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Transient and steady-state photoconductivity of a solid C_{60} film

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We report the experimental results of the subnanosecond time-resolved transient photoconductivity (PC) of solid C_{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_{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.[1,2] Band-structure calculations show that an fcc C_{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).[3] The optical transitions between these two states are dipole forbidden for an isolated C_{60} cluster, but they are weakly allowed in solid.[3] Indeed, measurements of absorption,[4,5] photoluminescene[6–9] on solid C_{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_{60} film.

Recent combined experiments of photoemission and inverse-photoemission spectra[10] of C_{60} film indicate that the direct band gap in solid C_{60} is about 2.3 eV and that the on-site molecular C_{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 $h_u \rightarrow t_{1u}$ intramolecular excitations. In particular, electron-energy-loss spectroscopy studies have identified the singlet and triplet exciton states at 1.79 and 1.55 eV, respectively.[11] Recent studies of transient photoinduced absorption[12–14] (PIA) and time-resolved degenerate four-wave mixing[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 biexciton annihilation processes in these experiments.[12–15]

Our work is aimed at investigating the mechanism of carrier generation in C_{60} film. The PC measurements reported to date have been carried out in the steady-state condition.[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 biexcitonic fusion processes prevail, while steady-state PC measurements are known to be dominated by trap-limited transport.[21]

Thin-film samples are prepared by evaporating purified C_{60} powder from a quartz crucible,[22] heated to 450 °C at a pressure of 5×10^{-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 Auston microstripline-switch technique.[23–26] The microstripline gold electrodes are deposited on top of about 5000-Å-thick C_{60} film leaving a gap of 100 μm between 600-μm-wide microstriplines, and a gold backplane is deposited onto the back surface of the alumina substrate to form a transmission line with 50-Ω impedance. One side of the microstrip is biased with 300 V (i.e., electric field of 3×10^4 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 N_2 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 early publications.[24–26]

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.[4] We observe the characteristic absorption peaks of C_{60} 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/cm^2 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 1.5×10^{-11} S/cm for the incident photon flux of $\approx 7.5\times 10^{14}$ photons/cm^2 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.[27]

Figure 2 shows the room-temperature transient photocurrent wave forms of the solid C_{60} 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.

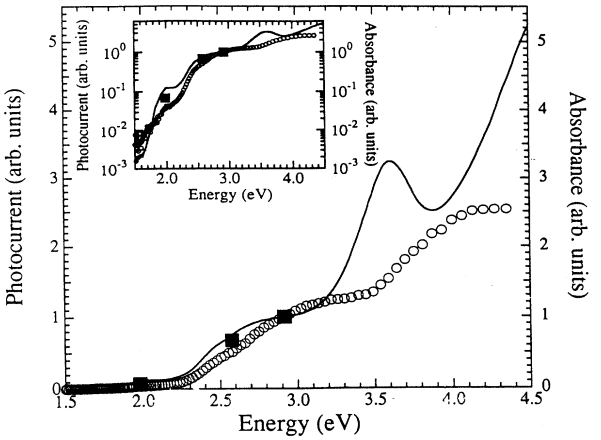

FIG. 1. The spectral response of both transient PC (■) and the steady-state PC (○) together with the optical absorption (solid line) of solid C_{60} at room temperature; inset shows the same data on a semilogarithmic plot.

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 C_{60} 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 regime 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-

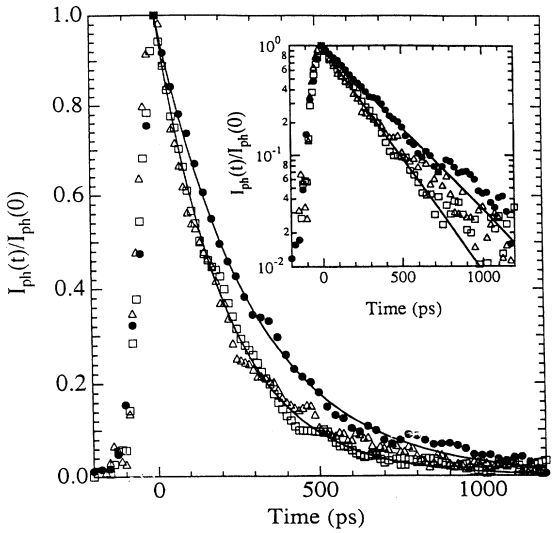

FIG. 2. The room-temperature transient photocurrent of the solid C_{60} film at three photon energies; 2.0 (●), 2.6 (△), and 2.9 eV (□), normalized at the peak value; the inset shows the same data plotted on a semilogarithmic plot, where the solid lines are fits to exponential decay function.

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 3×10^4 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 $\hbar\omega=2.9$ and 2.0 eV in a semilogarithmic plot. The transient PC data are measured with an incident photon flux of 2×10^{15} photons/cm^2 and an applied electric field of 3×10^4 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 $t<50$ 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[28] 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: $I_p\sim I_L^{1.26}$ and $I_L^{1.35}$ 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 $\hbar\omega\approx2.3$ eV (see Fig. 1) suggest interband photoexcitation above $E_g\approx2.3$ eV; these observations are consistent with recent photoemission and inverse-photoemission spectra of C_{60}.[10] Additionally, the superlinear intensity dependence at $\hbar\omega=2.0$ eV suggests that the exciton-exciton collision ionization[29–31] may dominate the carrier generation process at the weakly allowed absorption region (1.5–2.3 eV).

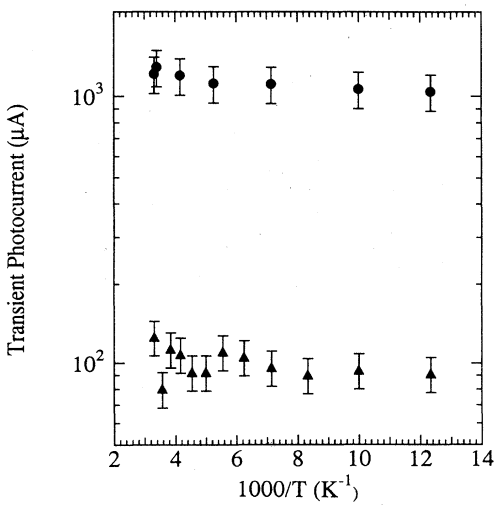

FIG. 3. The temperature dependence of the peak transient PC measured at 2.9 eV (●) and at 2.0 eV (▲) on a semilogarithmic plot.

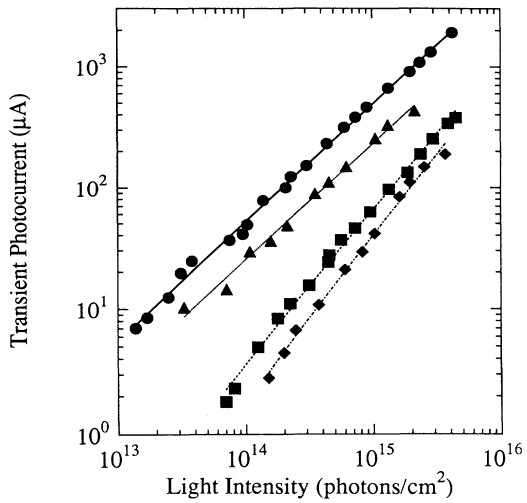

FIG. 4. The dependence of the peak transient PC on excitation light intensity. The data at $\hbar\omega=2.9$ (●) and 2.6 eV (▲), measured at 300 K, show a linear intensity dependence. The data at $\hbar\omega=2.0$ eV, measured at both 300 (■) and 80 K (◆), indicate the superlinear intensity dependences.

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 ($\tau\approx1$ ps), and it depends on the density of photoexcitation. The time-resolved DFWM experiments[15] show that at high laser fluences (at $\hbar\omega=2.0$ eV) the prompt signal is dominated by decay of the short-lived singlet 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.[12–15] Usually, a quadratic intensity dependence of the transient PC is expected when the charge carrier generation arises from singlet exciton-exciton collision ionization.[29–31] 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

$$I_p=N_{\rm ph}\eta eE\mu/d\ , \tag{1}$$

where I_p is the peak transient PC, $N_{\rm ph}$ the number of absorbed photons, η the quantum efficiency for carrier generation, μ the mobility, E the bias electric field, and d the distance between the electrodes. Assuming quantum yield $\eta=1$, we obtain carrier mobilities of 1.7×10^{-3} and 2.5×10^{-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[11–13] 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 $\eta\leq0.2$. Taking this

into consideration (the above underestimate μ by a factor of 5–10) we obtain at $\hbar\omega=2.6$ and 2.9 eV, $\mu\cong 2\times 10^{-2}$ $cm^2/V\,s$. This is in the range of mobilities typical to that of narrow-band molecular semiconductors.[32] However, a smaller value of the product $\eta\mu\cong 4\times 10^{-4}$ $cm^2/V\,s$ is obtained at $\hbar\omega=2.0$ eV. Assuming a similar mobility to that at $\hbar\omega=2.6$ and 2.9 eV ($\mu\cong 2\times 10^{-2}$ $cm^2/V\,s$), we find the quantum yield at $\hbar\omega=2.0$ eV, $\eta\cong 0.02$. 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 photoconductivity ($\sigma_{ph}\approx 0.02-0.03$ S/cm) varies linearly with light intensity but at $\hbar\omega=2.0$ eV it ($\sigma_{ph}\approx 0.002$ 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.[11–14] Our observations are also consistent with recently reported photoemission and inverse-photoemission experiments which suggest that below $\hbar\omega\cong 2.3$ eV photoexcitation creates strongly bound Frenkel-type molecular excitons.[10]

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 2×10^{-2} $cm^{-2}/V\,s$, and identify the initial fast photocurrent decay primarily due to carrier recombination.[12] 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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