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Partha P. Banerjee

University of Dayton, pbanerjee1@udayton.edu

S. H. Buller

Air Force Research Laboratory

C. M. Liebig

Air Force Research Laboratory

S. A. Basun

Air Force Research Laboratory

Gary Cook

Air Force Research Laboratory

See next page for additional authors

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Author(s)

Partha P. Banerjee, S. H. Buller, C. M. Liebig, S. A. Basun, Gary Cook, Dean R. Evans, Pierre-Alexandre Blanche, J. Thomas, Cory W. Christenson, and N. Peyghambarian

Time dynamics of self-pumped reflection gratings in a photorefractive polymer

P. P. Banerjee,^{1,2} S. H. Buller,¹ C. M. Liebig,^{1,3} S. A. Basun,^{1,3} G. Cook,^{1,3} D. R. Evans,^{1,a)} P.-A. Blanche,⁴ J. Thomas,⁴ C. W. Christenson,⁴ and N. Peyghambarian⁴

¹*Air Force Research Laboratory, Materials and Manufacturing Directorate, Wright-Patterson Air Force Base, Dayton, Ohio 45433, USA*

²*University of Dayton, Department of ECE and Electro-Optics Program, Dayton, Ohio 45469, USA*

³*Azimuth Corporation, 4134 Linden Avenue, Suite 300, Dayton, Ohio 45432, USA*

⁴*College of Optical Sciences, University of Arizona, Tucson, Arizona 85721, USA*

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The time dynamics of self-pumped reflection gratings in a commonly used photorefractive polymer PDCST:PVK:ECZ-BBP:C₆₀ with no additional electron sources or traps is investigated. While holes are normally the mobile charges and responsible for grating formation, our experimental observations, analyzed using multi-exponential fitting curves, show evidence of electrons in addition to holes as charge carriers, particularly above an applied field of 40 V/μm. The dependence of effective carrier mobilities on the applied electric field, deduced from experimental results, show stronger field dependence of electron mobility at high electric fields. At an applied field of 70 V/μm, electron and hole mobilities become approximately equal, and the contribution of electrons on grating formation becomes significant. © 2012 American Institute of Physics. [doi:10.1063/1.3672832]

The photorefractive (PR) effect is a nonlinear optical phenomenon due to an induced intensity-dependent refractive index in a doped material that is also an electro-optic (EO) photoconductor.¹ Under non-uniform illumination, e.g., an interference pattern, photoexcited charge carriers migrate from the higher intensity regions and subsequently become trapped in the lower intensity regions of the material. This charge displacement results in the build-up of an electrostatic space-charge field, which modulates the refractive index. The movement of photoexcited carriers can be predominantly effected by three different mechanisms: diffusion, drift, and photovoltaic effect.^{1,2} This motion gives rise to a spatial phase shift between the incident light intensity pattern and the refractive index modulation. An important consequence of this phase shift is energy transfer through two-beam coupling (TBC) between two light beams interfering in a PR medium. TBC can only occur in materials where there is a non-zero phase shift between the optical interference pattern and the induced refractive index grating.³

Doped polymeric composites are alternatives to inorganic crystals as PR media with the advantage of being able to optimize the properties responsible for the PR effect simultaneously and independently to a degree not possible in existing inorganic materials.⁴ The advantages of the multi-component composite (chromophore: photoconductor: plasticizer: photosensitizer) approach include (a) convenient engineering of the molecular structures of the components to optimize charge generation, transport, and trapping, (b) easy manipulation of energetics using dopants with suitable ionization energy, (c) flexibility of polymeric materials to be processed into different device forms, (d) easy processing and reproducibility, and (e) lower cost and fabrication time.

Reorientation of the chromophores in the PR polymer operating close to the glass temperature occurs due to the total electrostatic field, which comprises the externally applied bias field, E_0 , and the optically induced space charge field E_{sc} .⁵ The chromophore reorientation, together with the electro-optic effect, modulates the refractive index in the PR polymer.

While holes are the predominant mobile carriers in common PR polymers,⁶ researchers have deliberately designed PR polymers with a second mobile charge species to improve their performance.^{7–11} Wang *et al.*⁷ have shown that both electrons and holes are mobile in PR polymers, with the electron mobility becoming comparable to the hole mobility at high bias fields. However, a consequence of secondary charge species in PR materials is the presence of competing gratings, and the time dynamics are no longer single exponential in behavior.^{12,13} Grating formation dynamics in PR crystals that have a high coupling factor ($\Gamma L > 3$), a single charge carrier species, and an applied electric field have been described by Au and Solymar and Kukhtarev *et al.*;^{14,15} however, this is not pertinent to PR polymers, which typically have coupling factors much lower than the above value.

In this work, the temporal response of the PR polymer PDCST:PVK:ECZ-BBP:C₆₀ is investigated in a self-pumped reflection grating two-beam geometry and under different bias fields. In this configuration, the signal beam is self-generated by the Fresnel reflection of the pump beam off the rear surface of the polymer; the two beams interfere and power is transferred from one beam to the other. Details of self-pumped two-beam coupling can be found in Ref. 16, although, in the case of the polymer work in this paper, the incident laser beam remained unfocused. Although this polymer has no additional electron sources or traps, it is shown that bipolar charge transport still exists in our PR polymer

^{a)}Author to whom correspondence should be addressed. Electronic mail: dean.evans@wpafb.af.mil.

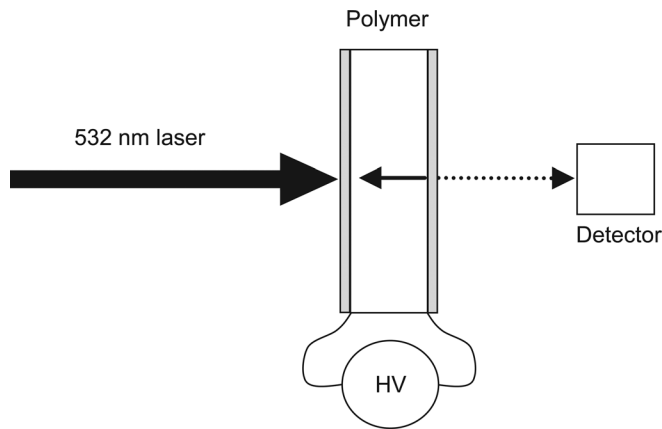


FIG. 1. PR polymer in self-pumped two-beam coupling geometry. The small arrow (signal beam) indicates the counter-propagating Fresnel reflection of the incident pump beam. The dotted line represents the transmitted signal beam. The signal beam is amplified at the expense of the pump beam.

samples for a range of applied bias fields. The dependence of their relative mobilities on the applied bias field is deduced from experimental results.

A schematic of the experimental arrangement is shown in Fig. 1. A linearly polarized CW frequency-doubled Nd:YVO₄ laser with a 532 nm wavelength (Coherent Verdi V) attenuated to approximately 10 mW output is normally incident on the PR polymer. A bias voltage from a high voltage (HV) source is applied across the approximately 100- μm -thick sample. The bias voltage is changed from 1.5 kV to 7 kV in steps of 0.5 kV. This corresponds to the variation of the applied bias field E_0 from 15 V/ μm to 70 V/ μm in steps of 5 V/ μm . 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. A measurement time of 50 s has been used to allow the PR response of the polymer to reach a steady state. Between measurements, the applied field is turned off for 50 s to allow for the 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). The transmitted power as a function of time is shown in Fig. 2 for the case where the applied bias field is opposite to the direction of the incident beam.

Figure 3 shows typical sets of experimental results for applied bias fields $E_0 = 20, 40,$ and 60 V/ μm . Multi-exponential fits (to be discussed later) are superimposed on the experimental data. It can be seen that the transmitted power rapidly decreases when the bias field is applied. For bias fields $E_0 < 40$ V/ μm , the transmitted power reaches steady state after the initial decrease. For $E_0 \geq 40$ V/ μm , the initial drop in transmitted power is followed by a subsequent rise to the steady state. The observed transient transmitted power for various applied bias fields is in agreement with Wang *et al.*⁷ The variation of the transmitted power is similar, even when the direction of E_0 is reversed. The unidirectional energy transfer in both cases¹⁵ may be indicative of

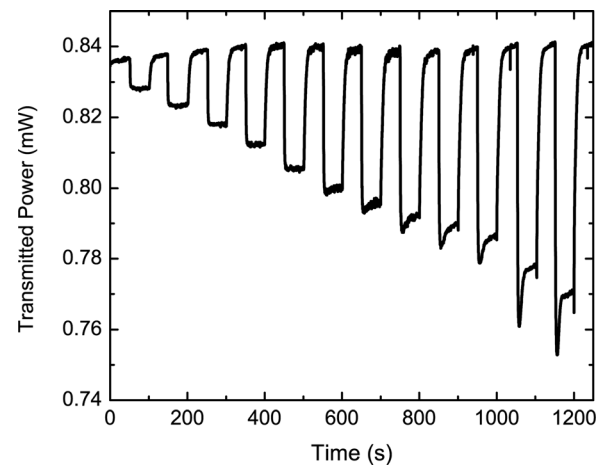


FIG. 2. Time response of the PR polymer to different bias voltages. The lowest bias field is 15 V/ μm , while the highest is 70 V/ μm , increased in steps of 5 V/ μm .

non-negligible diffractive energy coupling between the incident and the (weak) Fresnel reflected beams in the PR polymer rather than a true energy coupling. This can occur due to suboptimal ($\neq \pi/2$) field-dependent phase shift measured between the intensity grating and the induced refractive index grating during energy coupling in our PR polymer, in agreement with Grunnet-Jepsen *et al.*¹⁷ It should be mentioned that the role of absorption gratings for our geometry is shown to be negligible (see, for instance, Wang *et al.*).¹⁸ Also, Ref. 19 describes the effect of absorption gratings (which are in phase with the intensity grating) in our PR polymer using a transmission geometry with a zero bias across the sample. It is observed that the effect on diffraction efficiency of absorption gratings was less than 0.025%.

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

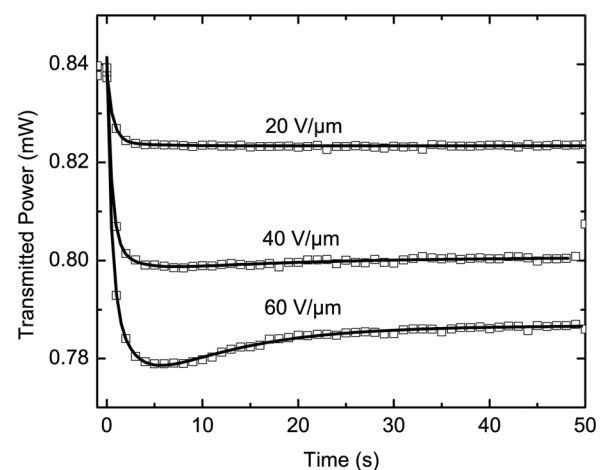


FIG. 3. Examples of time response of the PR polymer for applied fields E_0 of 20, 40, and 60 V/ μm . Superimposed on the experimental data are fitted curves formed from linear combinations of exponentials. No noticeable change (gain reversal) is observed for $E_0 = 20$ V/ μm , even for much longer times.

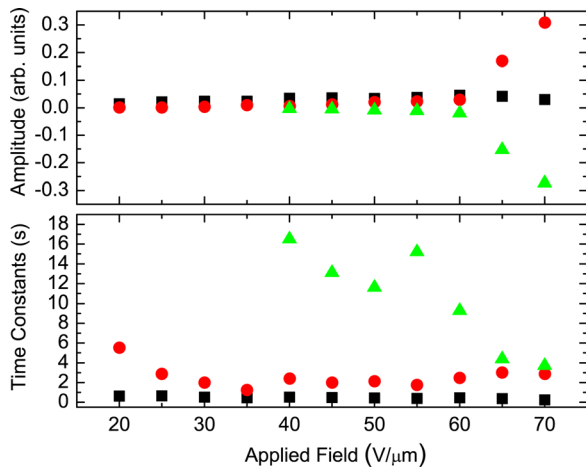


FIG. 4. (Color online) Variation of P_i (top) and t_i (bottom) P_i , $i=1$ (chromophores: squares), 2 (holes: circles), and 3 (electrons: triangles) with applied bias field E_0 .

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

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 4 shows (a) the powers P_i , $i=1, 2, 3$ and (b) the time constants t_i , $i=1, 2, 3$ as a function of the applied bias field E_0 . For applied fields $E_0 < 40$ V/ μ m, the transmitted power can be best fit with double exponential function rather than a triple exponential function. However, for $E_0 \geq 40$ V/ μ m, it is necessary to fit the data with triple exponential functions. As can be seen from Fig. 3, the fitted results are in good agreement with the experimental plots.

For all applied fields, it is worthwhile to consider the mechanisms that contribute to the time response of the transmitted power. For applied bias fields $E_0 < 40$ V/ μ m, there are two characteristic time constants. The shortest time constant t_1 (squares in Fig. 4), which shows little variation with E_0 , is attributed to the orientational time constant of the chromophores with the applied field. It is also observed that, if the optical beam is turned on *after* the bias field has been applied, the resulting time dependence of transmitted optical power (or resulting grating buildup) can be fit using a single exponential time constant similar to the second time constant t_2 (circles in Fig. 4). Our PR polymer, which is similar to commonly used PR polymers, have holes as primary charge carriers responsible for PR gratings.⁴ The time constant t_2 can, therefore, be attributed to the dynamics of grating formation due to holes. For bias fields $E_0 \geq 40$ V/ μ m, a third time constant t_3 (triangles in Fig. 4) becomes measurable. Other PR polymers^{6,7} have also shown a contribution of a secondary charge species of opposite sign, viz., electrons, as in the bipolar charge transport model.²⁰ In Ref. 7, the time constants have been deduced from four wave mixing (or diffraction efficiency) measurements as well as from time-of-flight measurements. Also, it is worthwhile to note that the time response of the TBC of Fig. 3 for $E_0 = 40$ and 60 V/ μ m

is in agreement with the expected behavior of PR materials with two species of charge carriers.¹³ Similar temporal behavior has been observed with other samples of the PR polymer at different wavelengths (viz. 633 nm) and during holographic readout in a transmission TBC geometry.

The following observations can be made from Fig. 4:

- the time constant t_2 associated with hole migration decreases with an increasing applied field for $E_0 < 40$ V/ μ m. The time constant t_3 associated with electron migration, which becomes relevant for $E_0 \geq 40$ V/ μ m, decreases at a faster rate than t_2 with increasing applied fields. At $E_0 = 70$ V/ μ m, the two time constants t_2 and t_3 are *approximately* equal;
- opposite signs of the associated coefficients P_2 and P_3 for $E_0 \geq 40$ V/ μ m support the existence of both holes and electrons. P_2 and P_3 become *approximately* equal and opposite at $E_0 = 70$ V/ μ m.

Although the source of the electrons is beyond the scope of this paper, one can consider that a plausible source of the complementary charges is from excitons.²¹ In this case, an applied electric field would break the exciton, allowing for free charges (such as electrons) to contribute to an opposing space charge field.²² This proposed source of electrons could explain the field dependence observed in the two-beam coupling gain reversal strength, and the competing space charge fields would be explained by the well-known bipolar transport model.²⁰

The *effective* mobility μ of charge carriers is inversely proportional to the effective response time.⁷ The mobility has been shown to change with the applied bias field, and a model for the variation of μ for PR polymers with E_0 is given by Gill's equation for mobility (or Poole-Frankel effect),²³

$$\ln \mu_i \propto \ln(1/t_i) \propto a_i + b_i E_0^{1/2}; \quad i = 2, 3. \quad (2)$$

The reciprocals of the effective time constants $t_{2,3}$ (proportional to the mobilities) have been plotted on a log scale as a function of the square root of the applied bias field E_0 and are shown in Fig. 5. As seen from Fig. 5, the variation of $\ln(1/t_2)$ is approximately linear and in general agreement with Gill's law^{23,24} up to $E_0 = 40$ V/ μ m. A linear dependence of the logarithm of the reciprocal of the time constant (or exponential dependence of the mobility) arises purely from the interaction of the charge with randomly distributed dipoles, although, in general, the variation is nonlinear and complicated; different scenarios giving rise to different variations of the mobility with the applied field are extensively discussed in Ref. 24. It is also seen from Fig. 5 that, when both charge carriers are present ($E_0 \geq 40$ V/ μ m), the mobility of electrons is more strongly dependent on the applied bias field than the hole mobility. Along with the increase in the electron mobility with the applied bias field, the effect of electrons on the PR grating also increases, as can be seen from the increase in P_3 in Fig. 4. At $E_0 = 70$ V/ μ m, the time constants and, hence, the mobilities of holes and electrons are approximately equal (see Fig. 5). It is speculated that, at even higher applied bias fields, the dominant charge mobility

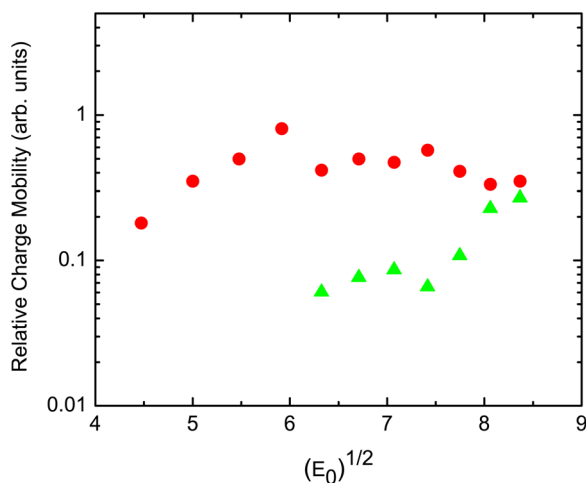


FIG. 5. (Color online) Variation of relative charge mobilities of holes (circles) and electrons (triangles) for t_2 and t_3 .

mechanism will be related to hopping among the localized states and would be described by kinetic theory, but this occurs at applied fields beyond those used in this study.⁷

In conclusion, the time dynamics of self-pumped reflection gratings in the PR polymer PDCST:PVK:ECZ-BBP:C₆₀ has been investigated as a function of the applied bias field. The evolution of the PR gratings from the time of application of the bias field has been analyzed using multi-exponential fitting curves. One of the time constants, which is independent of the applied bias field, is attributed to chromophore reorientation; this is determined by the self-pumped TBC experiment, where the applied field remains on at all times and the laser source is switched on and off. Analysis of the other pertinent time constants show evidence of a single species of charge carriers (holes) for $E_0 < 40$ V/ μ m and a second species of charge carriers (electrons), which is only measurable for $E_0 > 40$ V/ μ m. Similar behavior has been observed with other samples of the PR polymer at 633 nm. The dependence of the effective carrier mobilities on the applied bias field is deduced from experimental results. It is shown that the hole and electron mobilities become comparable at high values of the applied field due to the fact that the electron mobility is more strongly dependent on the applied field than the hole mobility. The source of electrons is presumed to be from excitons, which is suggested by the field dependence of the electron grating formation and electron mobility. Furthermore, the contribution of electrons in

the formation of gratings becomes significant for high applied fields. While it is generally true that higher fields enhance TBC gain in PR polymers, the presence of electrons and holes at high bias fields may considerably reduce the peak and steady-state TBC gain due to formation of competing gratings.

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