Terahertz emission from biased conjugated polymers excited by femtosecond laser pulses

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We perform terahertz emission spectroscopy to investigate the ultrafast motion of electrons and holes in conjugated polymer films excited by femtosecond laser pulses under in-plane bias electric field. The terahertz waveforms are found to exhibit not the features of free carrier acceleration along bias electric field but a characteristic shape reproduced well by the second time derivative of a delta-function-like polarization. Linear-to-quadratic relations between the terahertz emission amplitude and the excitation intensity are observed for three different conjugated polymers, indicating that the polarization is created by either exciton formation or optical rectification involving two-step excitation via localized states.

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Table I. Film thicknesses and absorption peak energies of conjugated polymer samples.

| Sample  | Film thickness (μm) | Absorption peak energy (eV) |
|---------|---------------------|-----------------------------|
| P3HT    | 30                  | 2.4                         |
| MEH-PPV | 30                  | 2.5                         |
| F8BT    | 100                 | 2.7                         |

Terahertz emission is a useful probe for elementary excitations and non-equilibrium charge transport relevant to higher performance of optoelectronic devices such as transistors and photovoltaic cells. This probe has been successfully applied to inorganic semiconductors, organic films, and nanocarbon materials. So far, there have been only a few reports on terahertz emission measurements of conjugated polymers, which are major organic semiconductors with easy processability, mechanical flexibility, and a unique one-dimensional nature. Soci and Moses have observed the terahertz emission from phenylenevinylene-based polymers in the time domain. However, it is not well understood whether the ultrafast motion of electrons and holes excited under bias electric field is common to various types of conjugated polymer. Such a character is complementary to those observed under highly doped conditions and will provide an essential insight into organic optoelectronics.

In this paper, we report the terahertz emission from three different films of typical conjugated polymers, i.e., poly(3-hexylthiophene) (P3HT), poly[2-methoxy-5-(2-ethylhexyl)oxy]-1,4-phenylenevinylene) (MEH-PPV), and poly(9,9-dioctylfluorene-alt-benzothiadiazole) (F8BT), excited by femtosecond laser pulses under in-plane bias electric field. The terahertz waveforms for the three films had the same order of magnitude; they exhibited not the features of free carrier acceleration along bias electric field but a characteristic shape that was nearly symmetric with respect to the main peak. This shape was found to be reproduced well by the second time derivative of a delta-function-like polarization. Furthermore, we observed linear-to-quadratic relations between the terahertz emission amplitude and the excitation intensity that depend on the conjugated polymers. This can be ascribed to either exciton formation or optical rectification involving two-step excitation via localized states.

The samples used here were P3HT (regioregular), MEH-PPV, and F8BT cast films made on glass slides from 3.0, 1.0, and 5.0 wt % chloroform solutions, respectively. The thicknesses of these films are listed in Table I. To apply in-plane bias electric fields to polymer chains, we fabricated a pair of aluminum half-plane-like electrodes (separated by a 0.5-mm-wide linear gap) on the front surface of each glass slide before casting a solution. More details on the samples, including the chemical structures and the electrode pattern, are illustrated in Fig. S1 in the online supplementary data at http://stacks.iop.org/APEX/9/121601/mmedia. The samples were excited by optical pulses with a duration of ~120 fs, which were delivered from a regeneratively amplified mode-locked Ti:sapphire laser at a repetition rate of 1 kHz and transmitted through the back surfaces of the glass slides perpendicularly, under in-plane bias voltages of up to 600 V. The central photon energy of the optical pulses was 1.55 eV, at which P3HT, MEH-PPV, and F8BT have small but finite absorption coefficients due to the low-energy tail of broad π–π* resonance. The absorption spectra of thinner films can be seen in Fig. S2 in the online supplementary data at http://stacks.iop.org/APEX/9/121601/mmedia; absorption peak energies are shown in Table I.

The time-varying current on the picosecond scale, which can arise from the true photocurrent and the displacement current (polarization current) through the conjugated polymers under in-plane bias voltage, serves as the source of transient terahertz emission. The terahertz electric field, proportional to the time derivative of the current, was emitted into the free space on the front side of the samples and recorded in the time domain by using a 0.2-mm-thick (110) ZnTe electro-optic sensor. The measurement geometry can be seen in Fig. S1(b) in the online supplementary data at http://stacks.iop.org/APEX/9/121601/mmedia. The terahertz signal increased linearly with in-plane bias voltage for each sample. The temporal waveforms of the terahertz electric
field measured for the samples were compared with one another and with that measured for an undoped GaAs crystal, which has a well-known mechanism of charge transport under bias electric fields.\textsuperscript{24,25} When the excitation intensity was varied by an order of magnitude between 0.13 and 1.8 mJ/cm\textsuperscript{2}, the terahertz signal retained its shape but substantially changed its amplitude for each sample; a thicker electro-optic sensor (2.0-mm-thick ZnTe) was used to measure terahertz emission amplitudes even for low excitation intensities. All the measurements were performed at room temperature.

Figure 1 shows the terahertz waveform emitted from the P3HT sample (solid curve) under a bias electric field of 12 kV/cm for a medium excitation intensity of 0.76 mL/cm\textsuperscript{2}, with the time origin set to an arbitrary position. The terahertz electric field exhibits an initial small positive peak at 1.7 ps, the largest negative peak at 2.0 ps, and two subsequent positive peaks. This is quite different from the measurement result for the GaAs crystal shown by the dashed curve, which has large positive and negative peaks ascribed to the initial acceleration of photocarriers in the $\Gamma$-valley and the subsequent transfer into satellite valleys with larger effective masses.\textsuperscript{24,25} Note that the vertical axis values for the solid and dashed curves were measured with common polarity. The solid curve thus lacks the features of free carrier acceleration along bias electric field, suggesting mechanism(s) for terahertz emission other than that proposed in Ref. 6.

Figure 2(a) shows the terahertz waveforms emitted from the MEH-PPV and F8BT samples together with that emitted from the P3HT sample. Here, the vertical axis values for the MEH-PPV and F8BT samples have been magnified by factors of 1.7 and 4.5, respectively. The three terahertz waveforms have the same order of magnitude and closely resemble one another in shape, indicating that the underlying physics of terahertz emission is common to conjugated polymers with different main chains. The terahertz signals were nearly symmetric with respect to the largest negative peak at 2.0 ps, which led us to consider the second derivative of a symmetric (i.e., delta-function-like) instantaneous polarization in the time domain on the basis of the displacement current contribution.

Here, we attempt to reproduce the observed terahertz waveforms by assuming a sharp Gaussian polarization peaking at 2.0 ps and furthermore by taking account of a possible waveform distortion due to the group-velocity mismatch between the terahertz pulses and optical pulses (sampling pulses) during the electro-optic detection with a finite sensor thickness.\textsuperscript{26,27} The second time derivative of the polarization is shown in Fig. 2(b), where the full width $\tau$ at half maximum of the polarization was set to 0.35 ps, i.e., a value comparable to the temporal resolution of our measurement system. Figure 2(c) shows the simulated terahertz waveform convolved with the response function of the 0.2-mm-thick ZnTe electro-optic sensor\textsuperscript{26,27} and compares it with the measured terahertz waveform for the P3HT sample. The agreement between the simulation and measurement is excellent, indicating that the terahertz electric fields shown in Fig. 2(a) were indeed emitted by the creation of instantaneous polarization and detected with little distortion through the 0.2-mm-thick ZnTe electro-optic sensor. The feature of instantaneous polarization described above has never been revealed by previous studies using a bolometer\textsuperscript{5} or a thicker electro-optic sensor.\textsuperscript{6}

Figure 3 shows the relations between the terahertz emission amplitude $E_{\text{THz}}$ and the excitation intensity $I$ for P3HT (circles), MEH-PPV (squares), and F8BT (triangles). First, the P3HT sample exhibited $E_{\text{THz}} \propto I^{0.97}$ for $I = 0.13$–1.8 mJ/cm\textsuperscript{2}. This indicates that the instantaneous polarization in

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Fig1.png}
\caption{Temporal waveform of the terahertz electric field emitted from a P3HT film (solid curve) under an in-plane bias electric field of 12 kV/cm for an excitation intensity of 0.76 mL/cm\textsuperscript{2}. Also shown by the dashed curve as a reference is the terahertz waveform emitted from an undoped GaAs crystal with the same pattern of electrodes. The vertical axis values were measured with common polarity.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Fig2.png}
\caption{Terahertz waveforms measured for three different conjugated polymers and simulated for instantaneous polarization. (a) Measurement results for P3HT, MEH-PPV, and F8BT films (with vertical axis values for MEH-PPV and F8BT magnified by factors of 1.7 and 4.5, respectively). (b) Simulation result for the second time derivative of a Gaussian polarization with a full width at half maximum of $\tau = 0.35$ ps. (c) Simulation result convolved with the response function of a 0.2-mm-thick ZnTe electro-optic sensor and then compared with the measurement result for P3HT.}
\end{figure}
P3HT was created either by the real excitation of electron–hole pairs due to one-photon absorption or by the optical rectification due to second-order optical nonlinearity, for which $E_{THz}$ should increase linearly with $I$. Second, $E_{THz}$ was proportional to $I^{1.8}$ for the MEH-PPV sample and to $I^{2.0}$ for the F8BT sample, suggesting that two-step excitation was involved in the creation of polarization. Note that two-step excitation needs localized states, such as polaron states due to the partial oxidation by air and low-energy exciton states due to structural disorder, which allow the absorption at 1.55 eV for the first step; these localized states may have partly contributed to the absorption coefficients shown in Fig. S2 in the online supplementary data at http://stacks.iop.org/APEX/9/121601/media.

Now, we discuss in more detail how the instantaneous polarization can be created in the two possible mechanisms mentioned above. For the real excitation of electron–hole pairs, polarization is expected to be coherently created by excitons with electron and hole wave functions shifted in the opposite directions under in-plane bias electric field and then to be rapidly dephased by phonons on a time scale of less than 0.35 ps. This process is induced by the one-photon absorption at 1.55 eV directly (owing to the tail of broad $\pi-\pi^*$ resonance) or by the two-step absorption via the localized states (with the second step being the excitation to less localized exciton states). For the optical rectification under in-plane bias electric field, on the other hand, polarization is expected to appear with a duration similar to those of optical pulses. This process is induced by virtual excitation alone or by two-step excitation (with the first step being the real excitation to the localized states and the second step being virtual excitation). Here, we recall that the P3HT sample had the narrower $\pi-\pi^*$ energy gap and presumably the better crystallinity than the MEH-PPV and F8BT samples. The observed relations between $E_{THz}$ and $I$ can be explained by either exciton formation or optical rectification when the two-step excitation (leading to $E_{THz} \propto I^2$) is resonantly enhanced and more efficient than the ordinary excitation (leading to $E_{THz} \propto I$) depending on the width of energy gap and also on the degree of disorder.

In summary, we performed terahertz emission measurements of P3HT, MEH-PPV, and F8BT films excited by femtosecond laser pulses under in-plane bias electric field. We found that the terahertz waveforms for the three conjugated polymers have the same order of magnitude; they exhibit not the features of free carrier acceleration along bias electric field but a characteristic shape reproduced well by the second time derivative of a delta-function-like polarization. Furthermore, we observed an almost linear relation between the terahertz emission amplitude and the excitation intensity for P3HT, a quadratic relation for F8BT, and an intermediate relation for MEH-PPV. This can be ascribed to either exciton formation or optical rectification involving two-step excitation via localized states. Thus, we have presented possible major mechanisms for terahertz emission common to typical conjugated polymers with different main chains.

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also available for excitation pulses. However, much larger absorption coefficients (or smaller absorption depths) at 3.10 eV led to the thermal degradation of polymer–glass interfaces for high excitation intensities. The below-gap excitation at 1.55 eV allowed us to prepare suitable experimental conditions more systematically.

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