Carrier dynamics in α-octithiophene solids: Comparison of the transient photoconductivity and excited-state absorption in single-crystal and polycrystalline film

D. Moses,* J. Wang, and A. Dogariu†
Institute for Polymers and Organic Solids, University of California, Santa Barbara, Santa Barbara, California 93106

D. Fichou‡ and C. Videlot
Laboratoire des Materiaux Moleculaires, CNRS (UPR 241), 2 rue Henry Dunant, F-94320 Thiais, France
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We demonstrate that the transient photoconductivity, photoluminescence, and excited-state absorption (PA) in single-crystal α-octithiophene (8T) are radically different from those in 8T-oriented polycrystalline film. These observations suggest that structural disorder in the 8T system introduces sub-band-gap energy levels that reduce the photocurrent lifetime, facilitate radiative transitions in the near-IR region, and enhance PA. [S0163-1829(99)04711-6]

I. INTRODUCTION

One factor that has hampered progress toward reaching a consensus in regard to the nature of the photoexcitation in organic solids has been the lack of single crystalline materials.[1] However, recent development of α-octithiophene (8T) solids, both in crystalline and oriented polycrystalline forms, presents an opportunity to study the intrinsic properties of the photoexcitation in such a model system and to determine the effect of structural defects on their properties.[2–6] This paper is dedicated to comparing the transport and optical properties in these two 8T forms as revealed from transient photoconductivity and ultrafast spectroscopy.

The transport properties of high purity α-8T thin films have been investigated previously in field-effect transistors;[7] recent studies reveal hole mobility at room temperature in the range 0.06–0.09 $cm^2/V\,s$, i.e., three times higher than in α-6T.[8] The 8T crystal consists of a herringbone packing of the planar α-8T oligomers (each consisting of 16 conjugated C═C double bonds) in a monoclinic structure. The obtained crystals are rather thin (a few microns) in the direction along the molecular axes (which is off by 24° from the *a* axis), but reach approximately 2 mm along the *b*-*c* crystalline plane. In the polycrystalline film the average grain diameter is approximately 50 nm. Although this film is not highly oriented, the grain packing is such that the long molecular axis is maintained roughly normal to the substrate. In our studies of both the 8T crystals and polycrystalline film we examine the transport properties in a direction roughly normal to the α-8T molecular axis (i.e., the field is applied in the *a*-*b* crystalline plane); for the photoluminescence (PL) and PA studies the light beams are aimed perpendicularly to the *a*-*b* plane.

As will be demonstrated, the optical and transient transport properties in the 8T crystal are drastically different than those in the 8T polycrystalline film: These systems manifest different carrier lifetime, photoconductivity (PC) dependence on external field, and recombination mechanisms. The existence of bimolecular recombination in the 8T crystal implies a significantly larger carrier delocalization in this system. The PC dependence on external field (E) is almost linear in the 8T crystal but sublinear in the 8T film. The 8T crystal manifests smaller PA and larger PL in comparison to the 8T polycrystalline film, where the emission extends into the near-IR region.

II. EXPERIMENTAL METHODS

The synthesis, purification, and crystallization of octithiophene (α-8T) have been described previously.[2,3] The α-8T films (200 nm) were vacuum deposited on alumina and silica substrates at a rate of 1–5 nm/second to provide partially oriented polycrystalline films with grain size of ~50 nm.

Transient photoconductivity was measured using the Auston microstrip-switch technique.[1] Gold microstrips were deposited on top of the 8T film, leaving a gap of about 16 μm between 600-μm-wide microstrips; a gold ground plane was deposited on to the backsurface of the alumina substrate to form a transmission line with 50Ω characteristic impedance. One of the microstrips is biased with a dc voltage while the other was connected to a boxcar system fitted with a 25-ps resolution and 50Ω input impedance sampling head. A similar sample configuration was used for the 8T crystal; conducting adhesive was used to secure the Au microstrips deposited directly on the crystals and the Au microstrips on the substrate.

An amplified Ti-sapphire laser system followed by an OPA system was used to produce 120-fs pulses at a repetition rate of 1 KHz with tunable wavelength. Most of the data was obtained with a photon energy of 3.1 eV. The same laser system was used for the nonlinear spectroscopy measurements; the excited state spectra were probed with a continuum light pulse in conjunction with 0.3-m spectrometer, with a sensitivity of 1%. Higher sensitivity measurements of 10^{-4} at single wavelength were obtained by using a mechanical chopper for modulating the pump and phase sensitive detection for the probe.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Transient photoconductivity

Figure 1 compares the transient PC waveform in the 8T crystal and the 8T film. The data indicate a significantly

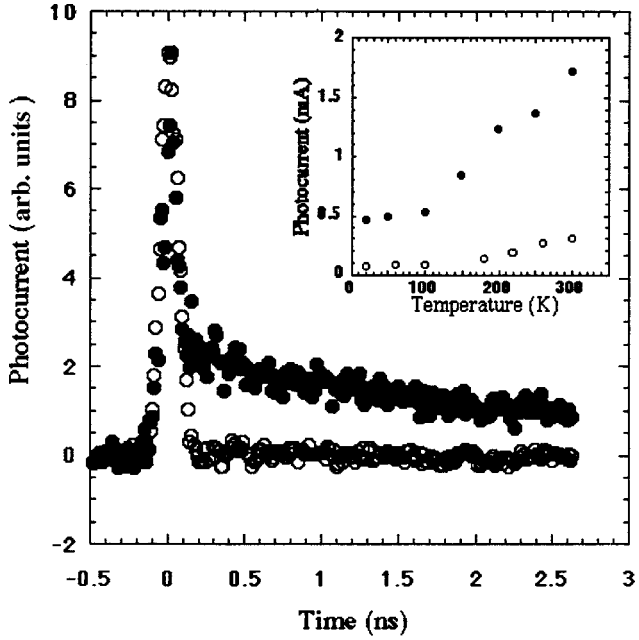

FIG. 1. The normalized photocurrent waveform in the 8T crystal (●) and 8T film (○); inset shows the T dependence of the peak transient PC in the 8T crystal (●) and the 8T film (○).

larger PC lifetime in the 8T crystal as compared to that in the 8T film that is shorter than our temporal resolution ($\Delta t < 50$ ps), indicating the existence of deep traps associated with the structural defects at the crystalline grain boundaries.

The PC waveform in the 8T crystal measured at various temperatures indicate that the long-lived photocurrent component decreases slightly at low temperatures, most likely due to the temperature effect on multiple trapping transport in shallow traps. The T dependence of the peak transient PC in the 8T crystal and film is depicted in the inset of Fig. 1. The PC in the 8T crystal is larger by a factor of ~6 than that in the film; in both systems the PC decreases by a factor of about 4 from room temperature to ~100 K, and below that temperature it remains almost constant. The reason for this behavior is not clear; it may arise from a structural phase transition similar to the one observed in long oligophenylenes at ~110 K.[9]

The dependence of the peak PC on light intensity (I) is sublinear ($\sim I^{0.67}$) in the 8T crystal and almost linear ($\sim I^{1.09}$) in the 8T film. The data suggest a bimolecular carrier recombination mechanism operating in the 8T crystal, as compared to a nonomolecular one in the 8T film due to the localized nature of the carriers in the latter system.

We can derive an approximate value for the bimolecular coefficient (β) for the 8T crystal. Assuming monomolecular and bimolecular mechanisms operating at short time scale, the time dependence of the carrier density (N) follows: $dN/dt = -N/\tau - \beta N^2$; the solution of this equation is given by $N(t) = N_0/[1+\beta N_0 \tau(1-\exp(-t/\tau)]$, where N_0 is the initial carrier density (at $t=0$), and $1/\tau$ is the monomolecular coefficient. Since the PC lifetime is much greater than Δt, $\Delta t \ll \tau$, and assuming that the peak PC (PC_0) arises from the time integral of the photocurrent during Δt, it follows that [Eq. (1)]

$$PC_0 \sim \frac{1}{\Delta t}\int_0^{\Delta t} N(t)dt = \frac{1}{\Delta t \beta}\ln(1+\beta N_0 \Delta t).$$

From the fitting of the measured PC_0 versus the light fluence F [and hence N_0, since $N_0 = F\alpha/(\varphi * h\nu)$] using the above expression, we obtain $\beta\varphi \sim 10^{-22}$ cm^3/ps, where φ is the carrier quantum efficiency.

The 8T crystal and film exhibit distinctly different dependence of the peak transient PC on external field (see Fig. 2). In contrast to the 8T crystal that manifests a linear dependence below about 5×10^4 V/cm and slightly superlinear dependence above this field, the 8T polycrystalline film manifests a sublinear behavior. This latter behavior in the 8T film may arise from an increasing rate of photocarrier trapping at

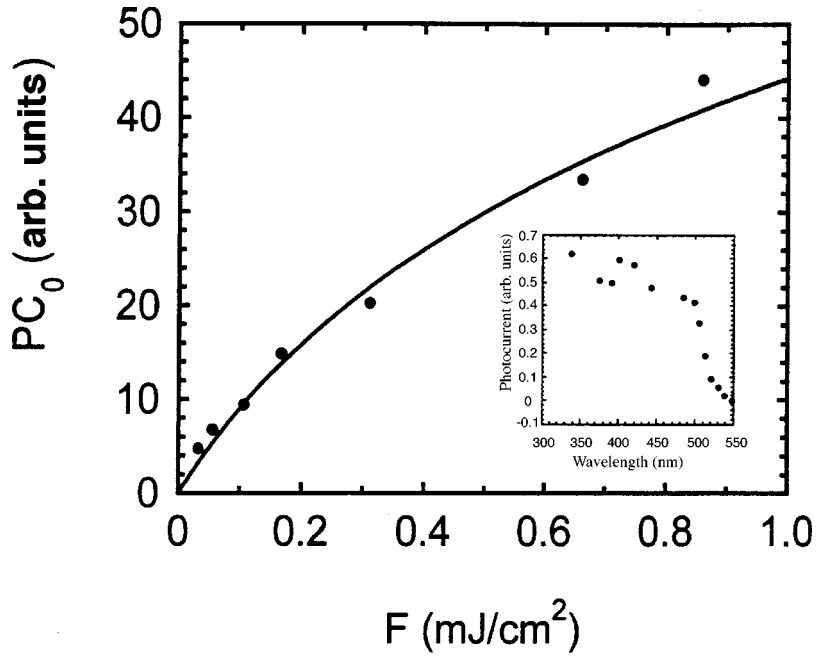

FIG. 2. The peak photocurrent vs pump fluence; the line is a fit to Eq. (1); inset depicts the peak transient PC vs excitation wavelength.

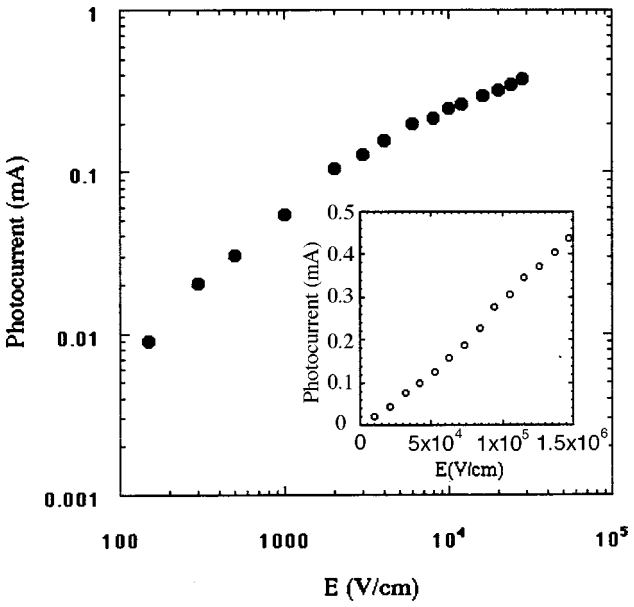

FIG. 3. The field dependence of the peak transient photocurrent in 8T film; the inset shows the data for the 8T crystal.

high fields, as the carrier drift velocity increases and thereby the carrier approaches faster the trap sites at the crystalline grain boundaries.

We also measured the dependence of the peak transient PC on the laser wavelength in the 8T crystal. The data (shown in the inset of Fig. 3) indicate an onset energy for the photocurrent of approximately 2.4 eV. However, deducing the exciton binding energy, from comparing the photocurrent onset energy to the absorption edge is not straightforward, since the absorption edge for light polarized along the *b-c* crystalline plane is not sharp but exhibits few vibronic peaks and shoulders (as shown in Fig. 4).

B. Transient spectroscopy and luminescence

Figure 4 shows the linear absorption spectra (left) and PL spectra (right) in 8T film (dashed lines) and 8T crystal (solid lines). The vibronic peaks in the absorption spectrum of the crystal are separated by approximately 0.12 eV, a slightly smaller value than in sexithiophene (0.18 eV).[10] For the PL and PA measurements, both 8T systems were pumped at 462

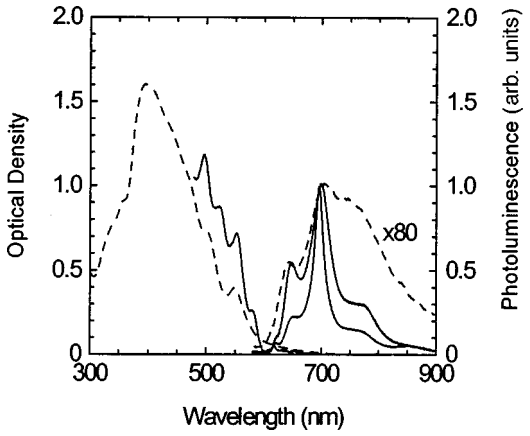

FIG. 4. Absorption (left) and luminescence (right) of the 8T crystal (solid lines) and 8T polycrystalline film (dashed lines).

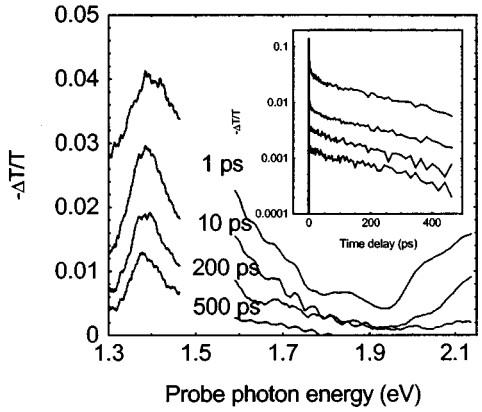

FIG. 5. The PA spectra for 8T polycrystalline film at 1, 10, 200, and 500 ps after photoexcitation; the inset shows the rate of decay of the PA at various light intensities: 0.13, 0.28, 0.85, and 4.4 mJ/cm^2 pulse.

nm, at a wavelength where the optical density of these samples differs by less than a factor of 2. Under the same pumping conditions, however, the luminescence spectra from the two samples are very different: The obtained emission from the film is about 72 times smaller than the one from the crystal and it extends farther into the IR region. In an accurate measurement of the PL quantum efficiency (QE) using integrating sphere, while pumping at 488 nm, we found that QE equals 4% and 0.4% in the single crystal and polycrystalline film, respectively. This behavior is most likely due to disorder that introduces emissive states into the band gap[6,11] and/or due to excimer formation.[12,13]

With increasing pumping fluence the PL manifests gain narrowing in the 8T crystal, as shown by the narrow emission (solid curve) in Fig. 4. The gain narrowing in 8T crystals due to the amplified spontaneous emission (ASE) (facilitated by the waveguide configuration formed by the thin sample in air) clearly implies that stimulated emission (SE) must be present in the 8T crystal at approximately 700 nm. However, ASE was not seen in 8T film because the SE is smaller than the PA in this system.

We find the excited state absorption in the 8T crystal much smaller (e.g., ~1%) than the PA in the 8T film, which shows a PA signal over the entire visible and near-IR regions. Figure 5 shows the PA spectra for the 8T film at various time delays. The PA peaks appear at ~890 nm (1.4 eV); within our experimental accuracy, the curve shapes do not change as time progresses.

Comparison of the PA dynamics in the two 8T systems was obtained from pump-probe experiments at a single wavelength. This allows us to obtain the PA with higher resolution. The inset in Fig. 5 depicts the PA decay rate in the 8T film at various light intensities, probed at 775. With increasing F, the rate of decay increases in the first few picoseconds, indicating a bimolecular interaction.[14]

Figure 6 compares the PA rate of decay in 8T crystal and 8T film when pumped by identical fluence of 1.5 mJ/cm^2. A similar PA rate of decay is observed in the two systems, characterized by a time constant of ~320 ps. Note the much smaller PA in 8T crystal (by a factor of ~8), an observation that explains why the SE overcomes the PA in this system, leading to ASE. As is clear from the above data, disorder in

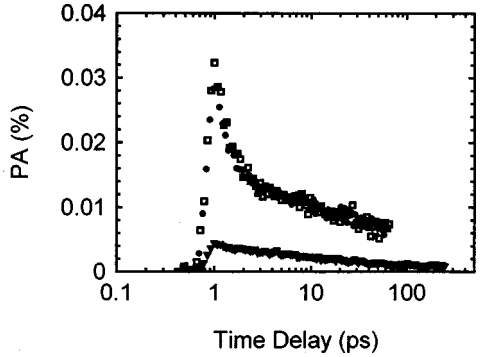

FIG. 6. Comparison of the PA in the 8T crystal (triangles) and 8T film at 295 K (circles) and 80 K (squares) when pumped at 462 nm and probed at 775 nm.

the 8T film magnifies the PA and diminishes SE. Figure 6 also indicates that the PA in the 8T film at room temperature is similar to the one at 80 K.

IV. CONCLUSIONS

Comparative study of the photoconductivity, transient spectroscopy, and luminescence in the α-octithiophene single crystal and partially oriented polycrystalline film reveals the distinct behavior of these two systems and the role of the structural defects on the transport and optical properties. In the 8T crystal we observed a rather long carrier lifetime and a bimolecular carrier recombination mechanism that suggest a larger extent of the carrier wave function in comparison with that in the 8T film. It appears that structural mismatch at grain boundaries introduces deep traps in the 8T polycrystalline film that reduce significantly the carrier lifetime and modify the ohmic behavior seen in the 8T crystal into a sublinear dependence of the PC on E in the 8T film. This latter behavior may arise from the faster carrier localization in deep traps as carrier drift velocity increases at high fields.

Studies of the spectral and temporal behavior of PL and PA in 8T single crystal and 8T film are consistent with the transport observations: They reveal PL efficiency (4%) as well as the ASE, but very small PA in the 8T crystal, in contrast to a much higher PA, smaller PL efficiency (0.4%) and the absence of SE in the 8T film. In addition, higher relative PL emission in the near-IR region was observed from the 8T film. These observations suggest that sub-band-gap energy levels, introduced by disorder, allow both, radiative transitions in the near-IR region as well as higher transition probability to higher states, which underlie the greatly enhanced PA in the 8T film.

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*Electronic address: moses@ipos.ucsb.edu
†Electronic address: arthur@ipos.ucsb.edu
‡Electronic address: fichou@glvt-cnrs.fr

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