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D. Moses [a], C. H. Lee [a], B. Kraabel [a], G. Yu [a] & V. I. Srdanov [b]
[a] Institute for Polymers and Organic Solids, University of California, Santa Barbara, California, 93106, USA
[b] Center for Quantized Electronic Structures, University of California, Santa Barbara, California, 93106, USA
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EFFECTS OF OXYGEN ON THE PHOTOCARRIER DYNAMICS IN C_{60}: STUDIES OF TRANSIENT PHOTOCONDUCTIVITY AND TRANSIENT PHOTOINDUCED ABSORPTION

D. MOSES, C. H. LEE, B. KRAABEL, G. YU, V. I. SRDANOV*

Institute for Polymers and Organic Solids, University of California,
Santa Barbara, California 93106, USA
*Center for Quantized Electronic Structures, University of California,
Santa Barbara, California 93106, USA

Abstract The intrinsic dynamics of photoexcited carriers in oxygen-free C_{60} film and their remarkable evolution as the film is exposed to oxygen are revealed by transient photoconductivity (PC) and transient photoinduced absorption (PA) measurements at various temperatures, light intensities and photon energies. We demonstrate that exposure C_{60} film to oxygen creates deep traps which effectively localize the photocarriers, and in particular strongly effecting the long-lived transport mechanism.

INTRODUCTION

Photoexcitations and photocarrier dynamics in solid C_{60} have been of great interest but almost all previous studies have been carried out on samples that were exposed to air. However, it has been recently reported that exposure of C_{60} film to oxygen modifies its electronic properties[1-8] and in particular decreases its dark conductivity and steady-state photoconductivity.[1-4] 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 PC and transient PA of pristine C_{60} film and how the carrier transport evolves as the film is progressively exposed to air. As will be demonstrated, oxygen in C_{60} film creates deep traps which drastically reduces the carrier lifetime and effectively quenches the transport mechanism associated with multiple trapping at shallow traps that prevails in oxygen-free C_{60}.[9,10]

EXPERIMENTAL

Thin-film samples were prepared by evaporating purified C_{60} powder, heated to 450 °C at a pressure of 5×10^{-6} Torr, onto alumina substrates (for Transient PC) and onto sapphire

(for the transient PA). 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 for the PC measurements. 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 for the PC measurements. After measuring 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, after which the same measurements 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. Similar procedure has applied to the PA measurements. Details regarding the transient and steady-state PC and transient PA experiments are given elsewhere.[9-11]

RESULTS AND DISCUSSION

Fig. 1 displays the transient PC waveform of oxygen-free C_{60} measured at photon energy $\hbar\omega$=2.0 eV at various temperatures. The photocarrier lifetime is drastically reduced at the

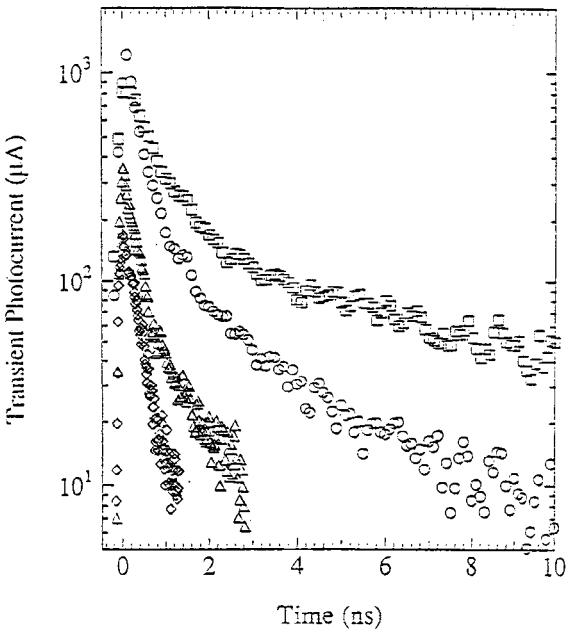

FIGURE 1 The time-resolved transient photocurrent measured at $\hbar\omega$=2.0 eV in pristine C_{60} film at various temperatures.

low temperature regime, from about 40 ns at 300 K to about 1 ns at 20 K. Moreover, these results indicate the existence of two PC components: a short lived one that persists at low temperatures and a longer lived one that vanishes as the temperature approaches zero.

The transient PC of the pristine C_{60} film and how it evolves upon exposing the film to air is shown in Fig. 2; the solid lines are the best fits of the experimental data to double-exponential function. The bottom curve in Fig. 2 is taken after the C_{60} film was exposed to air for more than a week, after which its dark conductivity reduced by more than 5 orders of magnitude from the initial value measured in oxygen-free C_{60} sample. The data in Fig. 2 clearly indicate that the carrier lifetime drastically decreases upon exposing the sample to air, from about 40 ns in the pristine C_{60} film to less than 2 ns in a film fully exposed to air. The results strongly suggest that oxygen in the C_{60} film creates efficient deep traps which effectively localize the photocarriers.[10]

The data in Fig. 2 demonstrates that oxygen affects much more the longer-lived component than the short-lived one. Moreover, the short- and long-lived PC components vary differently with light intensity and photon energy: The initial short-lived PC component shows a linear or slightly superlinear dependence on light intensity, depending on the photon energy, whereas the long-lived component a sublinear dependence;[9,10] 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. 2 where the normalized transient PC of pristine C_{60} is plotted at various laser intensities. As seen from the inset of Fig. 2 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 of 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.[9,0]

Fig. 3 displays the temperature dependence of the peak transient photocurrent in oxygen-free C_{60}, C_{60} partially exposed to air, and C_{60} fully exposed to air. The results indicate that the behavior of the transient PC varies appreciably with the oxygen content: The transient PC of oxygen-free C_{60} film manifests a maximum at about $T \approx 240$ K, below which it decreases exponentially in the 60-200 K range (with $E_a \sim 14$ meV), whereas below 60 K it remains constant. In contrast, in C_{60} film that is fully exposed to oxygen, the transient PC is almost independent of temperature.[10]

The inset in Fig. 3 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. We find that the long-lived PC does not exhibit the above maximum at 240 K (see the inset of Fig. 3); in addition, while the short-lived PC component remains almost constant at low temperatures the longer-lived component exhibits thermally activated behavior with $E_a \approx 18$ meV. Similar temperature dependences were observed at $\hbar\omega$ of 2.3, 2.6, and 2.9 eV.

The different dependences of the short- and long-lived PC components on

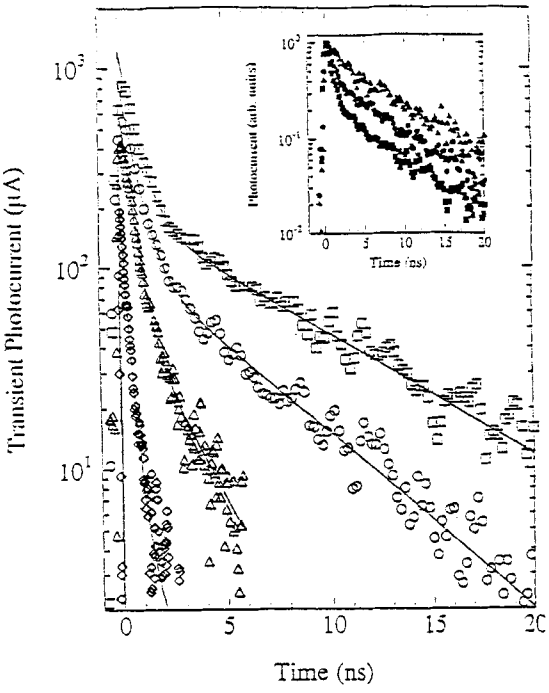

FIGURE 2 The time-resolved transient photocurrent (T=300 K, $\hbar\omega$=2.0 eV) in pristine C_{60} film and in the film at various levels of oxygen content. The dark current and relaxation time of each curve are indicated: I_d=3.6 nA (□; oxygen-free C_{60}, τ_1=693 ps and τ_2=7.2 ns), I_d=0.00567 nA (○; τ_1=640 ps and τ_2=5.0 ns), I_d=0.00024 nA (△; τ_1=463 ps and τ_2=2.2 ns), and I_d<0.00001 nA (◇; τ_1=238 ps and τ_2=1.0 ns); The inset shows the normalized transient PC of pristine C_{60} at different laser intensities: 2.7×10^{14} (▲), 1.1×10^{15} (●), and 5.4×10^{15} photons/cm^2 (■).

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[12,13] as well as states at the band tails at which the carriers tunnel to progressively lower energy levels[14] 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.[15] The contribution of the latter mechanism, which dominates the transport in oxygen free C_{60} at the high temperature regime, completely freezes out at the low temperature regime; moreover, Figs. 2 and 3 indicate that the multiple trapping mechanism is effectively quenched by oxygen.

The maximum of the peak transient PC 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 to a simple-cubic structure at low temperatures (characterized by more restricted rotational degree of freedom).[16] The observation of such a maximum indicates that evaporated oxygen-free C_{60} film contains regions of small crystalline regions imbedded in disordered C_{60}, consistent with recent X-ray scattering studies.[17] The disorder in a pristine C_{60} film is apparent from the existence of the thermally activated long-lived PC component. However, the structural order is severely modified by exposing the C_{60} film to oxygen, as indicated by the disappearance of the PC maximum in samples exposed to air.

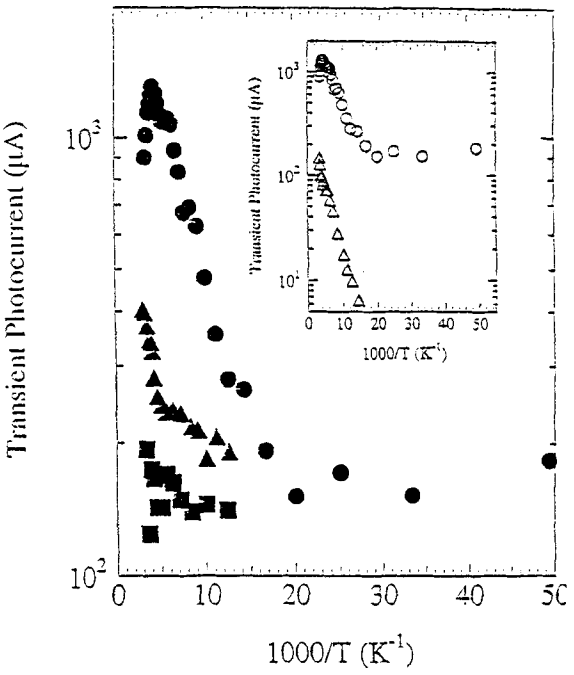

FIGURE 3 Temperature dependence of peak transient photocurrents measured at $\hbar\omega$=2.0 eV in oxygen-free C_{60} (●), partially-oxygen-exposed C_{60} (▲), and fully-oxygen-exposed C_{60} (■); the inset compares the transient photoconductivity in oxygen-free C_{60} at the peak (○) and at 2 ns after excitation (△).

Fig. 4 compares the rate of decay of the transient PA signals in the picosecond time regime in Oxygen free C_{60} film and in the film after it had been exposed to air, while the inset of Fig. 4 shows the PA spectrum measured at 0, 1, and 100 ps after photoexcitation. The data reveal a somewhat longer lived PA response in the Oxygen free sample, but the relaxation rate of the transient PA is on the order of that of the PC response. Since the PA

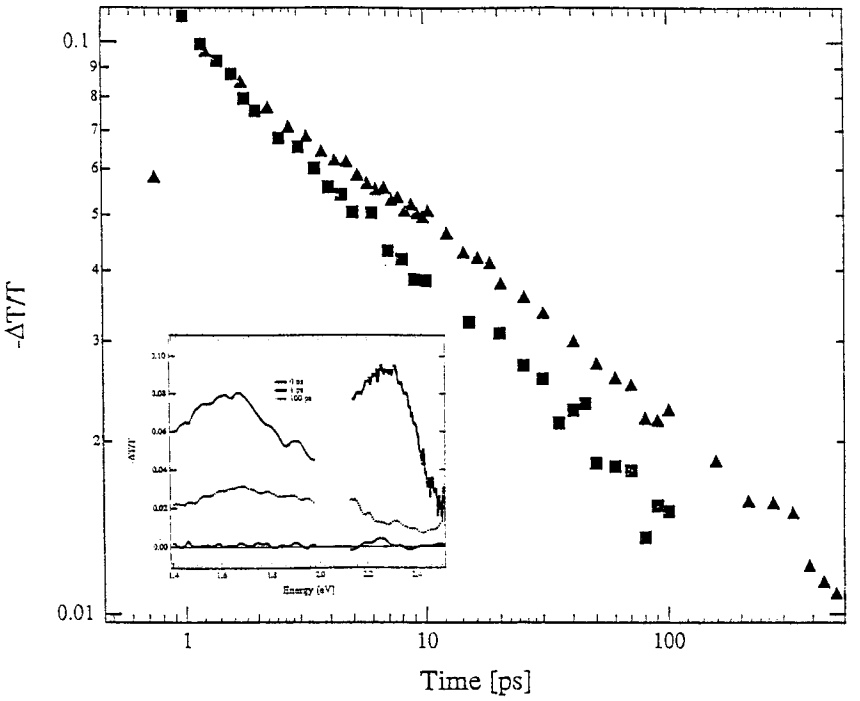

FIGURE 4 Comparison of the rate of decay of the transient PA signals in the picosecond time regime in Oxygen free C_{60} film (▲) and in the film after it had been exposed to air (■) (pump=2.05 eV, probe=1.6 eV, T=85 K); the inset shows the PA as a function of probe energy at 0, 1, and 100 ps after photoexcitation (pump=2.05 eV, T=305 K).

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 τ independent of light intensity (monomolecular kinetics), whereas for non-geminate recombination n(t) decays non-exponentially and τ decreases with increasing light intensity (bimolecular kinetics). Thus, the experimental observations of non-exponential decay of the PC and PA as well as τ being dependent on light intensity imply that non-geminate carrier recombination prevails in both oxygen-free C_{60} and C_{60} film exposed to air.[10]

Since the PA in C_{60} does not exhibit a peak at T≈240 K, it appears that the PC 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 C_{60} film exposed to oxygen as the oxygen molecules occupy the octahedral interstitial sites of the fcc C_{60} lattice.[18]

We note that 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.[10] 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 change significantly the optical absorption (it only slightly broadens the absorption peaks) and the transient PA (it reduces somewhat the photoexcitation lifetime) it modifies significantly 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 sates via nonlinear optical processes[9,10], carriers may be excited directly into localized states at the band tails. 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.

CONCLUSIONS

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 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 pristine C_{60} film: in both cases the magnitude of the steady-state PC is severely reduced, where the reduction is particularly fast for photoexcitation at $\hbar\omega$<2.3 eV. These observations indicate that oxygen in 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 structural phase transition.

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