Terahertz generation from poly(*p*-phenylene vinylene) photoconductive antenna

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Abstract

We report on terahertz (THz) emission from a photoconductive antenna made of stretch-oriented poly(*p*-phenylene vinylene) (PPV) obtained by two-photon optical excitation. The spectrum of the THz emission was detected by an autocorrelation technique with about 1 ps time resolution, limited by the antenna bandwidth. The ultrafast generation of the photocurrent is compatible with a direct carrier excitation mechanism operating in PPV.
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1. Introduction

Spectroscopy in the terahertz (THz) spectral region (10 μm to 1 mm) has been rarely investigated even though many interesting physical properties, such as those related to mobile carriers are amenable to THz spectroscopy. The reason for this deficiency has been mainly due to the lack of efficient and convenient THz sources. In recent years, however, a great effort has been devoted to the development of new THz sources, based on high mobility semiconductors [1], sources that opened a new window to studying the charged carrier transport properties in the sub-picosecond time regime [2]. So far, this new approach has been applied mostly to inorganic semiconductors [2]; a recent work has demonstrated the utility of THz spectroscopy to organic molecules as well [3]. The use of THz emission properties to investigate transient photoconductivity provides a powerful experimental approach to studying the charge transport in conjugated polymers, systems that can exhibit mobility comparable to that of amorphous silicon [4]. Additionally, the possibility of using electrodeless techniques to investigate the transport properties is useful in order to avoid the problems (such as carrier injection from the metallic contacts into the semiconductor) inherent in various contact geometries [5]. Reports on studying the carrier mobility in conjugated polymers using electrodeless techniques in the microwave spectral region, with sub-nanosecond tempo-ral resolution, appeared in recent years [6]; however, such studies in the THz region are scarce [7].

In this paper, we demonstrate the utility of an organic semiconductor, such as highly oriented poly(*p*-phenylene vinylene) (PPV), as an active material for generating THz radiation. The emission is due to photocarriers generated via sub-gap two-photon absorption, that are accelerated by an external field.

2. Experimental

We prepared a small aperture photoconductive antenna (see Fig. 1) by evaporating gold contacts on top of a free-standing PPV film (with thickness of about 15 μm) that was oriented by tensile drawing to an elongation ratio of $l/l_0 = 4$. The gap between the electrodes in the Auston switch configuration [8] was ~17 μm and the length of the antenna (*d*) was ~2 mm. The contacts were oriented so that the applied dc electric field was parallel to the polymer's chain axis. The antenna was attached to a hyper-spherical silicon lens in order to improve the THz radiation collection efficiency, which in our setup led to a 10-fold signal gain. A black polyethylene long-pass filter was interposed between the photoconductive antenna and the silicon lens in order to avoid a leakage of the excitation light into the detector.

For the generation of the THz radiation, we employed an amplified Ti:Sapphire laser system (100 fs pulses at 800 nm, pulse energy up to ~1 mJ, repetition rate of 1 kHz). The detection of the THz radiation spectrum was obtained by using

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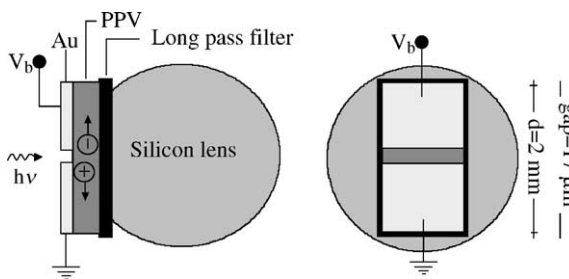*E-mail address:* moses@ipos.ucsb.edu (D. Moses).

Fig. 1. Structure of the PPV small aperture photoconductive antenna, coupled to the hyper-spherical silicon lens used for collimating the THz radiation.
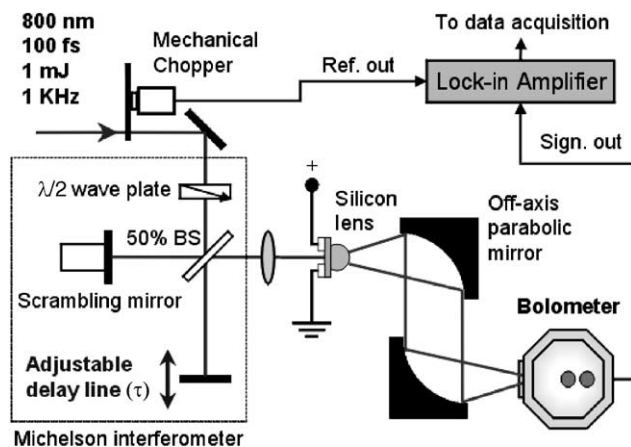

Fig. 2. Schematic of the autocorrelation setup used for THz detection.

an autocorrelation technique, where pairs of coherent laser pulses delayed by a time τ were generated by a Michelson interferometer (see Fig. 2). These pulses illuminated the antenna and thereby generated corresponding pairs of THz bursts with the same time delay (τ). This delay was varied by a mirror mounted on an optical translation stage, that constituted one arm of the Michelson interferometer. On the other arm of the interferometer, the mirror was attached onto a piezoelectric transducer that oscillated with amplitude comparable to that of the light wavelength, and thus prevented optical interference of the two laser beams on the sample when they overlapped in time. The pairs of delayed collinear THz beams were collected by the silicon lens and then collimated and focused by a pair of gold plated off-axis parabolic mirrors onto a QMC bolometer operating at liquid helium temperature [9].

3. Results and discussion

In the photoconductive approach, THz radiation is generated by the acceleration of charges due to an external bias. According to Maxwell's equations, this acceleration results in the generation of an electromagnetic wave, whose electric field amplitude is proportional to the first time derivative of the underlying photocurrent excited in the antenna.
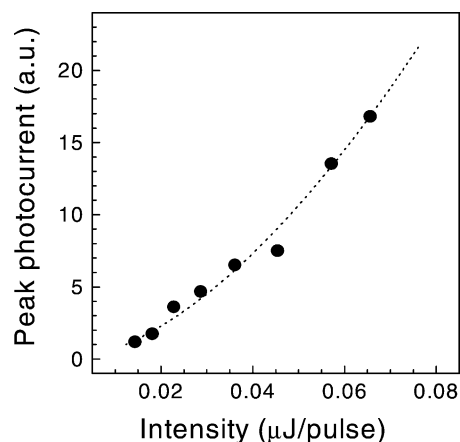

Fig. 3. The dependence of the peak transient photocurrent on laser intensity, pumped at 800 nm. The dotted line is the fitting to a power law with 1.7 exponent.

Our first attempt to obtain THz emission from the PPV sample was made by utilizing one-photon absorption at 400 nm (i.e. via inter-band excitation). In this case, the required photocurrent needed to generate sufficient THz signal resulted in high current density at a narrow absorption depth region ($\sim$100 nm) near the polymer surface that exceeded the damage threshold. Therefore, we opted of using a two-photon excitation (at 800 nm) that resulted in a larger absorption depth (in the intensity range used in our experiments) that almost comprised of the entire sample thickness of 15 μm; thus, in spite of the higher light fluence, the significantly smaller photocurrent density prevented sample deterioration [9].

In Fig. 3, we present the dependence of the peak transient photocurrent as measured by using a fast boxcar at $\sim$300 ps after excitation (the overall temporal resolution of our transient photoconductivity setup) as a function of the pump intensity [5]. The data can be fitted with a power law with exponent of 1.7, confirming that the excitation occurs via a nonlinear two-photon process. The smaller exponent observed (1.7 versus the theoretically expected 2) is most likely due to the early time carrier recombination during the 300 ps following photoexcitation.

In Fig. 4 (left panel), we show the THz autocorrelation signal ($I(\tau)$) as obtained with the pump polarized parallel and perpendicular to the applied electric field/polymer's chains direction. Since no signal was detectable at zero bias, we exclude the possibility that optical rectification or laser leakage through the sample contributed to the signal response [9]. Moreover, for both laser polarizations, the THz emission was polarized along the photocurrent flow direction, indicating the emission was solely due to the transient photocurrent generated in the PPV sample.

The long time oscillations of $I(\tau)$ may arise due to a cut-off frequency of the antenna, which shapes the spectral response; additionally, these long-lived oscillations may arise also due to a resonant coupling of the THz radiation
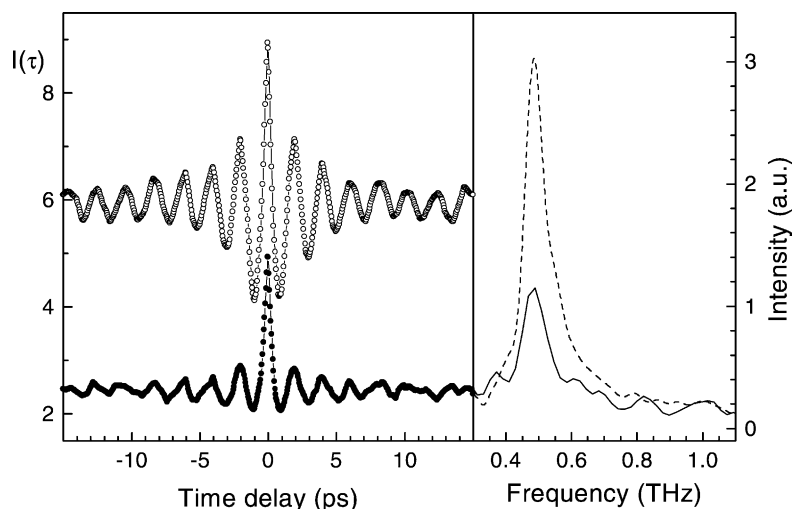
Fig. 4. Left panel: autocorrelation signal from a PPV photoconductive antenna, as obtained by two-photon excitation with the pump polarization parallel (open circles) or perpendicular (solid circles) to the polymer's chain axis. The pump excitation intensity was $35\,\mu J$ per pulse and the applied field $175\,kV/cm$. Right panel: THz spectra obtained by the Fourier transform of the autocorrelation signals shown in the left panel. Full line: perpendicular pump polarization; dashed line: parallel polarization.

with the *L–C* equivalent circuit formed by the characteristic capacitance and inductance of the antenna circuit. These factors affected the overall bandwidth and thereby limited the temporal resolution of our experiments to ~ 1 ps. The half-width half-maximum of the central peak of $I(\tau)$ corresponds to the first half-cycle of the THz field, and thus constitute an upper limit for the rise time of the transient photocurrent.

The THz spectra for the two pump polarizations were obtained by the Fourier transform of the autocorrelation signals (Fig. 4, right panel). The THz emission spectra for both polarizations indicate a cut-off frequency below 1 THz, that corresponds to the period of the above long-lived oscillations of the interferograms.

It is interesting to point out that the emitted THz intensity is strongly dependent on the polarization of the pump, as expected from the highly anisotropic optical polarizability of this material. Generally, the sequence of physical events leading to THz emission involves processes, such as photon absorption (via one- [10], or two-photon process as in our case), carrier generation, carrier transport and self-absorption in the THz spectral region. A deeper quantitative analysis of the anisotropic THz emission would require a precise knowledge of the anisotropic two-photon absorption coefficients which are currently unknown. In spite of this limitation, the prompt response of the underlying photoconductivity as detected by the THz emission occurring at $\tau < 1$ ps, within the temporal resolution of our setup, indicates ultrafast charge generation in PPV, in agreement with previous investigations [11].

In conclusion, we demonstrated for the first time THz emission from photoconductive conjugated polymer antenna. The temporal characteristics of the THz emission indicate a fast carrier photoexcitation.

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