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Photocarrier dynamics in C_{60}: studies of transient photoconductivity and transient photoinduced absorption

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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. These studies reveal the carrier transport and carrier recombination mechanisms, and provide an estimate for the initial mobility in pristine C_{60} film; these measurements also demonstrate that exposure C_{60} film to oxygen creates deep traps that localize the photocarriers and effectively quenches the long-lived multiple trapping transport mechanism.

1. 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. Recently it has been 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 they evolve upon exposure the film to oxygen have not been well understood. Here we report the results of a comprehensive study of the transient PC and transient PA in pristine C_{60} film and in a film which is progressively exposed to air. These measurements reveal the prevailing carrier transport and carrier recombination mechanisms, and demonstrate that oxygen in C_{60} film creates deep traps which drastically reduce 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]

2. EXPERIMENTAL

Thin-film samples were prepared by evaporating purified C_{60} powder, heated to 450 C at a pressure of $5x10^{-6}$ 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 similar 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 was applied to the PA measurements. Details regarding the transient and steady-state PC and transient PA experiments are given elsewhere.[9-11]

3. RESULTS AND DISCUSSION

Fig. 1 shows the transient PC waveform of oxygen-free C_{60} measured at photon energy $\hbar\omega$=2.0 eV at various temperatures on a log-log scale, whereas the inset of Fig.1 displays the data on a linear scale. The data indicate that the photocarrier lifetime is drastically reduced at low temperatures, from about 40 ns at 300 K to about 1 ns at 20 K. The temperature dependence of the PC waveform indicates 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; Fig.1 also shows that the long-lived component exhibits a power-law decay.

Fig. 2 depicts the temperature dependence of the transient PC at various delay times after the pulsed excitation on log vs. 1/T scale. The data clearly indicate that while the short-lived PC component remains almost constant at low temperatures,

the long-lived PC tail exhibits thermally activated behavior. The deduced activation energy $E_a(t)$ at various delay times is plotted in the inset of Fig. 2, which demonstrates that $E_a(t)$ increases logarithmically with the delay time.

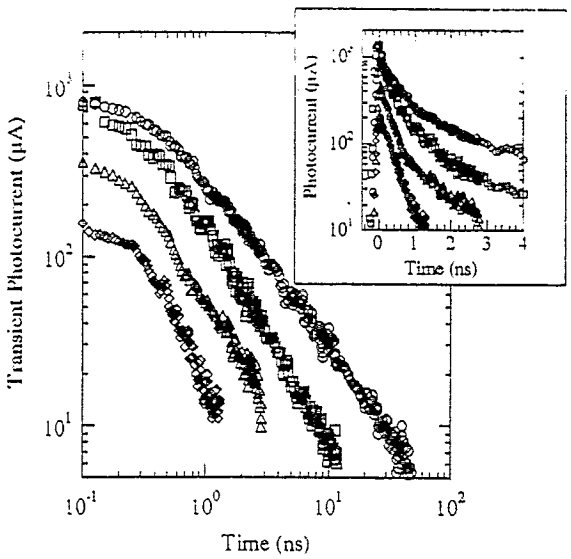

Figure 1. The transient PC decay measured in oxygen free C_{60} after pulsed excitation of 5.4×10^{15} photons/cm^2 at $\hbar\omega$=2.0 eV at various temperatures: 300(o), 160(□), 100(Δ), and 20 K(◇); inset shows the same data inearly time regime on a semi-log plot.

We find that the rate of decay of the transient PC depends on light intensity and photon energy: A faster rate of decay is observed at the higher photon energies as well as at the higher laser intensities.[9,10] In addition, at room temperature at $\hbar\omega$=2.0 eV, while the peak transient PC depends linearly on light intensity, the transient PC at 2 ns after excitation is proportional to the square root of the intensity. Thus, the observations of non exponential decay in conjunction with relaxation rates being dependent on the excitation density observed in both PC and PA unambiguously indicate that the prevailing carrier recombination is bimolecular, i.e. non-geminate.

The different dependence of the short- and long-lived PC components on temperature and light intensity clearly 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 - a model which predicts a power law decay rate of the transient PC as well as $E_a(t)$ increasing logarithmically with time.[15,16]

The transient PA signals in the picosecond time regime in Oygen free C_{60} film and in film exposed to air are shown in Fig. 3; the inset compares the transient PA in oxygen-free C_{60} at various temperatures. Since the transient PA response, which is sensitive to the density of surviving photoexcitations but not their mobility, is almost temperature independent, it follows that the temperature dependence of the transient PC stems from the mobility. We can estimate the mobility at 50 ps after excitation from the peak transient PC using the relationship: $Ip = \eta\phi\mu EN/d$, where $\eta\phi$ is the quantum yield, μ the mobility, E the external field, N the number of incident photons and d the length of the sample. We can infer the density of surviving carriers at 50 ps from the transient PA since its rate of decay at room temperature is similar to that of the transient PC. The PA data show that only about 10% of the initial density of excitation survives at 50 ps. Taking this into consideration and assuming unity quantum yield (i. e. $\eta\phi$=1 at t=0), the derived lower bound of the mobility in oxygen free C_{60} is in the range 0.03-0.3 cm^2/Vs for the photon energies 2.0-2.92 eV.

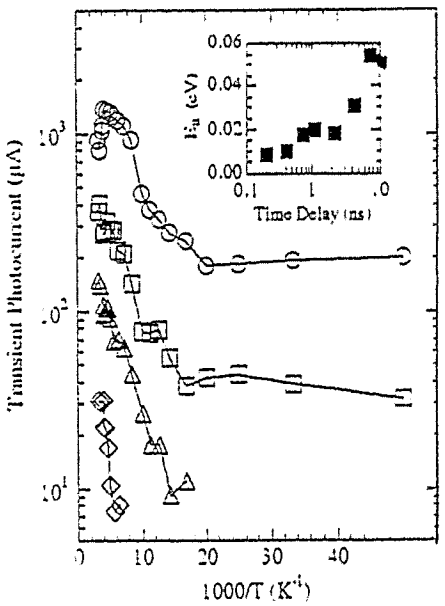

Figure 2. The temperature dependence of the transient PC at various delay times after the pulsed excitation at $\hbar\omega$=2.0 eV in oxygen free C60: t=0 (o), 0.7 (□), 2(Δ), and 10 ns (◇); inset shows the activation energy at various delay times.

We now examine the effect of oxygen on the carrier dynamics as revealed by PC and PA measurements. The transient PC of the pristine C_{60} film and how it evolves upon exposing the film to air is shown in Fig. 4. The data in 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 curve with the shortest lifetime in Fig. 4 was measured after the oxygen-free C_{60} film had been exposed to air for more than a week, after which its dark conductivity reduced by more than 5 orders of magnitude. These results strongly suggest that oxygen in the C_{60} film creates efficient deep traps which effectively localize the photocarriers.[10] These traps affect the longer-lived component more significantly than the short-lived one. As in oxygen-free C_{60}, the short- and

long-lived PC components in C_{60} fully exposed to air vary differently with light intensity and photon energy.

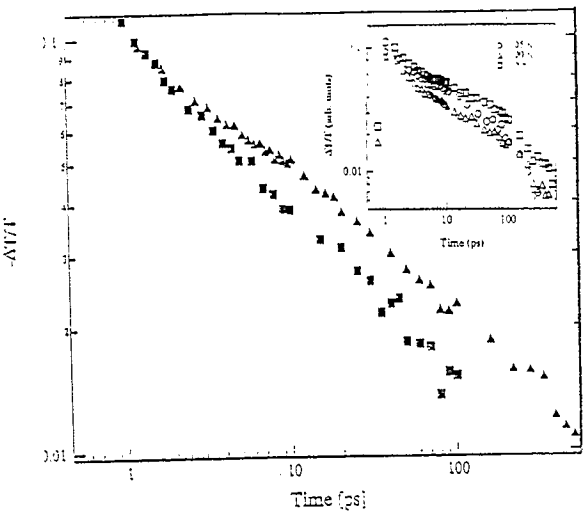

Figure 3. Comparison of the rate of decay of transient PA in the picosecond time regime in oxygen free C_{60} film (▲) and in the film after it had been expose to air (■) (pump 2.05 eV, probe 1.6 eV, T=85 K); inset shows The transient PA at various temperatures (pump 2.0 eV, probe 2.1-2.3 eV).

Fig. 5 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 peak transient PC of oxygen-free C_{60} film manifests a maximum at about T≈240 K, below which it decreases exponentially in the 60-200 K range (with E_a≅14 meV), while below 60 K it remains constant. In contrast, in C_{60} film that is fully exposed to oxygen, the transient PC is almost temperature independent.[10]

The inset in Fig. 5 compares the temperature dependence of the peak transient PC of oxygen-free C_{60} and the PC measured at 2 ns after excitation. These results indicate that the long-lived component does not exhibit the above maximum at 240 K, and while the short-lived PC component remains almost constant at low temperatures, the longer-lived component exhibits thermally activated behavior (with E_a≈18 meV). Similar temperature dependencies were observed at photon energies of 2.3, 2.6, and 2.9 eV.[10]

The local maximum of the peak transient PC in oxygen-free C_{60} film can be associated with a first-order structural phase transition of known to occur at 249 K, from a face-centered-cubic lattice to a simple-cubic structure prevails at low temperatures (which is characterized by a more limited rotational degree of freedom).[17] The observation of this 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.[18] The disorder in a pristine C_{60} film is apparent from the existence of a thermally activated long-lived PC component. This structural order is however severely modified by oxygen, as indicated by the disappearance of the local PC maximum in samples exposed to air.

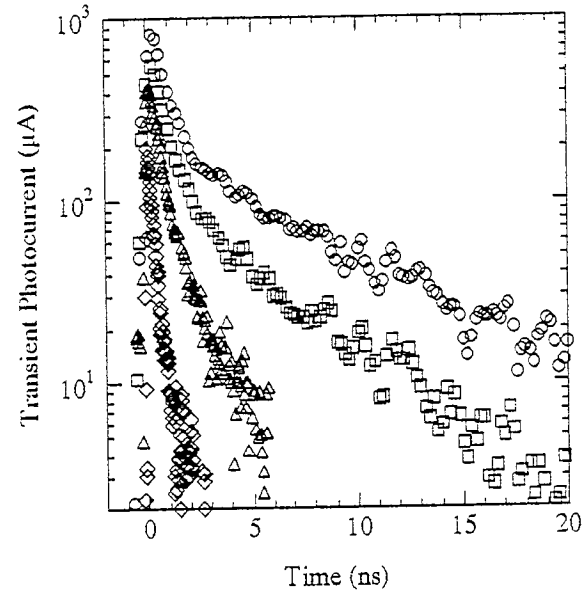

Figure 4. The room temperature transient PC decay measured at $\hbar\omega$=2.0 eV in oxygen free C_{60} film and in the film at various levels of oxygen content. The dark indicates the degree of exposure to oxygen: I_d=3.6 (o; oxygen free C_{60}), I_d=0.00567 (□), I_d=0.00024 (Δ), and I_d<0.00001 nA (◇).

Finally, 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 additional information regarding the spectral dependence of the PC. 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}. In addition, 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, as shown in Fig. 3) 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 the mobility edge in C_{60} is near 2.3 eV. Thus, in C_{60} film exposed to air at $\hbar\omega$<2.3 eV, in addition to carrier excitation into extended band states via nonlinear optical processes[9,10], carriers may be excited directly into localized states at the band tails; however their apparent contribution 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.

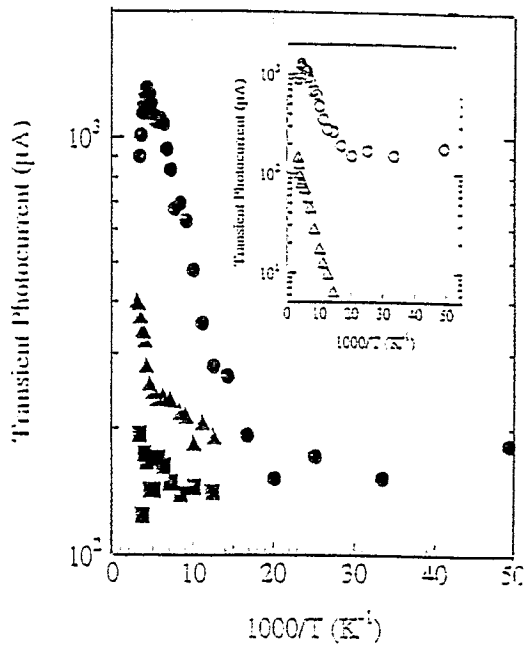

Figure 5. Temperature dependence of peak transient PC measured at $\hbar\omega$=2.0 eV in oxygen free C_{60} film (●), in the film partially exposed to air (▲), and in the film fully exposed to air (■); the inset compares the transient PC in oxygen free C_{60} at the peak (o) and at 2ns after excitation (Δ).

4. CONCLUSION

We have investigated the carrier dynamics in pristine C_{60} film and their evolution as the film is progressively exposed to oxygen by transient PC and transient PA measurements. We find that while oxygen in C_{60} slightly shortens the transient PA lifetime, it drastically reduces the long-lived transient PC component. The transient PC in oxygen-free C_{60} film indicates two distinct transport mechanisms: a short-lived one due to 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 and long-lived thermally activated transport that stems from carriers undergoing multiple trapping at shallow traps and phonon assisted releasing into the extended band states. The latter mechanism is identified by the power law decay of the transient PC and the behavior of the activation energy $E_a(t)$. At the high temperature regime, the non exponential relaxation of the transient PC in Oxygen-free C_{60} in conjunction with relaxation rates being dependent on the excitation density, observed in both PC and PA, indicate bimolecular recombination. However, at the low temperature regime, as the thermally activated long-lived PC component freezes out, the transient PC approaches an exponential decay, which may indicate a monomolecular carrier recombination.

From the transient PC and transient PA data we estimated the carrier mobility at 50 ps after excitation. Assuming that the transient PC follows similar rate of decay as the transient PA and $\eta\phi$=1 we deduce the lower bound for the mobility in oxygen free C_{60} to be in the range 0.03-0.3 cm^2/Vs at the photon energies 2.0-2.92 eV.

Finally, the peak transient PC in Oxygen-free C_{60} exhibits a local maximum at about 240 K, near a structural first-order phase transition temperature. This indicates that evaporated film of oxygen-free C_{60} contains structurally ordered regions, which apparently are in the form of micro-crystallites imbedded in disordered C_{60}.

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