# Effects of oxygen on the photocarrier dynamics in a $C_{60}$ film: Studies of transient and steady-state photoconductivity

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The intrinsic dynamics of photoexcited carriers in an oxygen-free $C_{60}$ film and their remarkable evolution as the film is exposed to oxygen are revealed by transient and steady-state photoconductivity (PC) measurements at various temperatures, light intensities, and photon energies. Exposure of $C_{60}$ film to oxygen creates deep traps that reduce drastically the carrier lifetime and, consequently, the room-temperature steady-state photoconductivity by three to six orders of magnitude. Oxygen affects the steady-state photoconductivity excitation spectrum in a qualitatively similar way, as does decreasing the ambient temperature; in both cases, the photoconductivity decreases faster when carriers are photoexcited into the band edges. The transient and steady-state PC of a $C_{60}$ film fully exposed to oxygen becomes temperature independent.

Photoexcitations and photocarrier dynamics in solid $C_{60}$ have been of great interest,[1-8] but almost all previous studies have been carried out on samples that were exposed to air. However, it has been reported recently that exposure of $C_{60}$ film to oxygen modifies its electronic properties,[9-16] and in particular decreases its dark conductivity and steady-state photoconductivity.[9-11] Nevertheless, the carrier dynamics in pristine $C_{60}$ and how it evolves upon exposure to oxygen have not been well understood. Here we report the results of a comprehensive study of the transient and steady-state photoconductivity (PC) of a pristine $C_{60}$ film, and how the carrier transport evolves as the film is progressively exposed to air. As will be demonstrated, oxygen in a $C_{60}$ film creates deep traps which drastically reduce the carrier lifetime and effectively quench the transport mechanism associated with multiple trapping at shallow traps that prevails in oxygen-free $C_{60}$.

Thin-film samples were prepared by evaporating purified $C_{60}$ powder, heated to 450 °C at a pressure of $5\times10^{-6}$ torr, onto alumina substrates.[17] After evaporation, while in vacuum, the samples were sealed in the quartz tube and transferred into inert (nitrogen) atmosphere of a glove box, which houses a vacuum evaporator used for the deposition of electrodes. Gold electrodes were deposited on top of the 5000-Å-thick *oxygen-free* $C_{60}$ film, leaving a gap of 200 $\mu$m between 600-$\mu$m-wide striplines; a ground-plane gold electrode was deposited onto the back side of the alumina substrate to form a transmission line with 50-$\Omega$ impedance.[2,18] The sample was then mounted onto a vacuum-tight sample holder that contains an optical window, transferred out of the glove box, and secured onto the cold finger of a cryostat. PC measurements were carried out in the temperature range of 20–300 K under a pressure of less than $10^{-4}$ torr. After measuring the transient and steady-state PC of the oxygen-free $C_{60}$ film, the sample was exposed to air until its dark conductivity decreased by approximately a factor of 10; then the measurements of the transient and steady-state PC resumed. This procedure was repeated until no further changes in the transient PC decay rate and/or the steady-state PC excitation spectrum could be detected.

Excitation pulses for the transient PC measurements were obtained from a PRA LN105A dye laser system pumped with a PRA LN1000 $N_2$ laser, and operated at a repetition rate of 3–5 Hz. The pulse width was approximately 20–30 ps, and the pulse intensity was about 2–3 $\mu$J. Transient PC data were taken at an electric field of $10^4$ V/cm using an EG&G PAR 4400 boxcar equipped with Tektronix S-4 sampling head. The overall temporal resolution of the measured system was about 50 ps. The excitation light source for the steady-state PC was a 150-W xenon lamp modulated at a frequency of 39 Hz, and the PC was detected by a lock-in amplifier.[2]

Figure 1 shows the transient PC of the pristine $C_{60}$ film measured at a photon energy of $\hbar\omega=2.0$ eV, and how it evolves upon exposing the $C_{60}$ film to air; the solid lines are the best fits of the experimental data to the double-exponential function. The bottom curve in Fig. 1 is taken after the $C_{60}$ film was exposed to air for more than a week when its dark conductivity was reduced by more than five orders of magnitude from the initial value measured in oxygen-free $C_{60}$ sample. The data clearly indicate that the carrier lifetime drastically decreases from about 40 ns in the pristine $C_{60}$ film to less than 2 ns in the film fully exposed to air. These results show that oxygen in the $C_{60}$ film creates efficient deep traps for the photocarriers, which diminish the probability of carrier release into the extended band states.

The transient PC in Fig. 1 consists of short- and long-lived components. Notice that oxygen affects the longer-

 

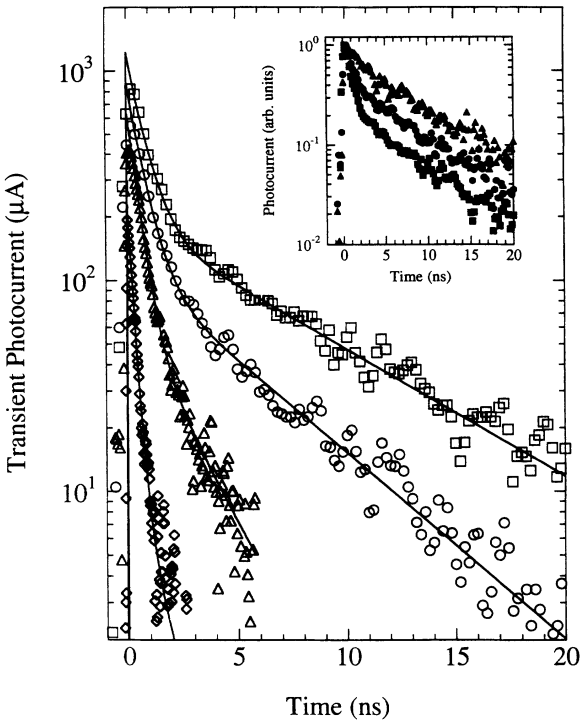


FIG. 1. The time-resolved transient photocurrent ($T=300$ K, $\hbar\omega=2.0$ eV) in pristine $C_{60}$ film, and in the film at various levels of oxygen content. The dark current and relaxation time of each curve are indicated: $I_d=3.6$ nA (□; oxygen-free $C_{60}$, $\tau_1=693$ ps and $\tau_2=7.2$ ns), $I_d=0.005\,67$ nA (○; $\tau_1=640$ ps and $\tau_2=5.0$ ns), $I_d=0.000\,24$ nA (△; $\tau_1=463$ ps and $\tau_2=2.2$ ns), and $I_d<0.000\,01$ nA (◇; $\tau_1=238$ ps and $\tau_2=1.0$ ns). The inset shows the normalized transient PC of pristine $C_{60}$ at different laser intensities: $2.7\times10^{14}$ (▲), $1.1\times10^{15}$ (●), and $5.4\times10^{15}$ photons/cm$^2$ (■).

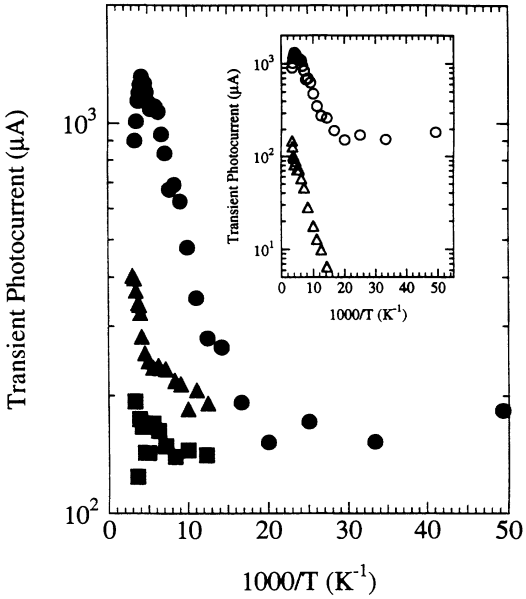


FIG. 2. Temperature dependence of peak transient photocurrents measured at $\hbar\omega=2.0$ eV in oxygen-free $C_{60}$ (●), partially oxygen-exposed $C_{60}$ (▲), and fully oxygen-exposed $C_{60}$ (■); the inset compares the transient photoconductivity in oxygen-free $C_{60}$ at the peak (○) and at 2 ns after excitation (△).

lived component much more than the short-lived one. Moreover, the short- and long-lived PC components vary differently with temperature, light intensity, and phonon energy: The initial short-lived PC component shows a linear or slightly superlinear dependence on light intensity, depending on the photon energy, the long-lived component a sublinear dependence;[2,19] hence, as the light intensity increases, the short-lived PC component increases faster than the long-lived one, as shown in the inset of Fig. 1, where the normalized transient PC of pristine $C_{60}$ is plotted at various laser intensities. As seen from the inset of Fig. 1, the relaxation of the transient photocurrent in pristine $C_{60}$ exhibits a faster decay rate as the light intensity increases. A faster rate of decay for the transient PC is also observed in oxygen-free $C_{60}$ at $\hbar\omega>2.3$ eV as compared to $\hbar\omega<2.3$ eV.[2,19]

The temperature dependence of the peak transient photocurrent at $\hbar\omega=2.0$ eV in oxygen-free $C_{60}$, $C_{60}$ partially exposed to air, and $C_{60}$ fully exposed to air is shown in Fig. 2. The data indicate that the temperature dependence of the peak transient PC varies appreciably with the oxygen content: The oxygen-free $C_{60}$ film manifests a maximum PC at about $T=240$ K, below which it decreases exponentially in the 60–200-K range (with $E_a\sim14$ meV), whereas below 60 K it remains constant. In contrast, in $C_{60}$ film that is partially exposed to oxygen, the peak photocurrent is activated at $T>240$ K and remains temperature independent at $T<240$ K, but in $C_{60}$ fully exposed to oxygen the transient PC is almost temperature independent.

The inset in Fig. 2 compares the temperature dependence of the peak transient PC of oxygen-free $C_{60}$ and the PC measured at 2 ns following the pulsed photoexcitation; similar temperature dependences were observed at $\hbar\omega$ of 2.3, 2.6, and 2.9 eV.[19] Note that while the short-lived PC component remains almost constant at low temperatures, the longer-lived component exhibits thermally activated behavior with $E_a\approx18$ meV. The above observations clearly indicate that the short- and long-lived PC components are dominated by two distinct transport mechanisms.

It is interesting to note that $C_{60}$ film exposed to oxygen does not exhibit the PC maximum near 240 K; also, this maximum is not exhibited by the long-lived PC component, as is evident from the inset of Fig. 2. The PC maximum in oxygen-free $C_{60}$ film can be associated with a first-order structural phase transition of $C_{60}$ known to occur at 249 K, from a face-centered-cubic lattice (characterized by a high rotational degree of freedom) to a simple-cubic structure at low temperatures (characterized by more restricted rotational degree of freedom).[20] Therefore, the observation of such a maximum indicates that an evaporated oxygen-free $C_{60}$ film contains regions of structurally ordered $C_{60}$, probably in the form of small crystalline regions imbedded in disordered $C_{60}$. This is consistent with recent x-ray scattering studies that in fact identify the existence of crystalline domains with 60-Å

coherence length.[21] The disorder in a pristine $C_{60}$ film is indicated by the existence of a large, thermally activated, long-lived PC component, which is generally manifested in conducting polymers[22] and amorphous semiconductors.[23,24] However, our results indicate that the structural order is severely modified by exposing the $C_{60}$ film to oxygen.

Since the transient photoinduced absorption (PA) in $C_{60}$ (see Refs. 4–6) does not exhibit a peak at $T=240$ K, it appears that this peak originates from the mobility. As the temperature of the sample is reduced, two competing mechanisms may operate: a decreasing mobility as the contribution of carriers occupying states at the band tails progressively freezes out, and an increasing mobility (at 300 K $> T >$ 240 K) due to reduced scattering of the photocarriers, in particular as the rotational degree of freedom of the $C_{60}$ molecules is inhibited. This latter mechanism of the mobility disappears in a $C_{60}$ film exposed to oxygen as the oxygen molecules occupy the octaheral interstitial sites of the fcc $C_{60}$ lattice.[25]

Our measurements reveal that the relaxation rate of the transient PC is similar to the decay of the PA.[4–7] Since the PA signal depends solely on the density of surviving photoexcitations, it follows that the transient PC decay is primarily due to carrier recombination rather than variation of the mobility. In general, the transient PC decay depends on the underlying carrier recombination kinetics: when geminate carrier recombination prevails, the carrier density $n(t)$ decays exponentially with carrier lifetime $\tau$ independent of light intensity (monomolecular kinetics), whereas for nongeminate recombination $n(t)$ decays nonexponentially, and $\tau$ decreases with increasing light intensity (bimolecular kinetics). Thus the experimental observations of nonexponential decay of the PC (Ref. 15) and PA (Refs. 19–21) as well as $\tau$ being dependent on light intensity imply that nongeminate carrier recombination prevails in both oxygen-free $C_{60}$ and $C_{60}$ film exposed to air.

The different dependences of the short- and long-lived PC components on temperature and light intensity indicate that they are dominated by two distinct transport mechanisms. The short-lived PC component stems from photocarriers occupying extended band states,[23] as well as states at the band tails at which the carriers tunnel to progressively lower-energy levels,[26] whereas the thermally activated long-lived PC component stems from carriers undergoing multiple trapping at shallow traps and (phonon assisted) releasing into the extended band states.[24] The contribution of the latter mechanism, which dominates the transport in oxygen-free $C_{60}$ in the high-temperature regime, completely freezes out at the low-temperature regime. Moreover, Figs. 1 and 2 indicate that this mechanism is effectively quenched by oxygen.

Studies of the steady-state PC corroborate the quenching effect of oxygen on the multiple trapping transport in $C_{60}$ film, and provide information on the spectral dependence of the PC. Figure 3 presents results that demonstrate the effect of oxygen on the excitation spectrum of the steady-state PC, taken at 300 K from the same sample used for the transient PC measurement. The results reveal a drastic reduction of the steady-state PC upon exposure to oxygen, by more than 4 orders of magnitude from its value in pristine $C_{60}$. While exposure of $C_{60}$ film to oxygen does not significantly change either the optical absorption (it only slightly broadens the absorption peaks[13]) or the transient photoinduced absorption [it slightly reduces the PA signal lifetime (Ref. 28)], it significantly modifies the PC excitation spectrum. In particular, as the film is exposed to air, the PC at $\hbar\omega < 2.3$ eV decreases faster than at $\hbar\omega > 2.3$ eV. Thus it appears that at $\hbar\omega < 2.3$ eV, in addition to carrier excitation into extended band states via nonlinear optical processes,[2,8,27] carriers may be excited directly into localized states at the band tails.[29] The contribution of these carriers to the PC is smaller than the one due to carriers occupying extended band states since they are more severely affected by the deep traps, as is suggested by the drastic quenching of the long-lived PC component.

The experimental results for steady-state PC action spectra of oxygen-free $C_{60}$ at various temperatures (depicted in Fig. 4) show that the PC decreases dramatically at low temperatures, by more than five orders of magnitude. This behavior is consistent with the reduction of the carrier lifetime as the temperature is reduced.[19] Below 80 K the PC decreases at a much faster rate at $\hbar\omega < 2.3$ eV, as more carriers are excited directly into localized states at the band tail, for which the contribution of the phonon-assisted multiple trapping transport mechanism freezes out. Thus reducing the ambient temperature affects the PC spectral dependence and the carrier lifetime of $C_{60}$ film in a similar quantitative way to exposing the film to oxygen, and the 2.3-eV energy appears to be the demarcation energy that separates extended and localized states.[2] The well-resolved PC structure in the

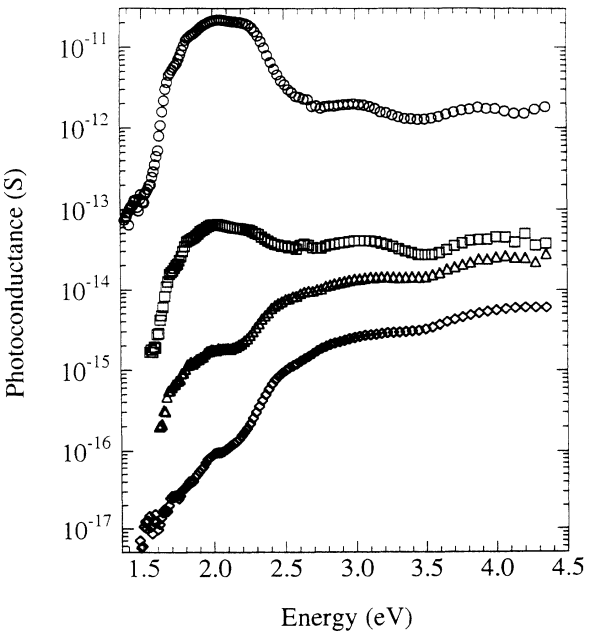


FIG. 3. The room-temperature steady-state PC action spectrum of pristine $C_{60}$ film and its evolution with increasing oxygen content. The dark current of each curve is indicated: $I_d = 0.55$ nA (○), $I_d = 0.000\,46$ nA (□), $I_d \approx 0.000\,05$ nA (△), and $I_d < 0.000\,01$ nA (◇).

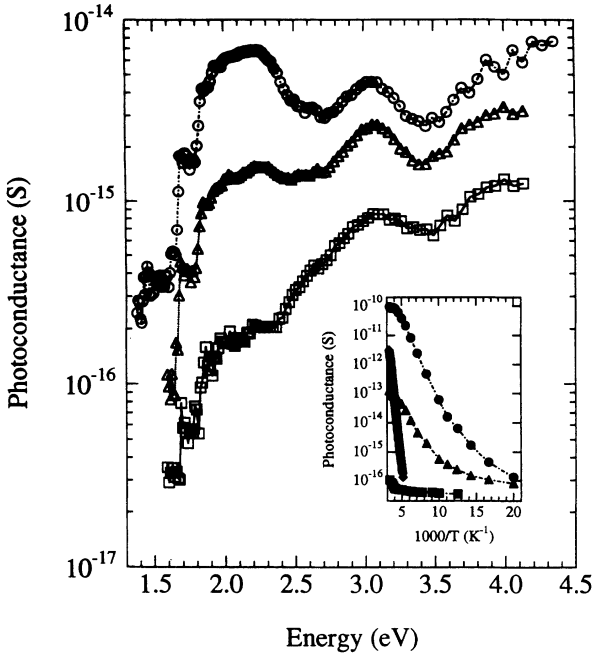


FIG. 4. The excitation spectra of the steady-state PC of oxygen-free $C_{60}$ at various temperatures: 80 (○), 70 (△), and 50 K (□); the inset shows the temperature dependence of the steady-state PC at $\hbar\omega = 2.0$ eV for oxygen-free (●), partially exposed (▲), and fully exposed $C_{60}$ to oxygen (■), as well as the dark conductance of oxygen-free $C_{60}$ (◆). The lines are plotted as a guide to the eye.

low-energy region in Fig. 4 has previously been associated with vibronic transitions.[29]

The inset of Fig. 4 displays the temperature dependence of the steady-state PC at $\hbar\omega = 2.0$ eV of oxygen-free $C_{60}$, partially contaminated $C_{60}$, and $C_{60}$ fully contaminated by oxygen; similar qualitative temperature dependences are observed at other photon energies as well. The temperature dependences of the steady-state PC are qualitatively similar to those of the peak transient PC, but the associated activation energies are higher; e.g., in oxygen-free $C_{60}$, $E_a \approx 14$ meV for the peak transient PC versus $E_a \approx 120$ meV for the steady-state PC. The higher activation energy of the steady-state PC originates from the prevailing contribution of long-lived carriers which occupy deeper subgap energy levels. The inset of Fig. 4 includes the dark conductance, which is characterized by $E_a = 0.5$ eV.

Similar to the peak transient PC, the steady-state PC of oxygen-free $C_{60}$ manifests a peak at $T \approx 240$, which disappears as the $C_{60}$ film is exposed to oxygen. As seen in the inset of Fig. 4, exposure to oxygen decreases the characteristic activation energy of the steady-state PC, reduces the temperature region at which the transport is activated, and eventually in film fully exposed to oxygen causes the steady-state PC to become almost temperature independent. The latter behavior demonstrates the quenching of the multiple trapping mechanism that we associated with the long-lived PC component.

Finally, we note that at the high-temperature regime ($T > 80$ K) the steady-state PC excitation spectrum of oxygen-free $C_{60}$ (top curves in Figs. 3 and 4) is antibatic with the optical absorption spectrum, i.e., the photoconductivity is higher at the spectral region characterized by a smaller absorption. Antibatic behavior may arise due to surface recombination[30] that is enhanced at the spectral region of high absorption, at which the absorption depth is small and hence the density of excitations near the surface is large. This process is consistent with our observation of a smaller transient PC lifetime at $\hbar\omega > 2.3$ eV, that may arise due to the faster recombination rate of a mobile carrier at the extended band states; it is also consistent with the dependence of the steady-state PC on light intensity in oxygen-free $C_{60}$, that manifests an increased recombination rate at $\hbar\omega > 2.3$ eV (e.g., the dependence of the steady-state PC on intensity is $I^{0.95}$ at 2.0 eV, whereas it is $I^{0.76}$ at 3.1 eV).

In conclusion, we have investigated the dynamics of photoexcited carriers in the pristine $C_{60}$ film and its evolution as the film is progressively exposed to oxygen by transient and steady-state PC measurements. Oxygen in a $C_{60}$ film effectively quenches the long-lived transient PC, and its effect on the excitation spectrum of the steady-state PC is qualitatively similar to the effect of reducing the ambient temperature of a pristine $C_{60}$ film: in both cases the magnitude of the steady-state PC is severely reduced, where the reduction is particularly fast for photoecxitation at $\hbar\omega < 2.3$ eV. These observations indicate that oxygen in a $C_{60}$ film creates deep traps that effectively localize the photocarriers and thereby modifies the carrier dynamics and recombination kinetics. In particular, the thermally activated long-lived transport mechanism in oxygen-free $C_{60}$, which is associated with multiple trapping transport, is effectively quenched in $C_{60}$ contaminated by oxygen, and consequently the transient and steady-state PC become almost temperature independent. In addition, exposing $C_{60}$ film to oxygen modifies the crystalline structural order; this is revealed by the disappearance of the maximum in the photoconductivity that is observed in pristine $C_{60}$ near 240 K which is associated with a structural phase transition.

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