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Mobile Charge Generation Dynamics in P3HT:PCBM Observed by Time-Resolved Terahertz Spectroscopy

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Abstract: Ultra-broadband time-resolved terahertz spectroscopy is used to examine the sub-ps conductivity dynamics of a conjugated polymer bulk heterojunction film P3HT:PCBM. We directly observe mobile charge generation dynamics on a sub-100 fs time scale.

OCIS codes: (300.6495) Spectroscopy, terahertz; (300.6500) Spectroscopy, time-resolved; (160.5470) Polymers

1. Introduction

Charge carrier generation in conjugated polymer bulk heterojunctions plays a determining role in the operation of solution based optoelectronics such as low cost and flexible photovoltaic cells [1]. Despite years of research, the mechanism for mobile charge generation is still not well understood, particularly within the first few picoseconds following photon absorption [2] . Optical probes with sub-ps resolution are typically not sensitive to the mobility of charge carriers, and so often rely on indirect evidence of free carriers. Here we apply ultra-broadband THz spectroscopy to directly probe the creation of mobile carriers on a sub-100 fs time scale in a device-ready, roll-to-roll processed poly-3-hexylthiophene / phenyl C60-butyric acid methyl ester (P3HT / PCBM) film.

2. Experiment

Our experiment is based on two-color THz generation in an air plasma yielding ultra-broadband pulses shown in Fig. 1(a) with a bandwidth of more than 15 THz (inset Fig. 1(a)) [5, 6]. Half of the 3.0 W output from the 1 kHz Ti:sapphire regenerative amplifier is split into three beams: generation, detection and excitation beams. The generation line undergoes second harmonic generation (SHG) in a 100 μm thick BBO crystal and the 800 and 400 nm beams pass through a zero order half waveplate for 800 nm (full wave at 400 nm) and are then focused by an off-axis parabolic mirror to produce a plasma in the dry nitrogen atmosphere inside the setup purge box, emitting a broadband THz pulse. The THz pulse is collimated and transmitted through a high resistivity Si beamsplitter before it is focused at the sample at normal incidence. The reflected beam is collimated and directed by the beamsplitter, a mirror and an off-axis parabolic mirror to share a focus with the 800 nm gating beam between two planar electrodes and the THz pulse is detected by air-biased coherent detection [3]. The 400 nm excitation beam is derived by SHG of the fundamental in a 100 micron thick BBO crystal and is co–linear with the THz probe pulse at a fluence of 570 μJ/cm^2. THz waveforms are recorded after reflection without ($E_{ref}(t)$) an excitation pulse simultaneously with the differential $\Delta E(t,\tau_p)=E_{ref}(t)-E_{pump}(t,\tau_p)$ at pump-probe delay time τ_p where $E_{pump}(t,\tau_p)$ is the transient recorded when the sample is pumped. Fourier transform and subsequent analysis treating the thin excited film as a uniform sheet conductor enables the extraction of the complex conductivity spectrum over the reference pulse bandwidth [7]. The sample is the technologically promising P3HT/PCBM bulk heterojunction on a PET plastic substrate coated with a thin layer of ZnO that acts as a transport layer in an actual device. Further details of the sample preparation are given elsewhere [4]. The samples are annealed at $140°$C for approximately 10 minutes during processing.

3. Results

Figure 1 shows $E_{ref}(t)$ and $\Delta E(t,\tau_p)$ transients taken 120 fs following excitation of the film. $\Delta E(t,\tau_p)$ reaches a maximum amplitude at 120 fs, which is 3 times the temporal resolution of the experiment given by the 40 fs pump pulse duration. As the THz modulation is sensitive to the photoinduced sheet conductance of the film, we therefore assign the buildup of $\Delta E(t,\tau_p)$ to the generation of mobile charge carriers in the P3HT:PCBM film.

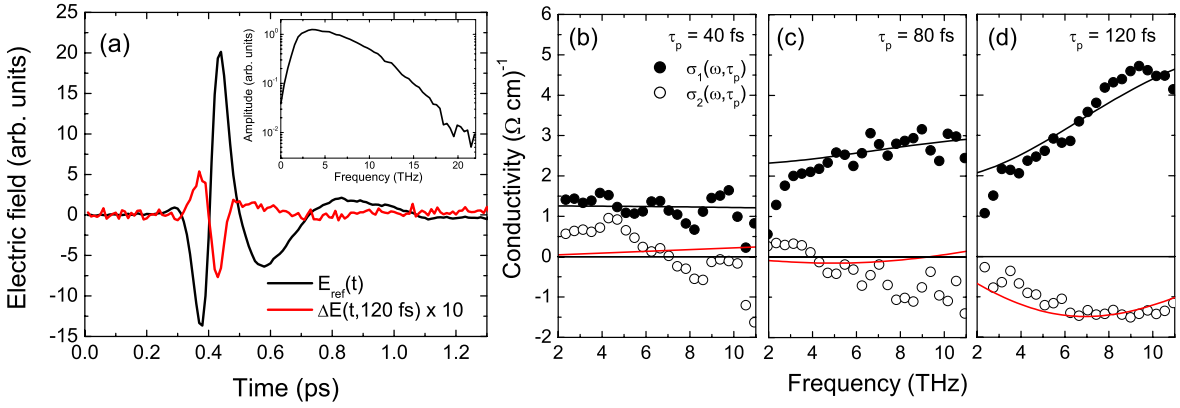

Fig. 1. (a) The time domain reference and differential THz transient at $\tau_p = 120$ fs with reference pulse Fourier amplitude spectrum shown in the inset. The transient real (solid) and imaginary (hollow) components of the complex THz conductivity of the P3HT:PCBM film following 400 nm photoexcitation at a fluence of 570 μJ/cm^2 and $\tau_p =$ (b) 40 fs, (c) 80 fs and (d) 120 fs.

The transient complex conductivity spectra, $\tilde{\sigma}(\omega) = \sigma_1(\omega, \tau_p) + i\sigma_2(\omega, \tau_p)$, for early τ_p are shown in Fig. 1(b-d) and can be best described by a phenomenological Drude-Smith model incorporating backscattering [8]. This model has the advantage of being able to continuously describe a material from a free carrier Drude response (c = 0) to a highly disordered insulating response (c = -1). For $\tau_p > 80$ fs, the main spectral features: 1) the increasing $\sigma_1(\omega)$ with frequency ω and negative imaginary conductivity $\sigma_2(\omega)$ have been observed previously at longer pump probe delays. However, for $\tau_p = 40$ fs the response is best described by a free-carrier Drude response indicating that immediately following photoexcitation, there is a population of carriers that are highly delocalized along the polymer chain. The extracted scattering time τ remained constant at a value of approximately 7 fs for all delay times. The plasma frequency $\omega_p = 18.9$ THz at the $\tau_p = 120$ fs peak, corresponding to a free carrier density of 7.5x10^{18} cm^{-3} using an effective mass of m*=1.7 m$_e$ (m$_e$ is the electron mass). Comparing to the photon density, this corresponds to an initial mobile carrier yield of 20%. Following the peak, the density is found to decay to 1/3 its peak value exponentially with a time constant of 950 fs (not shown). Considering other ultrafast studies finding exciton dissociation occurring on 4 - 9 ps time scales in annealed samples, we attribute this rapid decay to the formation of excitons or a bound charge transfer states from initially hot, delocalized population due to the excess photon energy of the 400 nm pump. Such an interpretation is in agreement with recent time-resolved photoluminescence measurements [9].

4. Conclusions

In conclusion, we have applied ultra-broadband reflective terahertz spectroscopy to observe the earliest photoconductivity dynamics ever observed in an organic semiconductor. We see evidence for delocalization of charges in band states on 40 fs time scales, followed by a 1 ps decay into a bound, possibly an excitonic, state.

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