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P. P. Banerjee, S. H. Buller, C. M. Liebig, S. A. Basun, G. Cook et al.

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


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

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

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

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.

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. 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. 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.

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. 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, E₀, and the optically induced space charge field Eₛ. 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, researchers have deliberately designed PR polymers with a second mobile charge species to improve their performance. Wang et al. 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. Grating formation dynamics in PR crystals that have a high coupling factor (TL > 3), a single charge carrier species, and an applied electric field have been described by Au and Solymar and Kukhtarev et al.; 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.

Author to whom correspondence should be addressed. Electronic mail: dean.evans@wpafb.af.mil.
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 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. The variation of the transmitted power is similar, even when the direction of \( E_0 \) is reversed. The unidirectional energy transfer in both cases may be indicative of 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 (≠ π/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. It should be mentioned that the role of absorption gratings for our geometry is shown to be negligible (see, for instance, Wang et al.). 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...
the respective time constants. The data is fit using a
mitted power. For applied bias fields
experimental plots.
secondary charge species of opposite sign, viz., electrons, as
E
40 V/μm, the transmitted power can be best fit with
double exponential function rather than a triple exponential
function. However, for \( E_0 \geq 40 \) V/μm, 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/μm, there
are two characteristic time constants. The shortest time con-
stant \( t_1 \) (squares in Fig. 4), which shows little variation with
\( E_0 \), is attributed to the orientational time constant of the chro-
mophores 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 for-
dation due to holes. For bias fields \( E_0 \geq 40 \) V/μm, a third
time constant \( t_3 \) (triangles in Fig. 4) becomes measurable. Other PR polymers6,7 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 dif-
fraction 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/μm
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:
(a) the time constant \( t_2 \) associated with hole migration
decreases with an increasing applied field for \( E_0 < 40 \) V/μm. The time constant \( t_3 \) associated with electron
migration, which becomes relevant for \( E_0 \geq 40 \) V/μm,
decreases at a faster rate than \( t_2 \) with increasing applied
fields. At \( E_0 = 70 \) V/μm, the two time constants \( t_2 \) and \( t_3 \) are approximately equal;
(b) opposite signs of the associated coefficients \( P_2 \) and \( P_3 \)
for \( E_0 \geq 40 \) V/μm support the existence of both holes
and electrons. \( P_2 \) and \( P_3 \) become approximately equal and opposite at \( E_0 = 70 \) V/μm.

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 cou-
ing gain reversal strength, and the competing space charge
fields would be explained by the well-known bipolar trans-
port model.20
The effective mobility \( \mu \) 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 \( \mu \) for PR polymers with \( E_0 \) is given
by Gill’s equation for mobility (or Poole-Frankel effect).23
\[
\ln \mu_i \propto \ln(1/t_i) \propto a_i + b_i E_0^{1/2}; \quad i = 2, 3.
\]
The reciprocals of the effective time constants \( t_{2,3} \) (pro-
tional 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 law23,24 up to \( E_0 = 40 \) V/μm. A linear depend-
ence 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 var-
iations 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/μm), the mobi-
licity 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 \( P_2 \) in Fig. 4. At \( E_0 = 70 \) V/μm, 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

\[
\begin{align*}
P_i(t) &= P_0 + \sum_{i=1}^{3} P_i \exp(-t/t_i),
\end{align*}
\]
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/μm, the transmitted power can be best fit with
double exponential function rather than a triple exponential
function. However, for \( E_0 \geq 40 \) V/μm, 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.

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 \( E_0 \).
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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