

## Oxygen effect on the photoconductivity behavior of C<sub>60</sub> thin films

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Conductivity ( $\sigma_d$ ) and photoconductivity ( $\sigma_{ph}$ ) measurements have been performed on polycrystalline C<sub>60</sub> thin films. C<sub>60</sub> films are characterized by an extended optical absorption edge ( $E_{gopt} \sim 1.7\text{eV}$ ) and a photoconductivity onset ( $E_{gel} = 1.7 \sim 2.1\text{eV}$ ).  $\sigma_d$  and  $\sigma_{ph}$  in the high temperature regime ( $T > 270\text{K}$ ) are thermally activated ( $E_a(\sigma_d) = 0.50 \pm 0.05$  and  $E_a(\sigma_{ph}) = 0.20 \pm 0.05\text{eV}$ ) whereas at low temperature regime ( $T < 270\text{K}$ ) they are weakly temperature dependent, for all excitation wavelength above the photoconductivity edge. Oxygen, in the octahedral interstitial sites of the fcc lattice of C<sub>60</sub>, has those effects in this material: decrease in  $\sigma_{ph}$  and  $\sigma_d$  by orders of magnitude, increase in  $\sigma_{ph}/\sigma_d$  ratio; decrease in photoconductivity response time. Moreover the oxygen effect on those properties is mostly reversible. Here carrier photogeneration and transport processes are invoked in the context of localized electronic states and oxygen effects are interpreted.

### 1. INTRODUCTION

Considerable interest exists in the properties, and possible applications of fullerenes, with particular focus on the electrical properties of C<sub>60</sub> films. Photophysical properties including UV-visible absorption, photoluminescence, photoconductivity have been already reported [1, 2].

Photoconductivity is for sake of simplicity a 2-step process: photogeneration and transport of charge carriers. Electronic transitions commonly found in photoconductors involved absorption of photon and concomitant excitation of the molecules. Excited materials can decay either radiatively or nonradiatively to the ground state. In the case where the excitation processes give a net electrical charge or e/h pair, requiring separation by thermal and/or electric field, photoconductivity can be observed. Once electrons and holes have been free they will remain free until they are captured at an imperfection or recombined or pass out of the material at the electrodes.

As far as we know, photocarrier generation and charge transport mechanisms have not been completely elucidated [3-8]. The outstanding question is, despite their molecular character whether the localized or delocalized state picture is most appropriated to describe the observed behavior. On the other hand oxygen effect on photoconductivity have been reported but the mechanism has not been conclusively established [8-12]. In this letter, we report complementary information obtained by means of steady-state photoconductivity. Wavelength and temperature dependence of conductivity and photoconductivity measurement for *in situ* and oxygen exposed samples are discussed.

### 2. EXPERIMENTAL

Deposition and measurement are performed strictly in vacuum. As it is well known electrical properties of C<sub>60</sub> film are affected by air, measurements made strictly excluding accidental contact with air seem particularly desirable [9-11]. As will be described later this precaution is found to be important to assess the electrical properties of C<sub>60</sub> film.

Films are deposited by sublimation using pure C<sub>60</sub> powder (99.9%, HPLC) on top of quartz plates with predeposited interdigitated gold electrodes; under vacuum (below  $10^{-6}$  Torr) at various substrate temperatures (298, 380K) at constant deposition rate of about 0.4nm/min. Based on the evidence that the diffusion and migration of C<sub>60</sub> molecules at the surface of the substrate are thermally activated, films grown at high temperature provided indeed clear thin film with large grain and smooth surface than those grown at room temperature (as observed by AFM). X-ray analysis of the films indicates polycrystalline material with fcc structure. In what follows only films grown at high temperature are considered.

Steady-state DC current (Digital electrometer Keithly 617) is measured under DC electrical field ( $10^4$  V/cm) before and after excitation in the wavelength range 260-800nm at constant number of photon  $2 \times 10^{14} \text{cm}^{-2} \text{sec}^{-1}$ . Then conductivity and photoconductivity were determined. Measurements are reported versus wavelength and temperature in the range  $\lambda = 260-800\text{nm}$  and  $T = 170-370\text{K}$  (temperature rate = 0.8K/min), respectively.

### 3. RESULTS

#### 3.1. Absorption and photoconductivity spectrum

Uv-visible absorption and photoconductivity spectroscopies might reveal some aspect of the electronic structure of the  $C_{60}$  film. For the purpose of comparison Uv-visible absorption of  $C_{60}$  in solution (hexane), thin film (air exposed) and photoconductivity spectra (air exposed) are represented in figure 1. Uv-visible absorption spectrum of  $C_{60}$  thin films is found to retain all the characteristic absorption bands observed in solution. However, the latter one shows neither a shoulder at 600 nor an extended tail in the region 700-800nm as clearly observed for films. In the range 260-800nm corresponding peaks are observed in both absorption and photoconductivity spectra of thin film confirming that photoconductivity is generated via the excitation of  $C_{60}$  molecules. The polycrystalline  $C_{60}$  films are characterized by: an extended optical absorption edge ( $E_{gopt} \sim 1.7eV$ ) and a photoconductivity onset ( $E_{gel} = 1.7 \sim 2.1eV$ ).

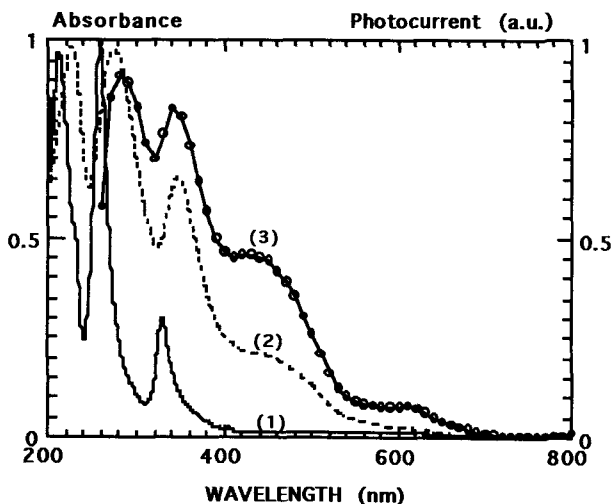


Figure 1: (1)Uv-visible absorption of  $C_{60}$  in solution (hexane), (2)thin film (air exposed) and (3)photoconductivity spectrum (air exposed).

#### 3.2. Temperature dependence

Conductivity and photoconductivity temperature dependence give interesting insight on the photo generation and carriers transport processes. Figure 2 (a) and (b) show the temperature dependence of the dark current and photocurrent ( $\lambda=300$  and  $600nm$ ) in the temperature range 170-370K, respectively. Two distinct temperature regimes are observed.

In the high temperature regime  $T > 270K$ , the observed behavior points to a thermally activated process. By taking an Arrhenius law the activation energy can be determined:

$$E_a(\sigma_d) = 0.50 \pm 0.05 \text{ eV and } E_a(\sigma_{ph}) = 0.20 \pm 0.05 \text{ eV}$$

for all excitation wavelength above the photoconductivity edge, within the experimental resolution. The activation energy  $E_a(\sigma_{ph})$  is constant for both excitations  $\lambda=300$  and  $600nm$ . As photoconductivity is thermally activated this result demonstrates that excitation process with energy above the absorption edge is insufficient to create directly free charge carriers. As conductivity is thermally assisted and if the Fermi level lies near midgap this implies an electronic band gap for  $C_{60}$  twice  $E_a(\sigma_d)$ , namely about  $1eV$ , which is inconsistent with an intrinsic activation energy. Thus the conductivity is mainly due to extrinsic carriers.

At low temperature regime  $T < 270K$ , conductivity and photoconductivity are weakly temperature dependent. Moreover here also the temperature dependence of the photoconductivity is similar for all excitation energy above  $1.7eV$ . Photogeneration and transport carrier mechanisms are not consistent with a thermally activated process but rather with Mott's law of variable range-hopping process.

At temperature around  $250K$  an order-disorder phase transition has been reported on powder, quartz and thin films. The anomaly observed on conductivity and photoconductivity in the temperature range  $250K$  is not reproducible and clearly established.

#### 3.3. Oxygen effect

Here we would like to emphasize the effect of the atmosphere in which the  $C_{60}$  samples are exposed and their electrical properties are measured. Figure 3 shows the experimental results obtained for  $C_{60}$  thin film kept strictly in vacuum after deposition, exposed to oxygen ( $T=298K$ ,  $1atm O_2$ , 12 hours, after which the vacuum is restored and measurements are performed) and heated oxygen exposed film (the previously oxygen exposed sample is heated under vacuum at  $T=380K$  for 4h, after which measurements are performed). Preliminary experimental results, after admission separately of pure nitrogen  $N_2$  and pure oxygen  $O_2$  both with a pressure of  $1atm$  at room temperature, show while  $N_2$  caused no change,  $O_2$  has those principal effects in this material: decrease in  $\sigma_{ph}$  and  $\sigma_d$  by orders of magnitude, increase in  $\sigma_{ph}/\sigma_d$  ratio; decrease in photoconductivity response time.

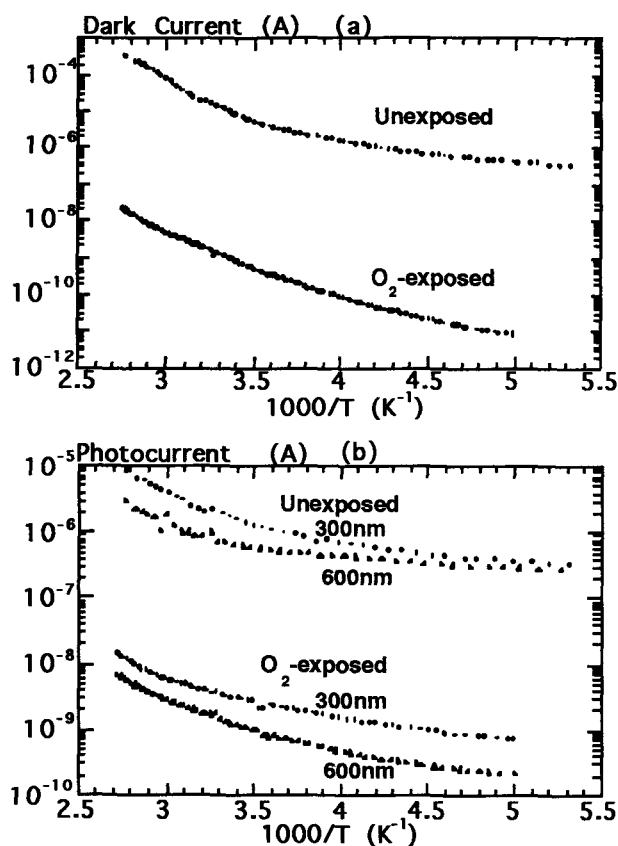


Figure 2: Temperature dependence: (a) the dark current and (b) photocurrent ( $\lambda=300$  and  $600\text{nm}$ ), in situ and oxygen exposed film (thickness= $220\text{nm}$ ).

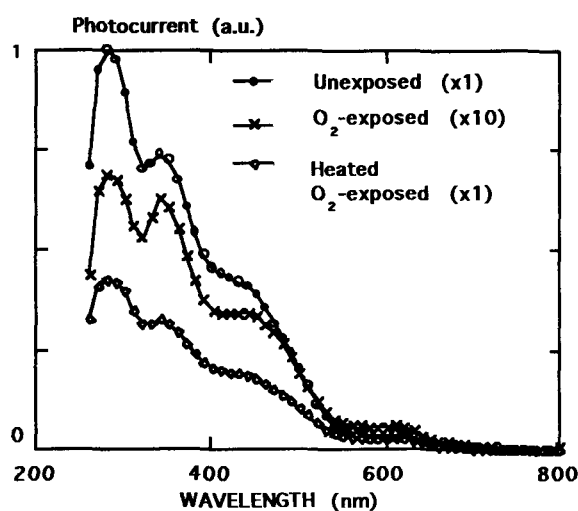


Figure 3: Photocurrent action spectrum at  $T=260\text{K}$ , for unexposed, oxygen exposed and heated oxygen exposed film (thickness= $13\text{nm}$ ).

On one hand this result indicates that oxygen has a strong electronic interaction with  $C_{60}$  sample once it adsorbed and diffused into the solid thin film.

Experimental result shows that only by reevacuation of the sample at room temperature it was not possible to recover the original conductivity and photoconductivity value at least for hours. However, most of the oxygen effect on  $\sigma_{ph}$  and  $\sigma_d$  can be reversed by heating the sample at  $380\text{K}$  under vacuum ( $p < 10^{-6}\text{Torr}$ ) for 4 hours, but the final state has a slightly lower photoconductivity and conductivity. As oxygen effect on those properties is mostly reversible, photoassisted transformations are excluded, at least with the experimental conditions used here. It is remarkable that the results obtained from temperature dependence of the photoconductivity and the conductivity for oxygen exposed sample are reproducible at least for 3 consecutive scans between  $170\text{--}370\text{K}$ . This means that no appreciable amount of oxygen has been desorbed during the temperature dependence measurements as far as the sample temperature is lower than  $370\text{K}$  and be kept at this temperature for a short time.

However, oxygen effect is imperceptible on temperature dependence of photoconductivity and conductivity. Neither the high nor the low temperature regime is significantly affected by oxygen: the activation energy is constant for temperature above  $270\text{K}$ , for both in situ and oxygen exposed example. As far as the photoconductivity spectrum is concerned all the characteristic bands observed in unexposed films were retained in oxygen exposed sample, neither alteration nor new bands appear.

#### 4. DISCUSSION

Carrier photogeneration and transport in  $C_{60}$  film involved localized electronic states. Evidences for this assignment come from optical, luminescence, PES/IPES spectroscopies and photoconductivity measurements [12-14]. It is remarkable that the electronic structure in polycrystalline  $C_{60}$  material preserves its molecular character. Some aspect of the electronic structure of  $C_{60}$  film observed by means of optical and photoconductivity spectroscopies revealed an extended optical absorption edge ( $E_{g,opt}=1.7\text{eV}$ ) and a photoconductivity edge ( $E_{g,el}=1.7\sim 2.1\text{eV}$ ). Moreover broadening and wavelength shift of the absorption bands in solid thin film with respect to solution might be assigned either to Coulombic interactions between  $C_{60}$  molecules and/or to structural disorder. The reported optical

transition at 600nm is dipole forbidden for isolated molecules but weakly dipole allowed in solid state.

It is interesting to mention that highly sensitive photothermal deflection spectroscopy measurements of the optical absorption spectrum of C<sub>60</sub> thin films have been carried out in the range 0.4-6.2eV(3100-200nm); measurements reveal a gap region that includes an Urbach edge from 1.5 to 1.8eV (830-690nm) with structure attributed to vibronic interations [12]. PES and IPES spectroscopy on C<sub>60</sub> thin film show: an electronic band gap LUMO(t<sub>1u</sub>)/HOMO(h<sub>u</sub>) in the range 2.3~2.6eV, an Hubbard energy U about 2eV, t<sub>1u</sub> and h<sub>u</sub> bandwidths about 0.4eV [13,14]. Those results suggest on one hand that C<sub>60</sub> behave as strongly correlated system, and on the other hand predicted the existence Frenkel-type excitons in the range 1.5-2eV.

Absorption and excitation of C<sub>60</sub> molecules above the photoconductivity edge might induce localized electronic states that generated e/h pairs. Subsequent motion of the carriers might happen in narrow conduction states by hopping from site to site. Consistent with this prediction are the results obtained at high temperature regime. The photocurrent is thermally activated with the same energy activation for all wavelength. On one hand this result shows that excitation process generates e/h that requires thermal and electric energies to create free carriers. On the other hand the excited molecules decay to the same localized electronic states irrespective of the excitation energy. At low temperature the photoconductivity is limited by the transport process rather than photogeneration mechanism. At high temperature transport mechanism as well as carrier photogeneration is thermally activated whereas at low temperature it is mainly governed by hopping transport process. This result is consistent with the estimated

mobility  $\mu_e=10^{-3}$ ,  $\mu_p=10^{-5}\text{cm}^2(\text{Vsec})^{-1}$  [15] and carrier mobility  $\mu_e\tau_e=10^{-7}$ ,  $\mu_p\tau_p=10^{-9}\text{cm}^2\text{V}^{-1}$  [3].

Oxygen effect on the photoconductivity and conductivity can be explained by assuming that oxygen diffuses in the octahedral interstitial sites of the fcc lattice of C<sub>60</sub> [16]. Oxygen acts both on photogeneration and transport properties as reflected by  $\sigma_{ph}$  and  $\sigma_d$ . A common feature is if electrons as major carriers are easily captured and recombined in energetically deep trap at oxygen site, the carrier density, the free lifetime and drift mobility would decrease then both conductivity and photoconductivity might also decrease. As the recombination mechanism is more efficient, the photoconductivity response time

is shorter, well in agreement with the experimental result. In addition, as reported above oxygen does not alter or creates new electronic states but rather might acts on the photogeneration process at the stage where the excited state needs to react with an electron donor before the formation of the e/h pair. Effect of oxygen on the activation energy at high temperature regime is weak. However at low temperature regime further consideration and experimental investigations are necessary.

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