Mechanisms for the Reciprocity Failure in Photorefractive Polymers

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ABSTRACT

We measured the diffraction efficiency response of two photorefractive polymer devices according to the duration of the single laser pulse used to record the hologram. The pulse duration was varied from 6 nanoseconds to 1 second, while the pulse energy density was maintained constant at 30 mJ/cm^2. This changed the peak power from 5×10^9 mW to 30 mW. We observed a strong reciprocity failure of the efficiency according to the pulse duration, with a reduction as large as a factor 35 between 1 second and 30 μs pulse duration. At even lower pulse duration (< 30 μs), the efficiency leveled out and remained constant down to the nanosecond exposure time. The same behavior was observed for samples composed of the same material but with and without buffer layers deposited on the electrodes, and different voltages applied during the holographic recording. We explained these experimental results based on the charge transport mechanism involved in the photorefractive process. The plateau is attributed to the single excitation of the charge carriers by short pulses ($\tau_p < 30$ μs). The increase of efficiency for longer pulse duration ($\tau_p > 30$ μs) is explained by multiple excitations of the charge carriers that allows longer distance to be traveled from the excitation sites. This longer separation distance between the carriers increases the amplitude of the space-charge field, and improves the index modulation. The understanding of the response of the diffraction efficiency according to the pulse duration is particularly important for the optimization of photorefractive materials to be used at high refresh rate such as in videorate 3D display.

Keywords: Photorefractive, polymer, holography, pulsed laser, reciprocity failure, sensitivity, efficiency, 3D display

1. INTRODUCTION

The present model for the photorefractive (PR) effect was initially developed for inorganic crystals, and was subsequently modified to take into account the specific mechanisms observed in polymers, such as charge transport dispersion by shallow traps, and the unexpectedly high value of the index modulation due to the orientational enhancement effect. This model has been proven to be robust, and explains a large variety of dynamic behaviors as well as relationship among experimental parameters. The PR process start by the absorption of a photon that is converted into an electron and hole pair. Under the influence of an external electric field, the principal charge carrier drifts into the material and get trapped in the a dark region where it cannot get re-excited. The different mobilities of the electrons and holes in the material ensures that there is dissociation of the charges and they don't just recombine when reaching the dark regions. This dissociation and relocation of the charges create an electrical space-charge field that orients the chromophore molecules, locally modifying the index of refraction.[1]

In this model, the PR process is directly proportional to the average optical energy density and should not depend on the way the photons are delivered. Optical peak power or pulse duration should not have any influence on the resulting diffraction efficiency. However, during the development of a fast refresh rate holographic 3D display,[2] we observed that the diffraction efficiency of the PR polymer used with a nanosecond pulsed laser was dramatically reduced from that when measured with a continuous wave (CW) laser.[3] This reduction happens at constant energy density and is referred to in the holographic recording media literature as

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"reciprocity failure".[4] When the reciprocity failure mechanism was studied into permanent recording materials such as silver halide,[5] dichromated gelatin,[6] and photopolymer,[7] it was found to be intrinsically connected to the light-matter interaction or the electronic mechanisms taking place in the material, opening a window of opportunity to better understand these types of phenomena.

Studying the diffraction efficiency according to the pulse duration not only contribute to a better understanding of the PR process in itself, but is also relevant for the development and optimization of new composites that will have better performance under pulsed illumination and high repetition rate. Such conditions of operation are found in application that require rapid refresh rates such as videorate 3D display or image restoration by phase conjugation.[1]

2. EXPERIMENT

Considering the lack of commercially available laser sources with a tunable pulse duration, we developed our own system based on a master oscillator power amplifier (MOPA) architecture.[8] In such a system, the initial beam from a distributed feedback laser diode is chopped by an acousto-optic modulator (AOM) in order to generate pulses of defined shape, duration, and repetition rate. Because of this external cavity pulse generation, the energy of the pulse is relatively low and has to be boosted by two stages of fiber power amplifiers. The light frequency of the amplified pulse is then doubled by a nonlinear crystal to reach the 515 nm wavelength at which the PR material used in the experiment is sensitive. Another AOM is used as a pulse selector to make sure the holographic grating is recorded with a single and unique pulse. Our particular MOPA laser can deliver pulses from 200 ns to 1 ms duration, with 500 mW and 1.2 mW average power respectively, at a repetition rate of 3 kHz. The beam coherence length was measured by interferometry to be 2 cm, long enough for holographic grating recording.

To extend the study of the diffraction efficiency at shorter and longer pulse duration, we also used a 6 nanosecond InnoLas SpitLight Q-switched laser system with 200 mJ of power per pulse; as well as a CW diode-pumped solid-state laser (Coherent Verdi V18) externally chopped with a Bragg cell to achieve a range of exposure times from milliseconds to seconds. This specific CW laser has a maximum power of 18 watts, which was the limiting factor for the available energy density (30 mJ/cm^2) used for the recording beams in our four wave mixing setup experiment.

The diffraction efficiency of the PR material was measured in a non-degenerated four-wave mixing (FWM) setup where the diffraction grating is recorded using a single pulse coming from one of the three laser sources described earlier. The beam energy density was kept constant between these sources at the sample location, and was 30 mJ/cm^2 for every measurement. The beam ration was set at 1:1 inside the sample for maximum interference modulation. The geometry of the FWM setup is presented in figure 1. The incidence angles with respect to the normal to the sample were 30° and 60° ensuring a large slant angle inside the material to obtain an ample projection of the grating vector **K** on the electric field vector **E**. The writing beams were s-polarized.

The diffraction was measured in real time using a p-polarized probe beam from an HeNe laser at 633 nm. This beam was incident to the sample at the Bragg angle corrected for its wavelength as well as for the average refractive index for the p-polarization, which is different from the s-polarization due to the chromophore alignment and birefringence. The incident intensity of the probe beam was set to be low enough to have no influence on the diffraction performance.

The dynamic of the diffracted intensity was recorded after a single pulse illumination from the recording beams. The efficiency was calculated as the ratio between the diffracted intensity over the incident intensity, and the maximum of the temporal evolution was reported.

Two PR devices were used in this study. Both were made out of the same polymer compound: the polymer matrix is a modified polyacrylic-tetraphenyldiaminobiphenyl (PATPD) in which carbaldehyde aniline (CAAN) was attached to the PATPD copolymer chain in a ratio of 10:1 (TPD:CAAN).[2] The chromophore was fluorinated dicyanostyrene 4-homo-piperidino benzylidine malononitrile (FDCST). The plasticizer was benzyl butyl phthalate (BBP), and the sensitizer was [6,6]-phenyl-C61-butyric acid methyl ester (PCBM). The weight ratio between the different components was PATPD-CAAN: FDCST:BBP:PCBM (56.23:33.74:9.84:0.2 wt%). Samples were
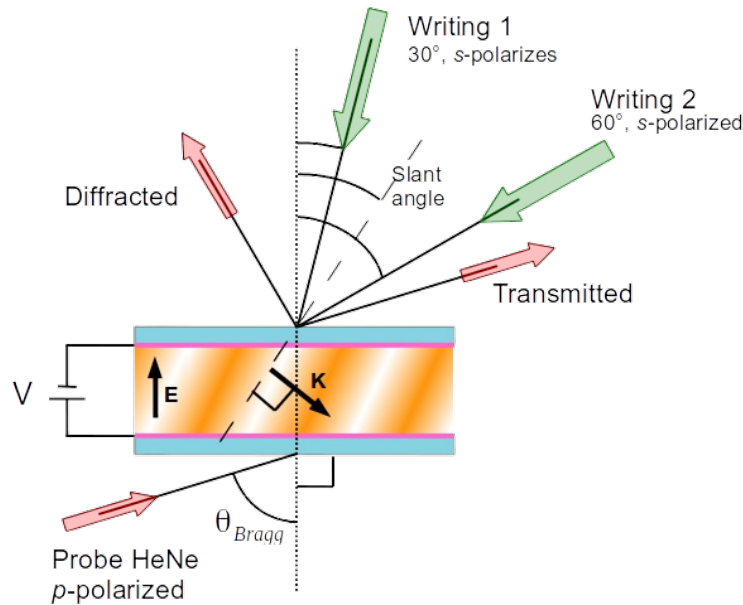
Figure 1. Non-degenerated four-wave mixing geometry. Writing beams are s-polarized. HeNe probe beam is p-polarized.

prepared by pressing the premixed compound between two heated ITO coated glass plates. Material thickness was set to 100 μm by glass bead spacers.

The difference between the two devices we studied was the presence (or absence) of buffer layers made of a 10 μm thick amorphous polycarbonate spin coated on top the ITO electrodes. These layers modify the electrical properties of the PR sample and allow much lower applied voltage due to the displacement of the over-modulation peak of the diffraction efficiency. It has been proposed that this modification is due to charge build up at the interface of the electrode and the material.[9–11] The external electric field at which the maximum diffraction efficiency was observed in the steady state with continuous illumination of the sample was 72.5 V/μm for the device without buffer layer, and 42.5 V/μm for the device with the buffer layers. These are also the values of the field at which the single pulse measurements were made.

3. RESULTS

The results of the diffraction efficiency measurement according to the pulse duration/peak power are presented in figure 2. Several noticeable features can be observed: First is the plateau of the efficiency for both devices in between 6 ns up to 30 μs. For pulse durations longer than 30 μs, the efficiency increases dramatically following a power law with an exponent of 0.12 for the sample without the buffer layer, and 0.34 for the sample with the buffer layers (lines are interpolated).

It can also be noted that whereas the sample with buffer layer is much less efficient ($\eta_{30\mu s} = 2\%$) than the sample without buffer ($\eta_{30\mu s} = 10\%$) at short pulse duration ($\tau_p < 30$ μs), the efficiency for the device with the buffer layers increases dramatically for longer pulse durations ($\tau_p > 30$ μs) that it becomes more efficient ($\eta_{1s} = 65\%$) than the sample without the buffer ($\eta_{1s} = 30\%$) for an exposure time of 1 second.

The dynamics of the diffraction efficiency were also observed in response to single pulse illumination. Very different time constants at the origin have been measured for the samples with buffer layers (65 ms^{-1}), and without buffer layer (16 ms^{-1}). The sample without buffer layer is clearly much faster.

Despite these very distinctive dynamic behaviors between the two devices, we observed that the transition between the plateau and the exponential region happens at the exact same value for the pulse duration ($\tau_p = 30$ μs), which is an indication of the material origin of the reciprocity failure.
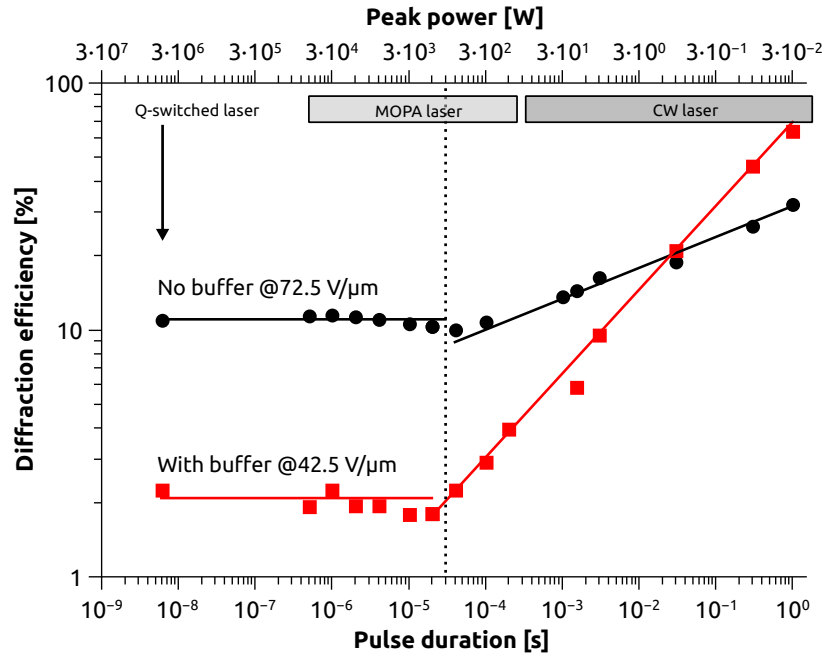
Figure 2. Diffraction efficiency according to the writing laser pulse duration for single pulse illumination of 30 mJ/cm^2. Black circle: sample without buffer layer at 72.5 V/μm applied electric field. Red square: sample with buffer layer at 42.5 V/μm applied electric field. Lines are interpolated using by a constant for $\tau_p < 30$ μs and a power law for $\tau_p > 30$ μs.

4. DISCUSSION

We already observed the dramatic reduction of the diffraction efficiency between CW illumination and nanosecond pulse recording from the results obtained with our holographic 3D display.[2,3] What the new measurements reveal is the behavior of the efficiency spanning 9 orders of magnitude in pulse duration and peak power. Equipped with this new measurement we can now interpret the origins of this variation according to the electronic properties of the PR material.

The photogeneration of the charge carriers by photon absorption has a response time on the order of a picosecond.[12] This is much faster than the time domain explored in our experiment. On the other hand, the time constant for transport and trapping of the excited charges in PR polymer is on the order of 0.1 to 5 ms.[13] This means that as long as the pulse duration (τ_p) is shorter than the lifetime of the charge carrier (τ_c), it can only excite the carriers once. Under this condition, the carriers can only travel a constant distance (φ) given by their mobility (μ) times the external electric field (E_0):

$$\varphi = \mu E_0 \tau_c, \qquad (1)$$

which is independent of the pulse duration. This mechanism explains the plateau we are observing for pulse durations shorter than 30 μs.

Since the same material is used for both devices, the plateau is expected to end at the exact same value of the pulse duration since the life time of the carriers is identical. However, because the external electric field is higher for the device without the buffer layer, the charge separation is larger, and the absolute value of the plateau is higher.

For pulse durations longer than the lifetime of the carrier ($\tau_p > \tau_c$), the same charge carrier can be re-excited from its trap and can move further away from where it was initially created. The distance traveled by the carrier becomes proportional to the pulse duration:

$$\varphi \propto \mu E_0 \tau_p. \qquad (2)$$

With larger separation distance between carriers of different signs (electron and holes), recombination is less likely to occur and the amplitude of the space-charge field increases. A larger space-charge field increases the index modulation and improves the diffraction efficiency as observed in our experiment.

The explanation of the different slopes observed for the efficiency at pulse duration larger than 30 μs for the two type of devices requires a more involved analysis including the rate equations of the charge generation and trapping under different applied electric fields.

5. CONCLUSION

We have measured the diffraction efficiency of two PR polymer devices over nine orders of magnitude of pulse duration. Both devices were made from the same PR polymer but one has amorphous polycarbonate buffer layers over the electrodes, and was operated at a lower external voltage.

For a constant energy density per pulse of 30 mJ/cm^2, we observed a plateau in the efficiency for pulse durations below 30 μs. For longer pulse durations, the efficiency increases according to a power law with different constants for the two devices.

We explained these behaviors as deriving from the limited lifetime of the charge carriers that are only excited once for short pulse durations. Under this condition, the charge carriers can only travel a fixed distance before being trapped, restraining the value of the space-charge field and the efficiency.

For longer pulse durations, the charge carriers can be re-excited by the tail of the pulse after being trapped. This allows a larger separation distance between the electrons and holes, reducing the chance of recombination, which increases the value of the space-charge field as well as the diffraction efficiency.

The understanding of the mechanism responsible of the reciprocity failure for the diffraction efficiency in PR polymers is important for the optimization of the material, especially when used with high frequency pulsed laser such as in applications requiring high speed refresh rates.

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