Enhanced gain dynamics in photorefractive polymers

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ABSTRACT

The complexity of photorefractive polymers arises from multiple contributions to the photo-induced index grating. Analysis of the time dynamics of the two-beam coupling signal is used to extract information about the charge species responsible for the grating formation. It has been shown in a commonly used photorefractive polymer at moderate applied electric fields, the primary charge carriers (holes) establish an initial grating which, however, are followed by a subsequent competing grating (electrons) that decreases the two-beam coupling efficiency. We show by upon using higher applied bias fields, gain enhancement can be achieved by eliminating the electron grating contribution and returning to hole gratings only.

1. INTRODUCTION

Photorefractive (PR) materials are low power nonlinear optical elements where an intensity- dependent refractive index is produced due to an electrostatic space charge field E_{sc} generated from charge carrier redistribution when light is incident on the material. Specifically, under a non-uniform illumination (such as an interference pattern) and applied bias field E_0, mobile charge carriers are generated and redistributed due to diffusion, drift, and photovoltaic effect [1-3]. While traditional PR materials are inorganic, doped polymeric composites offer an attractive alternative, with the advantage that properties responsible for the PR effect can be optimized simultaneously and independently to a degree not possible in existing inorganic materials [4]. A typical PR polymer composite, such as 7-DCST:PVK:ECZ-BBP:C_{60} used in our investigations, comprises a chromophore, a photoconductor, a plasticizer, and a photosensitizer. Reorientation of the chromophores, operating close to the glass temperature, occurs due to the total electrostatic field $E_T = E_0 + E_{sc}$. This reorientation, together with the electro-optic effect, modulates the refractive index in the PR polymer. In these polymers, there are no additional electron sources or traps, and holes are usually the predominant mobile charge carriers [4-6], although researchers have deliberately designed other novel PR polymers with a second mobile charge species to improve their performance [7]. Two-beam coupling (TBC) leading to efficient energy

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exchange between the participating beams is possible in PR materials when the phase shift between the refractive index grating and the intensity grating is ideally 90 degrees. In PR polymers, which exhibit no photovoltaic effect and negligible diffusion, the phase shift is non-ideal, but generally increases with the applied bias field [4].

In this paper, the time response of TBC in the PR polymer 7-DCST:PVK:ECZ-BBP:C_{60} in a self-pumped reflection grating geometry is investigated to identify the contribution of mobile charge carriers on grating formation. Using a nonlinear curve-fitting method to analyze the transient response of TBC when different bias fields E_0 are applied, it is shown that in addition to the expected chromophore reorientation time constant which is independent of E_0 and a bias-field dependent time constant associated with holes, there exists a third bias-field dependent time constant attributed to electrons. This, in turn, gives rise to a competing space charge field over an intermediate range of bias fields.

2. EXPERIMENTAL SETUP AND RESULTS

A schematic of the setup for self-pumped reflection grating geometry using the PR polymer is shown in Figure 1. A linearly polarized CW frequency-doubled Nd:YVO_4 laser at 532 nm (Coherent Verdi VI) or a 633 nm helium neon laser (Melles Griot: 05-LHP-925), both attenuated to 10 mW output, is normally incident on the PR polymer. A bias voltage from a high voltage (HV) source is applied across the approximately 100μm thick sample. The bias voltage is changed from 1.5 kV to 7.5 kV in steps of 0.5 kV. This corresponds to the variation of the applied bias field E_0 from 15 V/μm to 75 V/μm in steps of 5 V/μm. The applied bias field is opposite to the direction of the incident beam; this is similar to having the c-axis in a PR crystal contradirected to the incident beam, which ensures a decrease in transmitted beam intensity following grating formation. The transmitted optical power is monitored as a function of time after the application of the bias field E_0 using an optical power meter (Newport model 2832-C) and analyzed with a data acquisition system. The rise and fall times of the high voltage (HV) source has been measured to be approximately 10 ms. Sufficient time (typically 50-80 sec) has been allowed after application of the bias field to ensure that the response of the PR polymer reaches a steady state. In a similar fashion, the applied bias field is turned off for a sufficient time to allow for complete erasure of the PR grating. The on and off times for the applied bias field have been carefully chosen to be considerably greater than the time constants associated with the polymer and the space charge field(s).

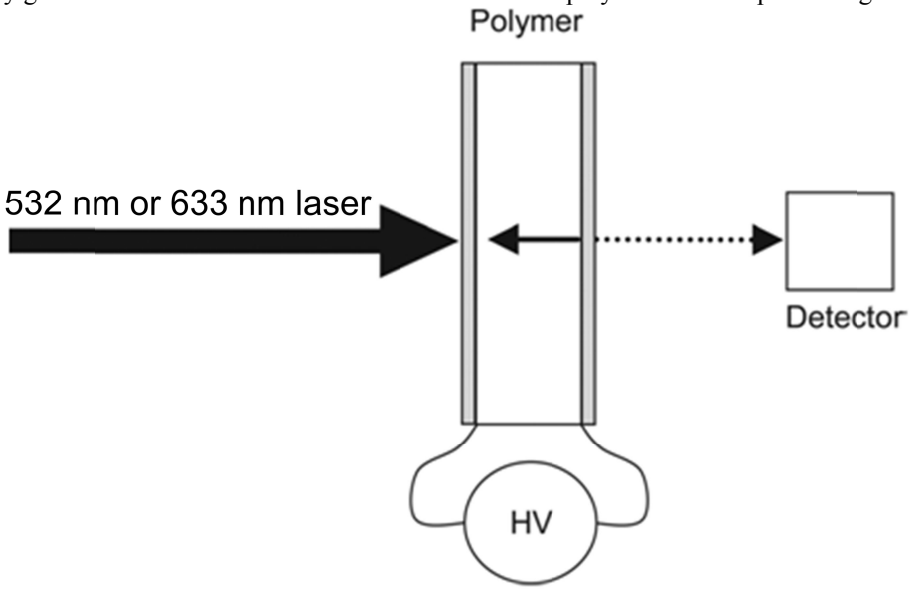

Figure 1. PR polymer 7-DCST:PVK:ECZ-BBP:C_{60} in self-pumped two-beam coupling geometry. The small arrow (signal beam) indicates the counter-propagating Fresnel reflection of the incident pump beam. The dotted line represents the transmitted pump beam. The signal beam is amplified at the expense of the pump beam.

Figure 2 shows the time dynamics for the change in normalized transmission for both 532 nm and 633 nm as a result of two-beam coupling in the reflection geometry. The resulting transmission of 532 nm light has been fit using a multi-exponential function for electric fields between 20 V/μm (small field) and 75 V/μm (large field). As previously reported [8], for relatively small applied fields (for instance, <40 V/μm at 532 nm) the decay can be adequately fit using a double exponential function with positive amplitudes for both exponential terms. These exponential terms correspond to the reorientation of the optical chromophore with the applied electric field and the formation of the PR grating formed by holes. For applied bias fields above a threshold (≈40V/μm for 532 nm illumination; lower for 633 nm illumination) a third component becomes measurable. This significant contribution is due to the competing grating formed by photo-excited electrons. It has recently been observed that for even higher applied bias fields, the contribution from photo-excited electrons decreases, and the time response can once again be fitted with the exponential resulting from the hole grating (and that corresponding to the reorientation of the optical chromophore).

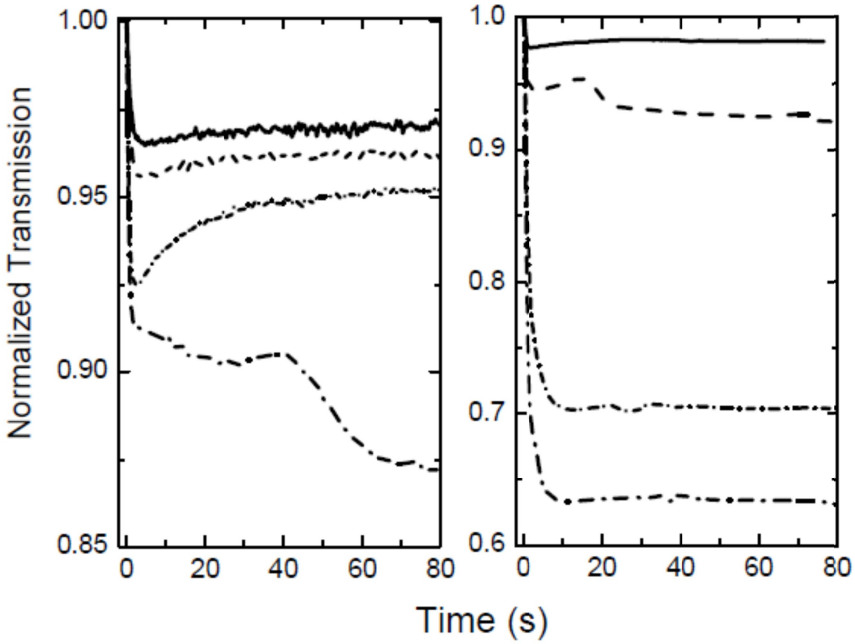

Figure 2. Time dynamics of the grating formation using (left) 532 nm and (right) 633 nm light to record the gratings for various applied fields (in order from top to bottom): 30 V/μm, 40 V/μm, 60 V/μm, and 70 V/μm.

3. ANALYSIS OF EXPERIMENTAL RESULTS

As stated above, the transmitted power $P_t(t)$, which is related to the two-beam coupling response, can been fitted with a linear combination of exponentials of the form [8]

$$P_t(t) = P_0 + \sum_{i=1}^{3} P_i \exp(-\frac{t}{t_i}), \quad (1)$$

where P_0 is the steady state transmitted power, $P_i, i = 1,2,3$ are the amplitudes of the exponentials, and $t_i, i = 1,2,3$ are the respective time constants. The data is fit using a Levenberg-Marquardt algorithm. Figure 3 shows the time constants $t_i, i = 1,2,3$ as a function of the applied bias field E_0 for the grating time dynamics at 532 nm illumination. For applied bias fields E_0<40 V/μm, the transmitted power can be best fit with double exponential function rather than a triple exponential function. However, for E_0> 40 V/μm, it is necessary to fit the data with triple exponential functions.

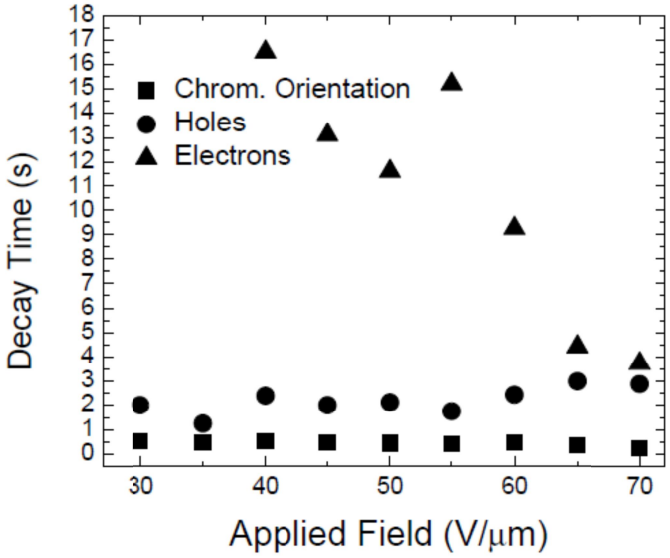

Figure 3. Variation of t_i, i=1 (chromophores: squares), 2 (holes: circles), and 3 (electrons: triangles) with applied bias field E_0 for 532 nm illumination.

As noted from Figure 3, the time constant t_1 (and the corresponding amplitude P_1, not shown here) associated with chromophores is relatively independent of the applied bias field. Incidentally, if the experiments are performed with a certain bias field on, and the incident illumination is instead switched on and off, the time response does not show the chromophore reorientational time constant, as expected. The sign of the amplitudes P_1 and P_2 are positive, which gives the exponential decay, while the sign of P_3 is negative. Our PR polymer, which is similar to commonly used PR polymers, has holes as primary charge carriers responsible for PR gratings. The time constant t_2 and the associated amplitude P_2 can, therefore, be attributed to the dynamics of grating formation due to holes. It is found that P_3 is negative, which implies that the associated time constant t_3 can be attributed to an opposite charge species, viz., electrons, and the formation of competing gratings. It is to be noted that the time constant t_3 associated with electron migration, decreases at a faster rate than t_2 with increasing applied fields, and for 532 nm illumination, they become approximately equal at a bias field of 70 V/μm. Since the mobility of charge carriers is inversely proportional to the response time, this means that the electron mobility increases faster than the hole mobility with applied bias field. Gill's equation models the mobility μ as a function of the applied bias field, and is given by [9]

$$\ln \mu \propto a + b{E_0}^{1/2}. \tag{2}$$

The variation of ln (μ) with ${E_0}^{1/2}$ has been plotted in Ref. [8] for holes and electrons, and shown to be approximately comparable at a bias field of 70 V/μm for 532 nm illumination. A similar behavior is found for 633 nm illumination, albeit at lower applied bias fields.

The temporal behavior of the transmission changes dramatically when applying bias fields at and above 70 V/μm (at 532 nm). Initially, there is a steep decrease of the transmission due to the chromophore reorientation and the formation of the hole grating, which is followed by a small increase in transmission due to the formation of the electron grating (i.e. the competing grating). Thereafter, at $t \approx 40$ s (for the case of 532 nm light) there is a further decrease in the transmission, suggesting gain enhancement. Gain enhancement beyond the regime of competing gratings occurs at lower applied fields using 633 nm illumination (≈40 V/μm compared to ≈70 V/μm), and the enhanced gain is far more dramatic for the case of 633 nm than 532 nm [10]. We attribute this reduction in the bias field threshold to the change in photocurrent, shown in Figure 4. Although at first glance this graph shows that there is an increase of a factor of 2.5 in the photocurrent comparing values measured at 532 nm and 633 nm, the two wavelengths have different absorption coeffcients ($\alpha_{532} = 162\ cm^{-1}, \alpha_{633} = 34\ cm^{-1}$). For a fair comparison, the absorption compensated photocurrent data for 633 nm

is redrawn with dashed lines by multiplying the 633 nm photocurrent data by the ratio of the absorption ($\frac{A_{532}}{A_{633}} = \alpha_{532}/\alpha_{633}$). This ratio has been measured and is of the order of 10. It is clear that the absorption compensated photocurrent for 633 nm is actually higher by a factor of 2 when compared to the photocurrent for 532 nm for the same applied field [10].

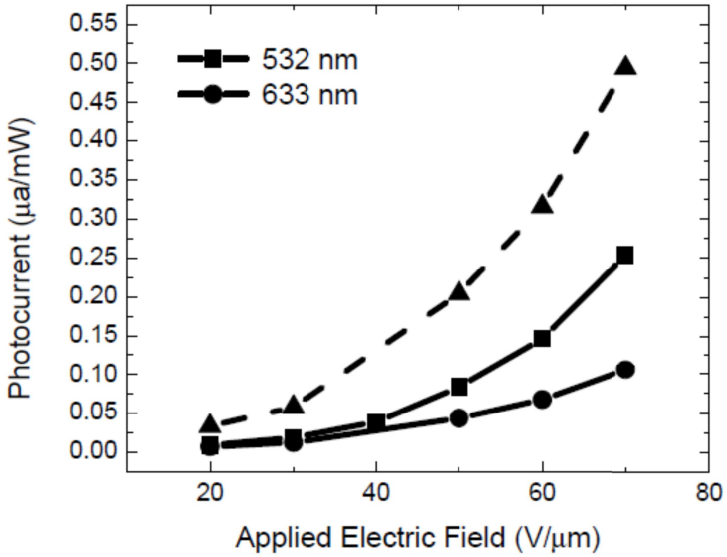

Figure 4. The steady-state photocurrent as a function of applied bias field (20 V/μm to 70 V/μm): (circles/lines) 633 nm and (squares/lines) 532 nm. The circle/dashed line trace in the photocurrent at 633 nm adjusted for the difference in absorption by multiplying the data with red circles/lines by the ratio of the absorption coefficients $\alpha_{532}/\alpha_{633} \approx 10$.

A possible mechanism for the gain enhancement, beyond the regime of competing electron gratings, can be identified upon examining the trend of the time constants $t_{2,3}$ (and hence, the mobility) as shown in Figure 3. At around 70 V/μm for 532 nm illumination, the time constants associated with holes and electrons are almost equal, i.e, $t_2 \approx t_3$ and from the trend in Figure 3, it is expected that above 70 V/μm, $t_2 > t_3$, implying that electron mobility should exceed the hole mobility. Due to this, the fast moving electrons can neither be trapped nor be able to recombine with the holes, and therefore no longer contribute to competing grating formation or reduction of the overall hole-formed grating. The same occurs for 633 nm illumination, albeit at smaller bias fields. Thus, hole-formed gratings should again dominate in the two-beam coupling measurements. This is further corroborated by the satisfactory single exponential fit to experimental data for normalized transmission as a function of time for 70 V/μm for 633 nm illumination [10]. The single exponential fit also supports the fact that positive ions do not play any role in gain enhancement.

4. CONCLUSION

In conclusion, grating formation and two-beam coupling have been investigated in a self-pumped reflection grating geometry in commonly used PR polymers, where holes have been conventionally assumed as the photogenerated mobile carriers responsible for grating formation. Upon analyzing the time dynamics of the transmission during self-pumped two-beam coupling using a novel multi-exponential fitting technique, it is shown that information about the charge species responsible for the grating formation can be deduced. The variation of the time constants, and hence the mobilities of holes and electrons with applied bias fields have also been investigated. Specifically, it has been shown in a PR polymer at moderate applied bias fields, the primary charge carriers (holes) establish an initial grating, followed by a subsequent grating (electrons) which decreases the two-beam coupling efficiency. At higher bias fields, electron contribution to competing gratings decreases, and gain enhancement occurs due to predominantly hole-formed gratings once again, due to enhanced mobility of electrons when compared to holes. The lower bias fields required for the onset of competing gratings and

gain enhancement for 633 nm illumination as compared to 532 nm is explained through examination of the absorption at the two wavelengths. It is also argued that other charges such as positively charged ions do not play any role in grating formation due to enhanced electron mobility. We show with using varying applied electric fields and illumination conditions, the steady-state two-beam coupling efficiency can be enhanced.

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