glass transition temperature (T_g) to near room temperature (25 °C). The sensitization at 1550 nm was achieved by use of a TPA dye,

2-[2-{5-[4-(di-*n*-butylamino)phenyl]-

2,4-pentadienylidene}-1,1-dioxido-1-benzothien-

3(2*H*)-ylidene]malononitrile (DBM)

at different loadings in the composites prepared. Uniform films of 105 μm thickness were fabricated by sandwiching these composites between two indium tin oxide-deposited glass electrodes that allow the application of a dc bias across the films, which is necessary for charge separation and NLO chromophore orientation.

In photorefractive polymers with a low Tg, the orientational nonlinearity (birefringence) is the dominant effect for

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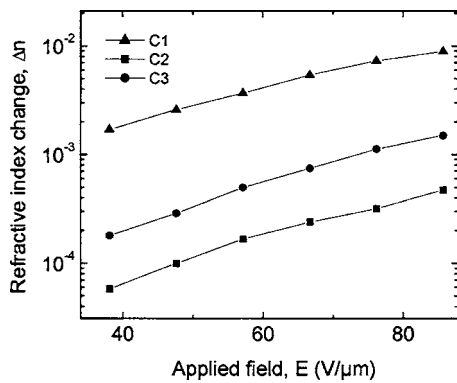
FIG. 1. Refractive index change as a function of the applied electric field for composites PATPD/7-DCST/ECZ/DBM (49:40:10:1 wt %) (C1), PATPD/7-DCST/ECZ/DBM (50:25:15:10 wt %) (C2), and PATPD/7-DCST/ECZ/DBM (50:25:20:5 wt %) (C3) measured by steady-state ellipsometry at 1550 nm.

FIG. 2. Internal diffraction efficiency at 1550 nm as a function of the applied electric field for composite C1. The writing beam pulse energy is 4.2 μJ (sum of both beams). The solid line is the theoretical fit.

the recording of holographic gratings.[2] The NLO chromophore aligns with the net electric field in the medium, resulting in a very large index modulation. Ellipsometric measurements[2] of photorefractive polymers provide valuable information on the strength of the index modulation that is due to birefringence. We have performed ellipsometric measurements on our composites in order to determine the optimum ratio of various functional components. The recipes for the composites were varied to obtain similar T_g around room temperature. The index change obtained at the highest applied fields for the composite PATPD/7-DCST/ECZ/DBM (49:40:10:1 wt %) (C1) was 9×10^{-3} (Fig. 1). For this composite, the refractive index modulation is more than an order of magnitude larger than that of the previously reported IR operating polymer composite,[14] PATPD/7-DCST/ECZ/DBM (50:25:15:10 wt %) (C2), which showed an index change of 4.5×10^{-4} at the same applied field. Increased NLO chromophore loading is usually the main reason for the improved index change in polymer composites with the same T_g. Interestingly, however, the index change in another composite, PATPD/7-DCST/ECZ/DBM (50:25:20:5 wt %) (C3)—which contained the same amount of chromophore as C2 but a smaller amount of sensitizer—showed an index change of 9×10^{-4} at the same applied field. The reduction of the DBM sensitizer dye loading from 10 wt % to 5 wt % increased the index modulation significantly. Considering that the T_g for these materials are similar, this result indicates that the room-temperature orientation of the NLO chromophore is adversely affected by higher sensitizer loadings. As a result of the ellipsometry measurements, the sensitizer concentration of 1 wt % that was used in C1 was found to be the optimum, giving the maximum index change with the fastest response.

To measure the diffractive strength of the refractive index gratings written in C1, we have performed four-wave mixing (FWM) experiments using a pulsed (130 fs) laser at 1550 nm. The *s*-polarized output from a Ti-sapphire pumped optical parametric amplifier tuned to 1550 nm and operating at a repetition rate of 1000 Hz was used for writing beams in a traditional FWM geometry with the addition of a delay line to ensure temporal overlap of the pulses in the polymer sample. Reading was achieved at the same wavelength using a counterpropagating *p*-polarized cw beam from a laser diode. Both the transmitted and diffracted beams were moni-
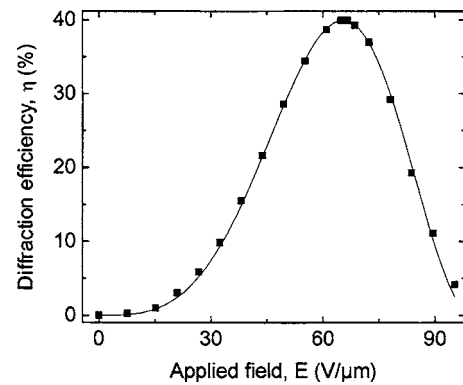
tored using photodiodes and a lock-in amplifier. The writing beams were focused to a spot size of 180 μm (diameter) at the sample position and the reading beam diameter was 60 μm. A smaller than usual reading beam diameter was used to ensure overlap of the reading beam and the photorefractive grating, which is confined to a small volume due to TPA writing. The pulse energy used for writing the holograms for these experiments was around 4.5 μJ. Figure 2 shows the internal diffraction efficiency as a function of applied electric field for C1 measured in the FWM setup described above. In this experiment we observed a 40% internal diffraction efficiency at an applied electric field of 65 V/μm at 1550 nm. This is more than an order of magnitude improvement compared to a previously reported two-photon photorefractive polymer composite.[14] The strong diffraction of IR light from this photorefractive thin-film device shows that the nonlinear writing scheme has important potential in holographic applications. Since the absorption of cw light was negligible at this wavelength, the use of the powerful cw reading beams (up to 20 mW) had no effect on the holographic writing/reading/erasure processes in this polymer. In these experiments, the grating decay time was independent of the cw reading beam power, in contrast to the case where pulsed reading beams were used. The easing of the restriction on reading beam intensities and nondestructive readout[14,15] are important advantages in read-only memory and laser communication applications of photorefractive materials.

The response time of photorefractive grating recording is an important parameter in practical applications, such as real-time beam clean-up.[4] To determine the temporal characteristics of our polymer composites, transient FWM experiments were performed using a fast photodetector and a computer interfaced data acquisition system. Figure 3 shows the diffraction efficiency as a function of time for C1 measured using the experimental setup described above. At $t=0$, the one of the writing beams is unblocked and photorefractive grating build-up is observed at an applied electric field of 93 V/μm and a pulse energy of 11.4 μJ focused to a spot with a diameter of 180 μm. The data fit to a biexponential function:

$$\eta = A \sin^2\{B \cdot [1 - m \exp(-t/t_1) - (1-m)\exp(-t/t_2)]\},$$

$$(1)$$

as described by the coupled wave equations for transmission gratings[18] provided a fast response time (t_1) of 35 ms with a
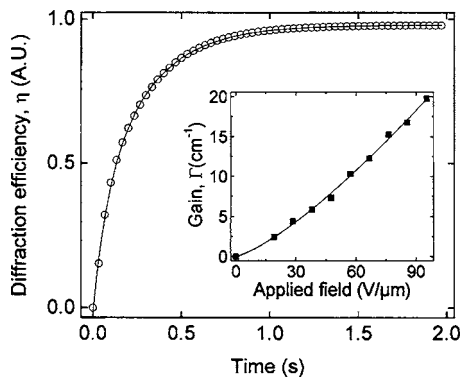
FIG. 3. Diffraction efficiency as a function of time for composite C1 showing grating build-up. At time zero, the writing beams were turned on. The data fits to the biexponential function (1) with a fast time constant (m =0.45) of 35 ms (solid line). Inset: TBC gain as a function of the applied electric field for p-polarized irradiation at 1550 nm.

weighing factor of $m=0.45$, which is very close to the so-called video rate response time of 33 ms.

With C1, we have also performed TBC measurements using the same source at 1550 nm (inset of Fig. 3). The TBC gain, which is the increase in the energy of one of the writing beams at the expense of the other, is the fingerprint of the photorefractive effect.[2] In these measurements, we have observed a net gain of 20 cm^{-1} at an applied electric field of 95 V/μm using p-polarized irradiation with total pulse energy of 6 μJ focused to a diameter of 180 μm. Together with the reversibility of the gratings, the demonstration of the TBC gain shows that the holographic gratings written in these composites are due to the photorefractive effect, and not due to other recording processes, such as photochromism, photobleaching, or optical damage.

In conclusion, the performance of IR sensitive photorefractive polymers composites was brought to a level where practical applications may be possible. FWM diffraction efficiency of 40% with a response time of 35 ms, net TBC gain of 20 cm^{-1}, and nondestructive readout show that the TPA writing scheme has important potential. Future work will focus on improving the sensitivity of our two-photon photorefractive polymer composites by employing sensitizers with larger TPA cross sections and demonstrating real-time holographic correction (beam clean-up) using thin-film devices made of this polymer. The combination of nondestructive

readout with thermal fixing for obtaining long-lived holograms is being investigated. Investigations of the physics and applications of the TPA writing scheme are also in progress.

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