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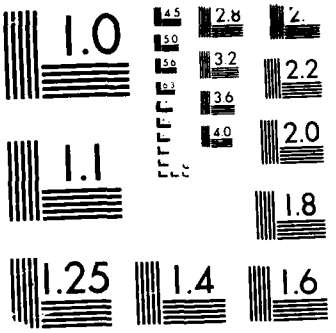

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Photoconductivity has been observed in vapor grown graphite fibers with a high quantum efficiency of carriers generated by photons. The photocurrent varies approximately as the square root of the intensity of illumination. No change in the growth or decay time of the photocurrent is observed as a function of illumination intensity or of the temperature. The photocurrent observed in semi-metallic graphite fibers is attributed to transitions between localized defect states which act as traps for photo-excited carriers. As the heat treatment temperature is raised above 1500 Kelvin, vapor grown graphite fibers show a decrease in the photocurrent due to the annealing of defects and an increase in the electron-hole recombination time.

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Photoconductivity in Carbon Fibers

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Abstract

Photoconductivity has been observed in conducting vapor grown carbon fibers. The photocurrent varies approximately as $I^{\frac{1}{2}}$ where I is the intensity of illumination and shows a quantum efficiency, E_Q, of ~ 1 carrier/photon. No change in the growth or decay times of the photocurrent is observed as a function of temperature, T, or I. The photocurrent is attributed to transitions between near–surface localized defect states which act as traps for photoexcited carriers. As the heat treatment temperature, T_{HT}, is raised above 1500K, vapor grown carbon fibers show a decrease in the photocurrent due to the annealing of defects. Some of these localized defect states can be passivated by gas adsorption at the graphite fiber surface.

Introduction

Previous observations of photoconductivity have primarily been confined to semiconductors and insulators where large illumination–induced changes in the carrier concentration are observed. The discovery of photoconductivity in carbon fibers is noteworthy as an example where the absorption of light by an electrical conductor significantly changes the electrical transport properties of the material.

Measurements of the photocurrent in vapor grown carbon fibers are reported as a function of the illumination intensity I. for heat treatment temperatures $T_{HT} \leq 3000$K. Measurements have also been made of the temperature dependence of the photocurrent and the growth and decay time of the photocurrent. The results suggest that the observed photocurrent in carbon fibers is directly related to hopping conduction between shallow localized defect states. The trapping of carriers by deep defect states provides an alternate decay mechanism to phonon scattering where the trapped carriers may contribute to enhancements of the electrical conductivity of the graphite fiber on a time scale considerably longer than the phonon scattering time. Since the photoconductance in carbon fibers is sensitive to the defect states, the measurement of the photoconductance may have potential uses as a non–destructive characterization technique for carbon fibers.

Experimental Overview

The photoconductivity measurements in this work have been done with vapor grown carbon fibers[1]. Fiber diameters ranged from 8 to 12μm. The transport properties of the fibers are dependent upon the heat treatment temperature, T_{HT}. The transport parameters of the fibers used in this work are given in table 1. The fibers were mounted on a mica substrate and connected to electrical leads in a four point probe configuration. The electrical leads were attached to the fiber by means of Epo–tek H20E silver epoxy and cured at 373K.

The illumination source was an Ar^+ laser operated at several wavelengths in the range $4550 \leq \lambda \leq 5145$Å and in the intensity range $6 \leq I \leq 200$mW. The maximum power density at the surface was 500W/cm^2. The laser was directed through focusing optics and a glass window in a dewar containing the electrical assembly. The beam was focused to a spot size $\sim 200\mu$m on the fiber

surface.

An electric field was applied to the fiber using a 1.5V battery connected in series with the fiber and a 100kΩ potentiometer. The dark current (no illumination) in the fiber was varied from 10 to 200μA to produce potential drops up to 300mV between the fiber electrodes.

Preliminary results indicated that the adsorption of air or He gas on the graphite fiber surface decreases the photocurrent by an order of magnitude. The adsorption of gas on graphite fiber surfaces is well known[2] and the decrease of the photocurrent due to gas adsorption at the surface of a photoconductor has been reported previously[3]. To eliminate this surface effect, all measurements were conducted on samples mounted in a dewar in a vacuum of 10^{-5} Torr.

The photocurrent was measured using a Tektronix differential amplifier and 4904A oscilloscope. The growth and the decay times of the photocurrent were also measured as a function of temperature T and illumination intensity I using the same experimental arrangement. For low temperature measurements, a nichrome–gold thermocouple was used with the temperature being displayed by an Air Products temperature controller.

Experimental Results

The measured photocurrent, i, versus the illumination intensity, I, for an as-grown graphite fiber with the illumination source at $\lambda = 4880$Å is presented as a log–log plot in Fig. 1. The figure also contains a fit of the photocurrent data with a line representing an $i = AI^{\frac{1}{2}}$ relationship between the photocurrent and the illumination intensity. This relation is characteristic of a photoconduction mechanism due to traps lying near the Fermi level[3]. This can easily be seen by balancing the photo–carrier generation rate with the recombination rate of decaying carriers

$$f = (n_0 + \Delta n)\nu SN \tag{1}$$

where f is the photo–carrier generation rate, n_0 is the intrinsic carrier density, Δn is the photocarrier density, S is the capture cross–section and N is the recombination center number density. For carbon fibers $\Delta n \gg n_0$ since the intrinsic carrier density in carbon fibers is less than 10^{19}cm^{-3}. Since most of the recombination centers will then be holes left by excited electrons, $N \sim \Delta n$.

Rearranging terms, we have

$$\Delta n = \left(\frac{f}{\nu S}\right)^{\frac{1}{2}} \tag{2}$$

which is the experimentally observed relationship for carbon fibers.

Measurements of the growth and decay time of the photocurrent as functions of both fiber temperature T and I show that the growth and decay times are independent of the fiber temperature and illumination intensity as T and I are varied over the range $10 \leq T \leq 300$K for intensities in the range $0 \leq I \leq 200$mW. The growth and decay times of the photocurrent are 50 and 100msec, respectively.

A sharp decrease in the photo-enhanced conductivity is found when T_{HT} is raised above 1500K (see Fig. 2). The decrease in photo-enhanced conductivity is correlated with the increase in the in-plane coherence length of the graphite fiber, L_a, from heat treatment. As T_{HT} is raised above 1500K, defects are expelled, decreasing the density of localized states, reducing the density of traps, and consequently reducing the photogenerated enhancement to the conductivity.

Discussion

To identify the mechanism by which photoconductivity occurs in graphite fibers, several possibilities were considered. Thermal carrier generation by a laser heating mechanism was ruled out for the following reasons: (1) The growth and decay of the observed photocurrent are independent of I. If the enhanced electrical conductivity were due to thermal effects, then a larger I should decrease the growth time due to an increased heating rate. There should also be a corresponding increase in the decay time of the electrical conductivity enhancement since more heat must be transported away from the illuminated region. Changes in both the growth and decay times should clearly be seen since I was varied by more than an order of magnitude in these experiments. Experimentally, the rise and fall times of the photocurrent are intensity independent. (2) For a train of illumination pulses, the conductivity enhancement maintains a characteristic "sawtooth" shape. If thermal effects were dominant, illumination pulse widths much smaller than the rise and fall times (e.g. $\leq$ 1msec) should make the changes in the electrical conductivity smoothly varying, contrary to

observations. (3) The behavior of the photo–enhanced electrical properties in carbon fibers is consistent with previously reported observations of photoconductance in evaporated carbon films[7]. The magnitude of both the rise and fall times for the photocurrent as functions of illumination intensity and temperature as well as the $I^{\frac{1}{2}}$ response of the photocurrent to illumination intensity are found for both carbon fibers and evaporated carbon films[7].

Previous measurements of the temperature dependence of the conductivity in vapor grown carbon fibers[5,8] have shown that in the low heat treatment temperature range ($T_{HT} < 1800$ K), the electrical conductivity is due to an activated or hopping process. It is only for the highest heat treatment temperatures ($T_{HT} > 3000$ K) that band conductivity is observed.

The hopping conductivity given by[10]

$$\sigma = Ne\mu = Ne^2\nu \exp(-E_a/kT) \tag{3}$$

where N is the density of active carriers, ν is the attempt frequency and E_a is the activation energy. Of these factors, it is the density of hopping carriers that is most sensitive to the optical absorption. The incident photons produce electron–hole pairs with unit quantum efficiency. The photon energies used suggest that most of the carriers are excited to band states far from the Fermi level E_F, indicated in Fig. 3a for two–dimensional graphite bands. These excited carriers quickly (< 1 picosecond) relax, via the electron–phonon interaction, to available states near the Fermi level. Here they can either rapidly recombine and give a negligible contribution to the photocurrent, or alternatively, the electron and hole can be separately trapped into the relatively large localized density of states indicated in Fig. 3a. The continuous distribution of the localized states is suggested by the temperature insensitivity of the photocurrent. The trapping retards recombination, so that either the electron or hole can be transported to the appropriate collection electrode before recombination and photoconductivity is observed. When the fibers are heat treated, the localized density of states decreases so that the density of conduction hopping states decreases. In the limit of high heat treatment temperatures ($T_{HT} \sim 3000$ K) the density of states becomes 3-dimensional as indicated in Fig. 3b. In this limit, one would not expect any significant photoconductance because of the rapid electron-hole recombination through band states[8,9].

The difference in the growth and decay times for the photocurrent may be understood in terms of the increased phonon scattering rate of the highly excited carriers during illumination, while the decay process only involves the

emptying of filled trap states. The insensitivity of the rise and fall times to external conditions is most likely due to photon energies which are much larger than the energy changes associated with carrier recombination processes.

Conclusions

The observed photo-enhanced electrical conductivity in vapor grown carbon fibers has been shown to be a photoconduction effect. The graphite fiber photocurrent increases as $I^{\frac{1}{2}}$ and has a growth and decay time insensitive to variations of T and I. The photoconductivity observed in carbon fibers is similar to the photoconductivity effect previously reported in evaporated carbon films[7]. The photoconduction in vapor grown carbon fibers is attributed to the activation of localized defect states by populating them with photoexcited carriers. The enhancement in the electrical conductivity comes directly from increased hopping among the defect states.

Photo-enhanced conductivity has also been observed in PAN[11] and pitch[12] based carbon fibers, but has not been studied in detail. Apart from the scientific significance of finding photoconductivity in a system which is intrinsically semi-metallic, photoconductivity measurements may provide a simple, nondestructive technique for the study of defects in carbon fibers.

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Figure Captions

Fig. 1: Log–log plot of the induced photocurrent, i, versus the the illumination intensity, I. The wavelength used was 4880Å. Note the good fit of a line of slope 0.5 to the experimental points showing the $i = AI^{\frac{1}{2}}$ relationship.

Fig. 2: Dependence of the photocurrent on heat treatment temperature for an incident power density of $\sim 40\mathrm{W/cm^2}$ with the Ar^+ laser source at 4880Å. Correlation between the in–plane coherence length, L_a, in graphite fibers with the photocurrent. Note the strong correlation between the photocurrent and the onset of long range two dimensional order in graphite through the temperature range 1000K to 2000K.

Fig. 3: Proposed density of states diagram for photoconductivity in vapor grown carbon fibers. Both band states and localized states are shown separately. In *a*) the density of states for an as–grown carbon fiber show two dimensional band states and a high density of localized states while *b*) presents the density of states for heat treated vapor grown carbon fibers showing the band overlap characteristic of graphite and a reduced localized density of states. The reduction in the density of localized states is due to the reduction of defects through heat treatment.

Table 1: Transport parameters as a function of heat treatment temperature, T_{HT}.

T_{HT} (K)	$\rho_{dark}(\Omega-\text{cm})$ $T = 300\text{K}$	$\mu_{dark}(\text{cm}^2/\text{V-s})$ $T = 4\text{K}$	$\mu_{dark}(\text{cm}^2/\text{V-s})$ $T = 300\text{K}$
as grown	9.3×10^{-4}	≤ 10	≤ 10
1000	7.9×10^{-4}	–	≤ 10
1500	5.1×10^{-4}	7.1×10^{3}	–
2000	2.3×10^{-4}	1.1×10^{4}	1.8×10^{2}
3000	9.9×10^{-5}	2.0×10^{4}	1.8×10^{2}

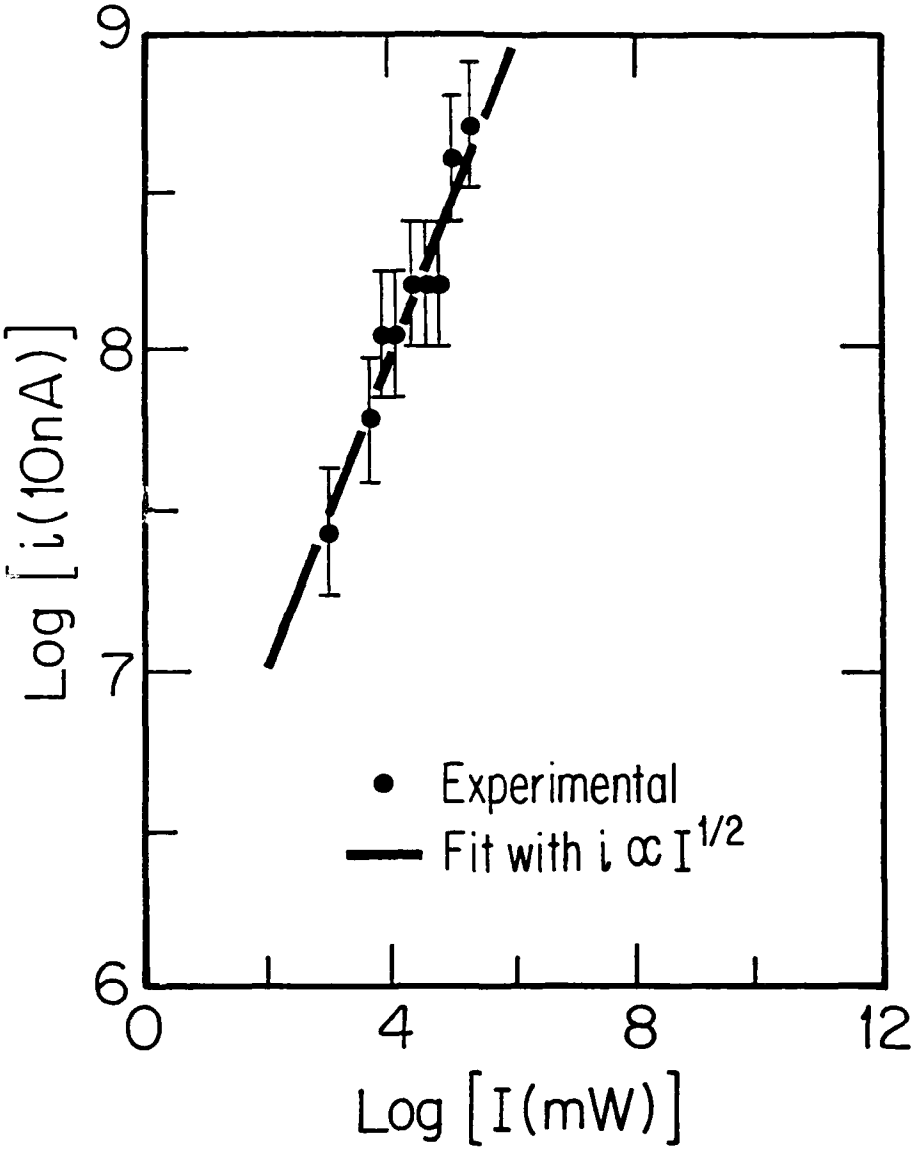
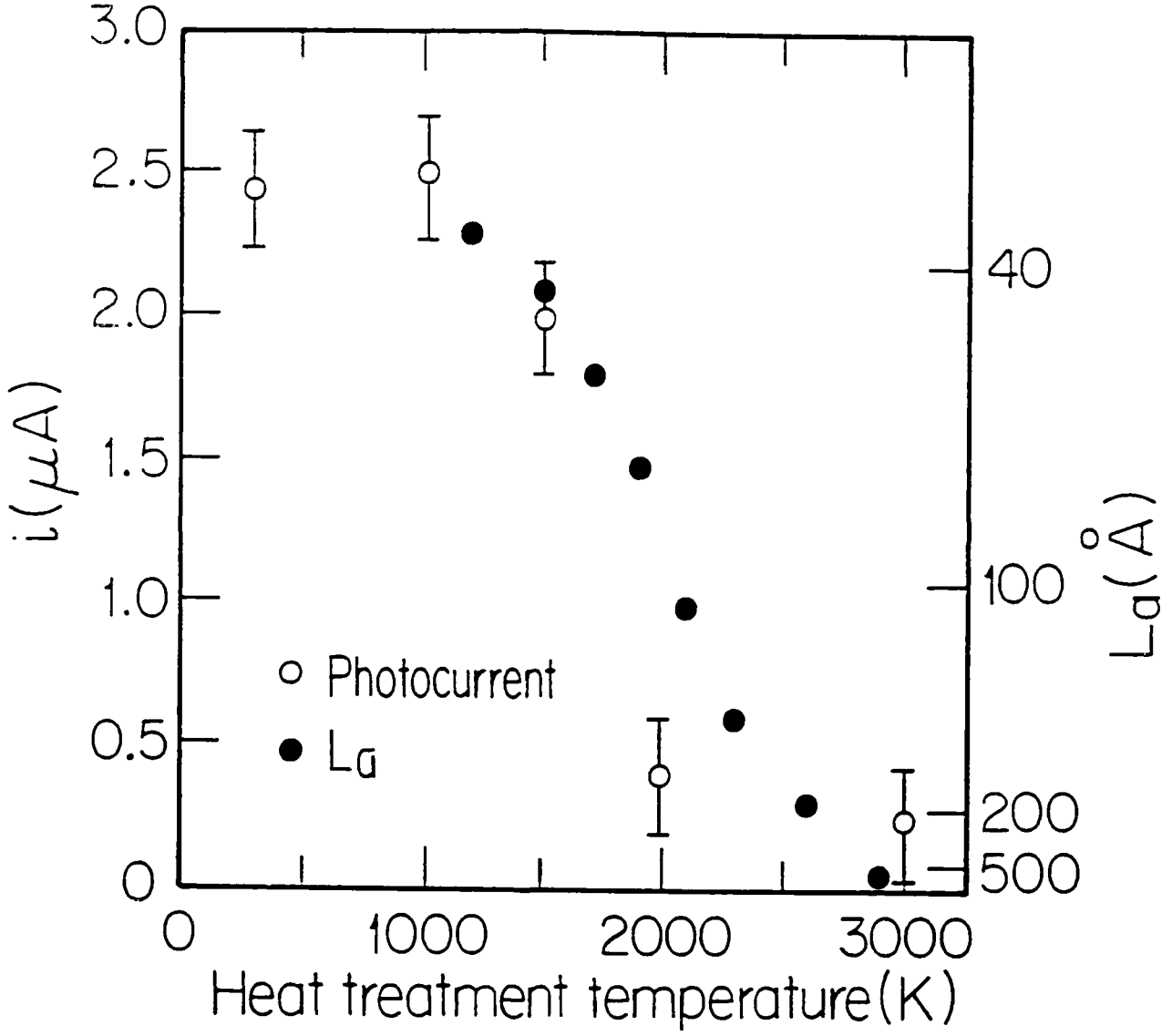


Fig 1


3.0
2.5
2.0
1.5
1.0
0.5
0
i(μA)
40
100
200
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La(Å)
Photocurrent
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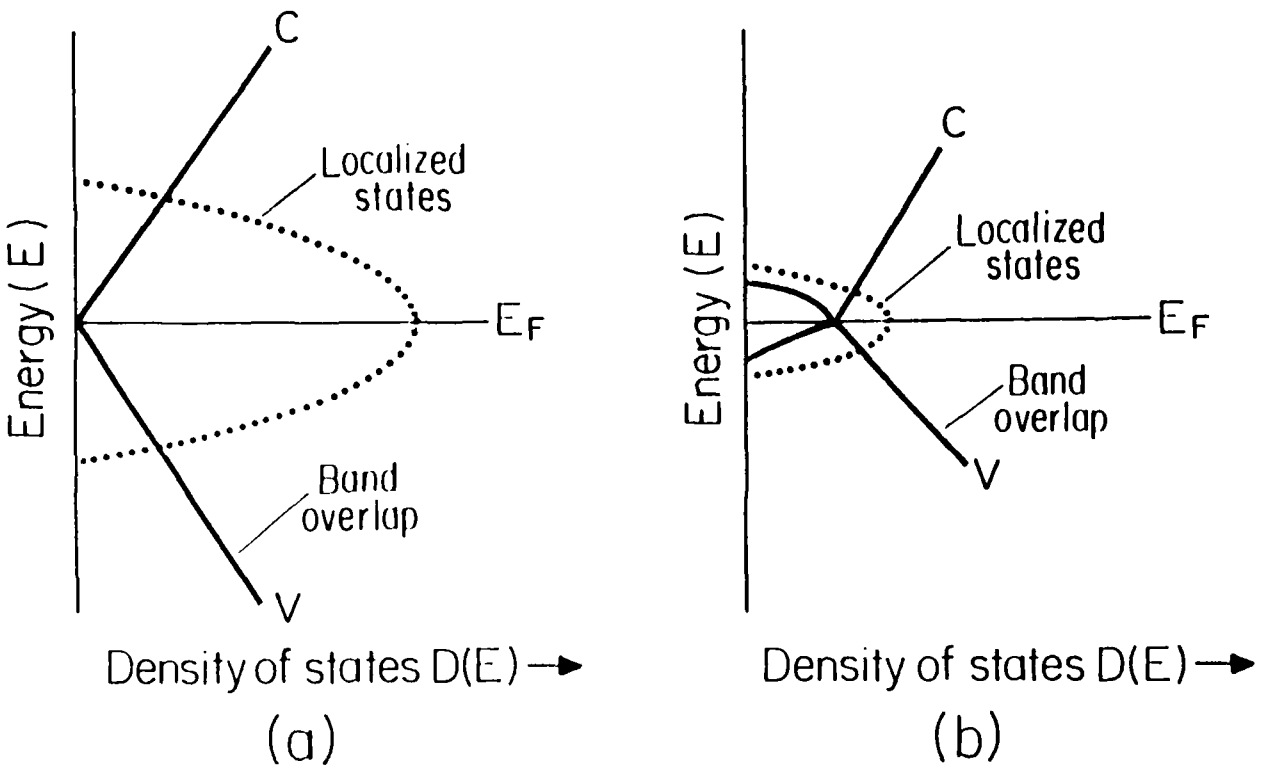
0
1000
2000
3000
Heat treatment temperature(K)

Fig 2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Localized states
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Energy (E)
Band overlap
V
Density of states D(E) →
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C
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E_F
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