Transient and steady-state photoconductivity of a solid C\textsubscript{60} film

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We report the experimental results of the subnanosecond time-resolved transient photoconductivity (PC) of solid C\textsubscript{60} film at various photon energies, and the spectral response of the steady-state PC in the energy range between 1.5 and 4.5 eV. The initial fast transient PC response decays exponentially in the subnanosecond time regime, followed by a weak slower component. Decay time at \(\hbar \omega = 2.0\) eV is longer than that at \(\hbar \omega = 2.6\) and 2.9 eV. At \(\hbar \omega = 2.0\) eV, transient PC peak shows a superlinear intensity dependence, suggesting carrier generation via exciton-exciton collision ionization, consistent with the recent results of fast photoinduced absorption. However, the linear intensity dependence of the transient PC at \(\hbar \omega = 2.6\) and 2.9 eV and a sharp increase of the transient and steady-state PC response at \(\hbar \omega \approx 2.3\) eV indicate direct photogeneration of free electrons and holes at \(\hbar \omega > 2.3\) eV.

As is well known, C\textsubscript{60} molecules condense at room temperature into a face-centered-cubic (fcc) lattice held by rather weak intermolecular van der Waals forces, with a high degree of rotational disorder.\textsuperscript{1,2} Band-structure calculations show that an fcc C\textsubscript{60} solid is a narrow-band semiconductor with a direct band gap of 1.5 eV between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).\textsuperscript{3} The optical transitions between these two states are dipole forbidden for an isolated C\textsubscript{60} cluster, but they are weakly allowed in solid.\textsuperscript{3} Indeed, measurements of absorption,\textsuperscript{4,5} photoluminescence\textsuperscript{6–9} on solid C\textsubscript{60} yield a HOMO-LUMO gap in the range of 1.6–1.9 eV. However, the nature of the photoexcitations at this region of photon energy and, in particular, the onset energy for generation of free carriers has not been determined conclusively. Measurement of photoconductivity (PC) provides crucial information on the carrier generation mechanism and carrier dynamics. In this paper we present the results of the time-resolved transient PC and the steady-state PC experiments on solid C\textsubscript{60} film.

Recent combined experiments of photoemission and inverse-photoemission spectra\textsuperscript{10} of C\textsubscript{60} film indicate that the direct band gap in solid C\textsubscript{60} is about 2.3 eV and that the on-site molecular C\textsubscript{60} Coulomb interaction (U) is about 1.6 eV, indicating a highly correlated electronic system. The weak optical absorption in the range 1.5–2 eV corresponds therefore to \(h \nu \rightarrow 1\alpha\) intramolecular excitations. In particular, electron-energy-loss spectroscopy studies have identified the singlet and triplet excitation states at 1.79 and 1.55 eV, respectively.\textsuperscript{11} Recent studies of transient photoinduced absorption\textsuperscript{12–14} (PIA) and time-resolved degenerate four-wave mixing\textsuperscript{15} (DFWM) suggest that the early temporal response is dominated by the decay of the singlet excited state; the relaxation dynamics at \(\hbar \omega = 2.0\) eV is found strongly dependent on the excitation density, suggesting the importance of bieexciton annihilation processes in these experiments.\textsuperscript{12–15}

Our work is aimed at investigating the mechanism of carrier generation in C\textsubscript{60} film. The PC measurements reported to date have been carried out in the steady-state condition.\textsuperscript{16–20} However, fast time-resolved transient PC measurement provides unique information regarding the photogeneration and recombination mechanisms of charged carriers; in particular, measurements of the photocurrent dependence on light intensity have been shown to provide a crucial test whether bieexcitonic fusion processes prevail, while steady-state PC measurements are known to be dominated by trap-limited transport.\textsuperscript{21}

Thin-film samples are prepared by evaporating purified C\textsubscript{60} powder from a quartz crucible,\textsuperscript{22} heated to 450°C at a pressure of \(5 \times 10^{-6}\) Torr onto either alumina substrates for the PC measurement or onto sapphire substrates for the optical absorption measurement. After preparation, the sample was transferred into the measuring system exposed to air, and therefore we can assume that it contained oxygen. The optical absorption spectra are taken using a Perkin-Elmer Lambda-9 spectrophotometer. Samples are mounted onto the cold finger of a cryostat, and the PC measurement is carried out in the temperature ranges from 300 to 81 K under a pressure of less than \(10^{-4}\) Torr.

The transient PC is measured using the Aston microstrip-line-switch technique.\textsuperscript{23–26} The microstrip gold electrodes are deposited on top of about 5000-Å-thick C\textsubscript{60} film leaving a gap of 100 μm between 600-μm-wide microstrips, and a gold backplane is deposited onto the back surface of the alumina substrate to form a transmission line with 50Ω impedance. One side of the microstrip is biased with 300 V (i.e., electric field of \(3 \times 10^4\) V/cm), and the other side is connected to the EG&G PAR 4400 boxcar system fitted with Tektronix S-4 sampling head. Excitation pulses are obtained from a
PRA LN105A dye laser system pumped with a PRA LN1000 N₂ laser, operated at a repetition rate of 3–5 Hz. The pulse width is approximately 20–30 ps and pulse intensity is about 2–4 μJ/pulse. The overall system temporal resolution is about 50 ps, limited by a combination of the boxcar gatewidth, trigger jitter of the boxcar, response of the cable transmission line between the probe and the boxcar, and the laser pulse width. The steady-state PC data are taken from the same samples used for the transient PC using standard modulation technique, where the excitation light from a 150-W xenon lamp is chopped at frequency of 9.3 Hz and the photocurrent response is detected by a lock-in amplifier. More details regarding the transient PC and steady-state PC measurements are summarized in earlier publications.⁴⁻⁻⁶

Figure 1 shows the spectral response of both transient PC and steady-state PC at room temperature together with the optical absorption spectrum, in the 1.5–4.5-eV range. The inset of Fig. 1 depicts the same data plotted on a semilogarithmic plot. The optical absorption data agree well with earlier reported results.⁸ We observe the characteristic absorption peaks of C₆₀ and a shoulder near 2 eV; below 2 eV the optical absorption is very weak. The measured transient PC (peak values) under the photoexcitation of \( \approx 2 \times 10^{15} \) photons/cm² per pulse at \( \hbar \omega = 2.0, \) 2.6, and 2.9 eV are approximately 0.002, 0.02, and 0.03 S/cm, respectively. In Fig. 1, the transient PC peaks are normalized to unity at \( \hbar \omega = 2.9 \) eV and to a constant incident photon flux. The steady-state PC data are also normalized to unity at \( \hbar \omega = 2.9 \) eV, for comparison with the transient PC data. The magnitude of the steady-state photoconductivity at 2.9 eV is about \( 1.5 \times 10^{-11} \) S/cm for the incident photon flux of \( \approx 7.5 \times 10^{14} \) photons/cm²/s. Thus, the magnitude of the transient photoconductivity in the subnanosecond time regime is about nine orders of magnitude larger than the steady-state photoconductivity.

The steady-state PC response shows an onset at \( \hbar \omega \approx 1.6 \) eV and a shoulder at 2.0 eV. Both transient and steady-state photocurrents increase sharply at \( \hbar \omega \approx 2.3 \) eV and follow closely the optical absorption spectrum up to about \( \hbar \omega = 3 \) eV, but above \( \hbar \omega \approx 3 \) eV the steady-state PC response deviates from the optical absorption. This behavior indicates that in the high absorption region surface recombination dominates the photocurrent; the rate of recombination increases as the absorption depth decreases since the density of excitations near the surface increases.

Figure 2 shows the room-temperature transient photocurrent wave forms of the solid C₆₀ film at three photon energies: 2.0, 2.6, and 2.9 eV (the three curves are normalized at the peaks). The same data are shown on a semilogarithmic plot in the inset, where the solid lines are fits to an exponential decay. As is evident, at the three photon energies the initial photocurrent decays exponentially in the subnanosecond time regime, followed by a slower decaying component after about 800 ps. Similar decay times of \( \tau \approx 210 \) ps are observed at both \( \hbar \omega = 2.6 \) and 2.9 eV but a distinct decay rate appears at \( \hbar \omega = 2.0 \) eV, of about \( \tau \approx 300 \) ps. These decay times are independent of the biasing electric field, light intensity, and temperature.

In order to identify the dominant mechanism of the PC decay (i.e., variation in the mobility or carrier recombination) we compare the transient PC data with the results of transient PIA experiments. The transient PIA data in solid C₆₀ films at \( \hbar \omega = 2.0 \) eV indicate an initial fast relaxation of the order of \( \tau \approx 1 \) ps and a slower one on a time scale of several hundred picoseconds.¹²⁻¹⁴ In the comparable time range that can be resolved by our transient PC measurements, \( t \geq 50 \) ps, the relaxation times of the transient photocurrent are similar to those of the transient PIA signal. Thus, since the PIA signal is sensitive solely to the number of photoexcited carriers, it follows that the transient photocurrent decays primarily due to carrier recombination. Both transient PC and PIA (Refs. 12–14) decay times are independent of temperature.

Traditionally, the dominating mechanisms for the pho-
togeneration and recombination have been studied by measuring the dependence of the PC response as a function of the light intensity, biasing field, and temperature. We find the peak transient photocurrent linearly proportional to the applied electric field up to $3 \times 10^4$ V/cm at all three photon energies at all temperatures between 300 and 80 K. Figure 3 shows the temperature dependence of the peak transient PC at $\hbar \omega = 2.0$ eV in a semilogarithmic plot. The transient PC data are measured with an incident photon flux of $2 \times 10^{15}$ photons/cm$^2$ and an applied electric field of $3 \times 10^4$ V/cm, from 80 to 300 K. The magnitude of the peak transient PC is independent of the temperature at all photon energies (as is indicated in Fig. 3); this behavior, and the observation of temperature-independent decay times of the transient PC and the transient PIA (Refs. 12–14) signals rule out thermally activated transport mechanism at the time regime $t \approx 50$ ps. Moreover, this observation, in addition to the linear dependence of the peak transient PC on the electric field, indicates that the Onsager geminate recombination model is not viable for the carrier generation mechanism in C$_{60}$.

A most important observation is the intensity dependence of the transient PC displayed in Fig. 4. The peak transient PC, $I_p$, at $\hbar \omega = 2.0$ eV shows a superlinear intensity dependence: $I_p \sim I_{ph}^{2.6}$ and $I_{ph}^{1.35}$ at 300 and 80 K, respectively. However, a linear intensity dependence is observed at both temperatures for photoexcitations at $\hbar \omega = 2.6$ and 2.9 eV.

The linear intensity dependence of the transient PC at $\hbar \omega = 2.6$ and 2.9 eV, the superlinear intensity dependence at $\hbar \omega = 2.0$ eV, and the sharp increase of the PC response (both transient and steady state) at $\hbar \omega = 2.3$ eV (see Fig. 1) suggest interband photoexcitation above $E_g \approx 2.3$ eV; these observations are consistent with recent photoemission and inverse-photoemission spectra of C$_{60}$. Additionally, the superlinear intensity dependence at $\hbar \omega = 2.0$ eV suggests that the exciton-exciton collision ionization may dominate the carrier generation process at the weakly allowed absorption region (1.5–2.3 eV).

Carrier generation via exciton-exciton collision ionization at $\hbar \omega = 2.0$ eV is consistent with recent results of the time-resolved transient PIA (Refs. 12–14) and DFWM (Ref. 15) experiments; the decay rate of the PIA signal (at $\hbar \omega = 2.0$ eV) is temperature independent ($\tau \approx 1$ ps), and it depends on the density of photoexcitation. The time-resolved DFWM experiments show that at high laser fluences (at $\hbar \omega = 2.0$ eV) the prompt signal is dominated by decay of the short-lived single exciton excited state whose lifetime is strongly dependent on the density of photoexcitation. The superlinear dependence of the signals at $\hbar \omega = 2.0$ eV of the transient PC, DFWM, and PIA suggest a distinct carrier generation mechanism at this photon energy mediated by excitons. Usually, a quadratic intensity dependence of the transient PC is expected when the charge carrier generation arises from singlet exciton-exciton collision ionization. The subquadratic intensity dependence observed at $\hbar \omega = 2.0$ eV indicates therefore a significant contribution due to first-order exciton decay processes such as decay at defects or impurities.

We now discuss the carrier mobility in C$_{60}$ film. We can estimate the mobility from the peak transient PC, using

$$I_p = N_{ph} \eta e \mu / d,$$

(1)

where $I_p$ is the peak transient PC, $N_{ph}$ the number of absorbed photons, $\eta$ the quantum efficiency for carrier generation, $\mu$ the mobility, $E$ the bias electric field, and $d$ the distance between the electrodes. Assuming quantum yield $\eta = 1$, we obtain carrier mobilities of $1.7 \times 10^{-3}$ and $2.5 \times 10^{-3}$ cm$^2$/V/s at photon energies $\hbar \omega = 2.6$ and 2.9 eV, respectively. However, since the time-resolved PIA experiments in the solid C$_{60}$ films show that at 50 ps the density of photoexcitation decays to approximately 10–20% of its initial value, we expect similar decay of the transient photocurrent, implying that the effective quantum yield in Eq. (1) is about $\eta \approx 0.2$. Taking this...
into consideration (the above underestimate $\mu$ by a factor of $5\to 10$) we obtain at $\hbar \omega = 2.6$ and 2.9 eV, $\mu = 2 \times 10^{-2}$ cm$^2$/Vs. This is in the range of mobilities typical to that of narrow-band molecular semiconductors. However, a smaller value of the product $\eta \mu = 4 \times 10^{-4}$ cm$^2$/V s is obtained at $\hbar \omega = 2.0$ eV. Assuming a similar mobility to that at $\hbar \omega = 2.6$ and 2.9 eV ($\mu = 2 \times 10^{-2}$ cm$^2$/V s), we find the quantum yield at $\hbar \omega = 2.0$ eV, $\eta = 0.02$. The smaller value of the quantum yield is in fact consistent with carrier generation mechanism via singlet exciton-exciton collision ionization at this photon energy.

In conclusion, we report the results of the transient PC in the subnanosecond time regime of solid $C_{60}$ films at three photon energies: 2.0, 2.6, and 2.9 eV as well as the steady-state PC in the 1.5–4.5 eV photon energy range. The initial fast transient PC response, at the three photon energies, decays exponentially in the subnanosecond time regime, followed by a weaker and slower component. At all photon energies, the peak transient PC is independent of the temperature (from 80 to 300 K). At $\hbar \omega = 2.6$ and 2.9 eV the peak transient photocconductivity ($\sigma_p \approx 0.02–0.03$ S/cm) varies linearly with light intensity but at $\hbar \omega = 2.0$ eV it ($\sigma_p \approx 0.002$ S/cm) varies superlinearly. These observations in addition to the sharp increase of the steady-state and transient PC responses at $\hbar \omega \approx 2.3$ eV are consistent with a band gap of 2.3 eV. The observation of superlinear intensity dependence of the transient PC at $\hbar \omega = 2.0$ eV suggests that the singlet exciton-exciton collision ionization underlies the carrier generation mechanism in this spectral region, consistent with previous studies of the dependence of the fast PIA and DFWM signals on excitation density. Our observations are also consistent with recently reported photoemission and inverse-photoemission experiments which suggest that below $\hbar \omega \approx 2.3$ eV photoexcitation creates strongly bound Frenkel-type molecular excitons.

By comparing the transient PC with the time-resolved PIA results, we estimate the initial mobility at $\hbar \omega = 2.6$ and 2.9 eV to be about $2 \times 10^{-2}$ cm$^2$/V s, and identify the initial fast photocurrent decay primarily due to carrier recombination. Assuming similar mobility at $\hbar \omega = 2.0$ eV we find the quantum yield at this energy smaller by a factor of about 10, which is also consistent with carrier generation mechanism via exciton-exciton collision ionization at $\hbar \omega = 2$ eV.

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