

Carrier mobilities and influence of oxygen in C_{60} films

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We have studied the intermolecular carrier transport in C_{60} films. Photoelectrical and optical experiments indicate charge transfer transitions to set in at photon energies of ~ 2.2 eV. The electron transport in the charge transfer state is by hopping with typical drift mobilities of $1 \text{ cm}^2/\text{V s}$ in as-grown films. Hole drift mobilities are in the $10^{-4} \text{ cm}^2/\text{V s}$ range. Upon oxygen exposure the carrier mobilities decrease significantly, while recombination lifetimes grow. These findings are interpreted as being due to transport-limited recombination kinetics. [S0163-1829(99)02539-4]

INTRODUCTION

The photoconductivity in C_{60} has attracted considerable attention from the applied physics field as well as in basic research. It was noted at an early stage that the onset of photoconductance occurs at ~ 1.85 eV with low-quantum efficiencies. These findings were quantitatively explained in terms of an Onsager generation mechanism involving excitonic molecular states.^{1,2} From photoemission measurements the band gap of C_{60} was determined to be 2.3 ± 0.1 eV.³ Optical investigations, however, indicate a charge transfer exciton state near 2.3 eV (Ref. 4) and the band gap to be 2.6 eV. Several studies into the electronic kinetic behavior showed that the carrier propagation in C_{60} films is trap limited and dispersive.⁵⁻⁷ Exposure to oxygen lowers the conductivity and gives rise to strong changes^{8,9} in the carrier kinetics.^{10,11} In the present paper we report results from photoelectric measurements, which complete this picture of charge propagation. Our transport experiments indicate that the electron drift mobility is in the $1 \text{ cm}^2/\text{V s}$ range, while the hole mobility is much smaller.¹²⁻¹⁶ The low mobility values and the temperature dependence of the carrier kinetics suggest that the carrier propagation is by hopping. We further show that the electronic transport properties are strongly affected when C_{60} is exposed to oxygen. Both, hole and electron drift mobilities are found to decrease with O uptake, while the recombination lifetime increases due to the slower transport.

PREPARATION

The films were prepared by sublimation of C_{60} powder, which was obtained from Merck Co.⁹ Before deposition the powder was chromatographically purified and outgassed in ultra-high-vacuum (UHV) for 1 day at $T=300^\circ\text{C}$. The sublimation and deposition occurred at 500°C in UHV conditions with the substrates kept at room temperature. This procedure gave polycrystalline films containing $>99.9\%$ C_{60} with grain size between 70 and 200 nm. An atomic force micrograph depicting the grain structure of a 100-Å-thick film is shown in Fig. 1. A more detailed description of the preparation is given in Refs. 17 and 18. Photoelectric measurements were performed on films of 1–2- μm thickness and were carried out outside the UHV chamber. Since oxygen has a strong effect on the electronic properties of C_{60} , the

films needed to be covered with an oxygen barrier. In the case of sandwich structures, a 100-Å Pt film, deposited without breaking the UHV conditions, served this purpose. The sample structure in the sandwich configuration was thus glass/ SnO_2 / C_{60} /Pt with diameters for the Pt dots of 2 mm. Films with coplanar contacts used 8-mm Cr strips on 7059 Corning glass with a separation of 0.5 mm. The samples were sealed with polymer tape inside the load-lock chamber at pressures of $\sim 10^{-5}$ mbar. Our experience showed that the tape sealing prevented oxygen uptake for ~ 5 h, which was sufficient to carry out the photoelectric measurements. After 5 h the samples showed degradation in the electronic transport properties.¹⁵

CARRIER TRANSPORT STATES IN C_{60}

First experiments to determine the band gap in C_{60} have been carried out by Lof *et al.*³ using a combination of photoemission and inverse photoemission measurements. Since the two experiments do not probe the same excitation state, a somewhat complicated estimate for the exciton binding energy had to be employed to derive a bandgap of 2.3 ± 0.1 eV from the experimental data. More recently optical investigations^{4,19} have shown that an excitonic charge transfer state is accessed with photon energies of 2.3 eV, and it was suggested that the single carrier band gap may be as large as ~ 2.6 eV.⁴ One may hope to confirm this assignment by a direct comparison of transport and absorption data on

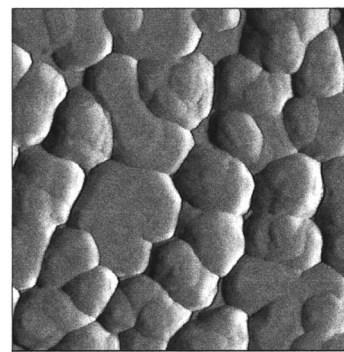


FIG. 1. Atomic-force micrograph of a 100-Å-thick C_{60} film grown on glass substrate. The side length of the micrograph corresponds to $1 \mu\text{m}$.

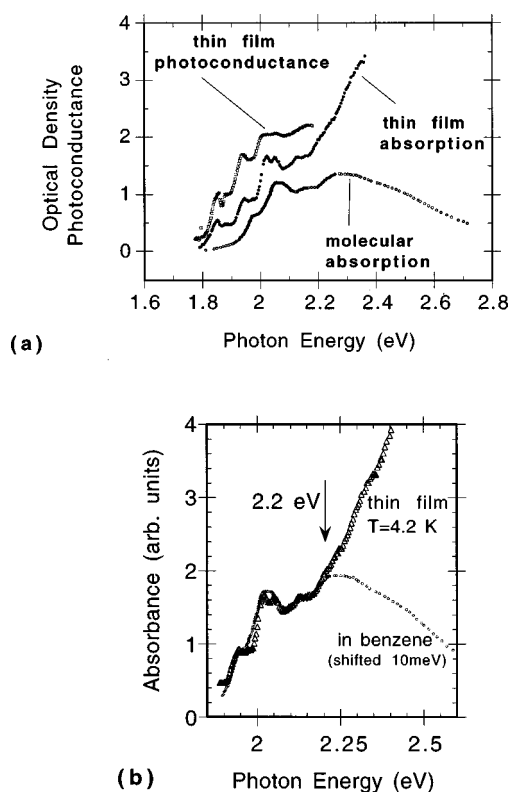


FIG. 2. (a) Absorbance spectra of C_{60} in benzene solution and C_{60} thin film, photoconductance spectrum of C_{60} thin film. (b) Solution spectrum shifted by +10 meV, and thin film absorbance spectrum. Note that scaling in the vertical axis corresponds to adjusting the differing optical thickness of the two samples.

thin films and on molecular C_{60} in solution. Figure 2 shows such a comparison involving a C_{60} /benzene solution and thin-solid films. At $T=4.2$ K the thin-film absorption spectrum is sufficiently structured to allow a direct comparison to the solution spectrum. Both spectra are very similar near the absorption onset except for a small shift in energy, which can be attributed to the different dielectric constants. A 10-meV shift of the solution spectrum brings the two spectra in nearly perfect coincidence, as shown in Fig. 2(b). The close similarity clearly indicates that the lower excited states are largely unaffected by solid-state effects, i.e., that they are excitonic molecular states. For photon energies in excess of ~ 2.2 eV there is strong absorption gain in the film. This absorption gain is interpreted as being due to the wavefunction overlap in charge transfer states. Considering the nature of these states we find the threshold value of 2.2 eV found here compatible with the assignment of 2.3 eV in Ref. 4. A similar comparison of room-temperature absorption spectra gives essentially the same result; there is hence no discernible difference in the energy of the charge-transfer states in the low-temperature simple cubic phase and the high-temperature fcc phase. Figure 2(a) shows that the photocurrent spectrum also exhibits the vibronic structure as seen in the absorption spectra below ~ 2.3 eV, indicating that the photoconductance in this regime is due to exciton dissociation. This interpretation is further corroborated by the energy dependence of the quantum generation efficiency shown in Fig. 3. The data were obtained from charge collection measurements using pulsed laser excitation.² The field and

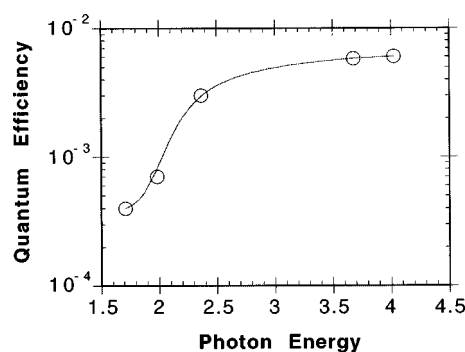


FIG. 3. Quantum generation efficiency vs photon energy in C_{60} (data from Ref. 2).

temperature dependence of these data is well described by the Onsager pair generation model.^{20,21} For photon energies below ~ 2 eV and small electric fields, the quantum efficiency typically lies in the 10^{-3} range. At ~ 2.2 eV a steep increase in quantum efficiency is observed, indicating that a different type of states is accessed with these higher photon energies. The limited quantum efficiency in the region above 2.5 eV indicates that the involved states are not extended Bloch states. Instead the data are compatible with the interpretation that excitonic charge-transfer states are involved.

PROPAGATION MECHANISM

We next turn to a discussion of the carrier propagation mechanism. Figure 4(a) shows typical decay curves of the photoconductance obtained after pulsed laser excitation. In the ns and μ s time region the photocurrent decay follows an algebraic decay law, approximately given by $i(t) \sim t^{-1}$, which we attribute to dispersive transport conditions. Measurements by others performed in the ps and ns time region have also observed decay kinetics slower than a single exponential behavior.⁷ We find the algebraic decay kinetic to be operative for excitation energies in the range $\sim 2.5 < h\nu < 4$ eV, which clearly indicates that in this time regime the trap occupation is independent of the states initially excited. As part (b) of the figure shows the kinetics is only weakly temperature-dependent throughout the range, $100 < T < 400$ K, the decay exponent changing by only $\sim 15\%$. This absence of a strong-temperature dependence strongly suggests that thermal emission is not the rate-limiting process for carrier transport, implying that multiple trapping should be ruled out as a propagation mode. Instead the data are compatible with hopping-type transport for the intermolecular charge transfer. In the hopping transport model the algebraic decay-law results from the spatial distribution of sites and the strong dependence of the transfer integral on the distance between the sites. The hopping model therefore predicts only a weak-temperature dependence of the kinetic behavior, in agreement with the data of Fig. 4.

ELECTRON AND HOLE DRIFT MOBILITIES, RECOMBINATION TIMES

For quantitative measurements of the transport parameters we have used the moving photocarrier grating technique, which allows to determine the electron and hole drift mobili-

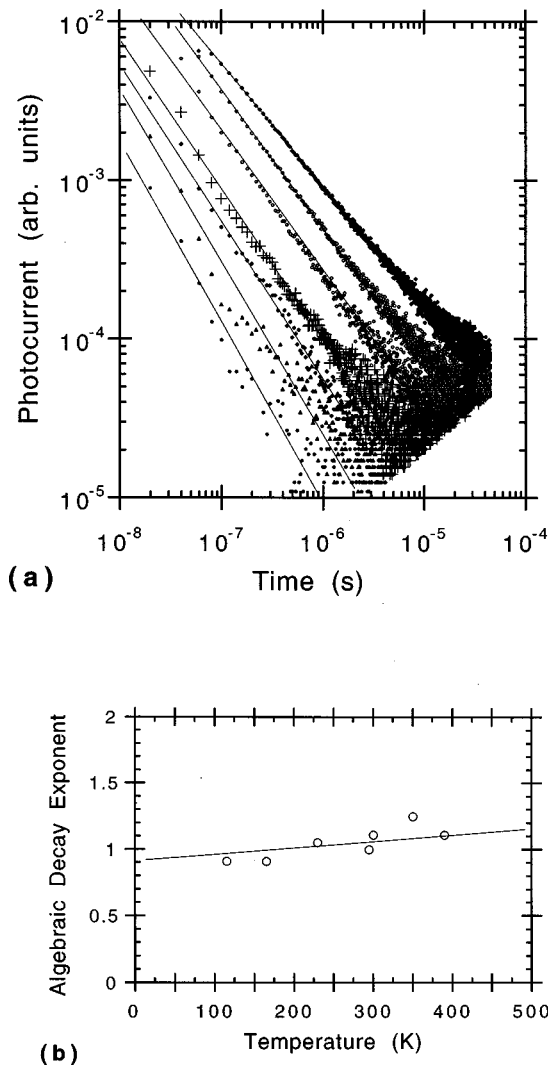


FIG. 4. (a) Photoconductance decay in C₆₀ films, following an algebraic decay law approximately given by $i(t) \sim t^{-1}$; (b) temperature dependence of the decay exponent

ties and the ambipolar recombination lifetime.^{22,23} The experiment involves an optical interference grating, which moves at constant velocity between two coplanar electric contacts. Due to their different mobilities, electrons and holes respond to the grating motion at different rates. This results in a net motion of charge, which is picked up as a photocurrent between the two contacts. The dependence of the photocurrent on grating velocity is evaluated in terms of the drift mobilities of the two carrier types and the ambipolar recombination lifetime by solving the transport and Poisson equations. The procedure is described in detail in Refs. 22 and 23.

Figure 5 shows the experimental results obtained for a polymer-sealed film at different stages of O exposure after deposition. The solid lines show calculated fits to the experimental data.^{15,23} The initial electron drift mobility, measured within 20 min after breaking UHV conditions, is $\mu_e = 1.3 \text{ cm}^2/\text{V s}$, a value comparable to that of other polycrystalline organic semiconductor films^{24,25} and to earlier results on C₆₀ crystals.¹³ The magnitude of the drift mobility is also compatible with the suggested transport by hopping. The hole mobility is found to be much smaller than the electron

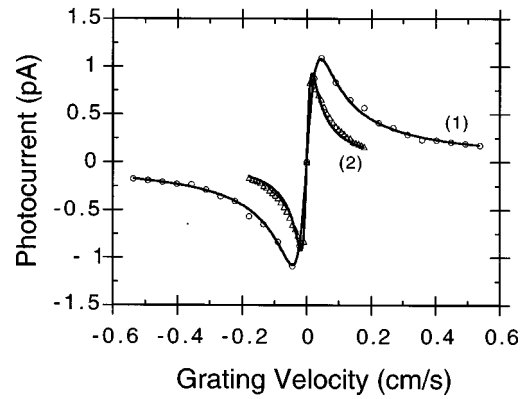


FIG. 5. Moving grating results for C₆₀. (a) Curve (1) shows results for a film ~ 20 min after deposition ($\mu_e = 1.3 \text{ cm}^2/\text{V s}$, $\mu_h = 2 \times 10^{-4} \text{ cm}^2/\text{V s}$, $\tau = 1.7 \mu\text{s}$), curve (2) shows results obtained after 5 h ($\mu_e = 0.45 \text{ cm}^2/\text{V s}$, $\mu_h = 7 \times 10^{-5} \text{ cm}^2/\text{V s}$, $\tau = 5 \mu\text{s}$).

mobility, $\mu_h \approx 2 \times 10^{-4} \text{ V/cm}^2 \text{ s}$. This value is considerably smaller than the $\sim 1.7 \text{ cm}^2/\text{V s}$ reported for crystals,¹³ but compatible with previous conclusions for thin films.^{12,14} It thus appears that one significant difference between C₆₀ single crystals and thin films is the much lower hole drift mobility in thin films. It remains to be investigated if this difference is due to impurity or grain boundary effects. The recombination time in the first measurement is $1.7 \mu\text{s}$. This value is considerably larger than typical decay times from time-resolved photoconductance studies.^{5,6} However, most of the kinetic measurements have focused on the ps and ns time region, and their basic result is that the decay becomes slower with progressing time. Our own data suggest an algebraic decay law, covering all of the ns time region and reaching several μs . A possible explanation to these observations is that fast trapping precedes a comparably slow recombination process. We believe that such an explanation is likely to apply in C₆₀ films. This explanation would also be in line with our finding of small $\mu\tau$ products under trapping conditions as shown in Ref. 2.

Strong degradation of the transport parameters due to the influence of oxygen is noticed from Fig. 6. The degradation is seen to set in after approximately 5 h. Electron spin resonance (ESR) and secondary ion mass spectroscopy (SIMS) were used to characterize the O content in the as-grown and degraded state.²⁶⁻²⁸ The ESR signal strength can be evaluated in terms of the chemically active O content in the films. In the as-grown state typical spin densities are in the 10^{15} cm^{-3} range, while the most strongly degraded samples had an ESR spin density of 10^{17} cm^{-3} . Comparing the ESR results to total concentration measurements by SIMS, indicates that only 1–10 % of the incorporated oxygen induces oxidation reactions.

The O-induced degradation involves a dramatic decrease in the carrier drift mobilities and an increase in the recombination time. Chemical studies have shown that the oxygen impurity state lies 0.3 eV below the excited triplet state.²⁹⁻³² It therefore constitutes a deep defect with an energy not far from midgap. This may explain a strong electronic compensation effect of O, apparent in the drastic lowering of the dark conductivity. The charge transfer in the oxidized

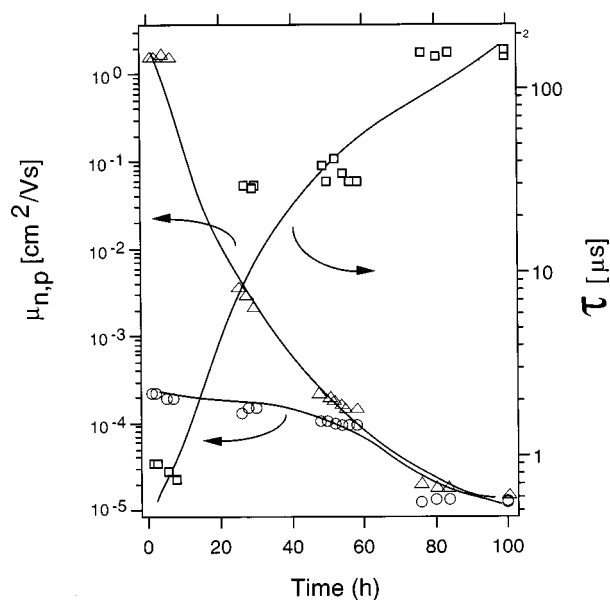


FIG. 6. Change in transport parameters due to O uptake in C_{60} films. In the course of these measurements the ESR spin density was found to rise from $\sim 10^{15}$ to $\sim 10^{17} \text{ cm}^{-3}$; (Δ) electron and (\circ) hole mobilities, (\square) recombination time.

molecule also gives rise to a negative charge on the impurity. It has been shown³³ that charge fluctuations in excess of $\sim 10^{17} \text{ cm}^{-3}$, may give rise to potential fluctuations of some 100 meV, which usually decrease the carrier propagation rate. If the transport process is the rate-limiting step for the recombination, it is to be expected that smaller drift mobilities and longer recombination lifetimes will result, as observed in Fig. 6.

The product of quantum efficiency, drift mobility, and recombination time, $\eta\mu\tau$, is the relevant photoconductance parameter for many applications, such as xerography, solar energy conversion or detector applications. For recombina-

tion conditions we obtain, $\eta\mu\tau \approx 7 \times 10^{-9} \text{ cm}^2/\text{V}$ in oxygen-free samples at low applied fields.

CONCLUSIONS

Our results suggest that localized excitonic states in C_{60} play a dominant role in charge carrier generation and transport. There is a finite probability for transitions into excitonic states above 1.85 eV. These transitions involve vibrational coupling in the lowest excited singlet state. The photoconductance accompanying these excitations is due to the subsequent ionization of excitons at defects or in internal electrical fields. Accordingly the carrier transport among these states is characterized by very low-quantum efficiencies.

Charge-transfer states lie ~ 2.2 eV above the ground state. These states lead to a sizable absorption in the solid as compared to molecules in the solution. The excitation into these states is associated with increased quantum efficiencies, but the overall quantum efficiencies remains below 1%. These findings suggest that the excitation is spread across several molecules.

Electron drift mobilities are in the $1 \text{ cm}^2/\text{V s}$ range and more than three orders of magnitude larger than hole mobilities. From the lack of a strong temperature dependence in the photoconductance decay it is concluded that the propagation mechanism is hopping. The $\eta\mu\tau$ product for recombination conditions is in the 10^{-9} to $10^{-8} \text{ cm}^2/\text{V}$ range. Oxygen acts as a compensating agent on the n -type conductivity and is found to degrade the carrier mobilities by several orders of magnitude. The slower transport goes along with longer recombination times, indicating that the recombination process is transport limited.

Since the low quantum efficiency results from intrinsic properties of the solid, there appears to be little prospect for substantial improvement of the transport properties of pure films. Modifications to the molecular subunit or changes in composition of the films can, however, alleviate some of these problems.^{34,35}

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