Long-decay-time photoconductivity in highly disordered carbon fibers

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A photoconductivity with a rather long decay time ($\simeq 0.3$ s at 290 K) is observed in a carbon material that is characterized by its huge specific surface area (1000 m^2/g). The decay time is temperature dependent at low temperatures (<100 K) with a small activation energy (3–5 meV), and is also dependent on the illumination power. A decrease in the mobility of the carriers during the illumination is strongly suggested. The relaxation of dangling bonds on the large surface area is proposed as the mechanism to screen the Coulomb attraction among the photocarriers and to build a recombination barrier, resulting in the long decay time. This photoconductivity is considered to be an effect analogous to the persistent photoconductivity in semiconductors, although some apparent differences are also observed.

I. INTRODUCTION

A photoinduced excess conductivity with an anomalously long decay time, called persistent photoconductivity (PPC), has been observed in GaAs,[1–4] a-Si:H,[5–10] and other semiconductors.[11,12] The main feature of this phenomenon is the long (seconds to weeks) decay time of the photoconductivity even at room temperature. Although the mechanism for the PPC has not been decided, it is evident that the recombination of the induced photocarriers is for some reason prevented. If the key mechanism for this effect is a coupling of the electrons to the lattice,[1,2,9,10] this effect should be universal in materials with flexible microstructures.

The long decay time of the photoconductivity in disordered carbons was first reported nearly 40 years ago. McMichael, Kmetko, and Mrozowski[13] investigated cellophane films as an infrared detector and observed a rather long decay time (50 ms) for the photoconductivity. A similar magnitude of the decay time (100 ms) was observed for vapor-grown carbon fibers[14] and an even longer decay time (several seconds) was observed for evaporated carbon films.[15] We previously measured the photoconductivity for highly disordered carbon fibers (activated carbon fibers) and reported the decay time of about 0.3 s at room temperature.[16] Although the magnitude of these decay times in carbon-based materials is smaller than reported values for other materials, it must be noted that the decay times for the disordered carbons are surprisingly long for materials with defects that usually behave as recombination centers and make the photocarrier lifetime remarkably short.

It seems, however, that nobody has discussed this long decay time of the photoconductivity in carbon-based materials in connection with the PPC. Obviously, defects in the carbon materials operate differently from usual recombination centers. In fact, defects are necessary to observe the photoconductivity in carbon materials in the first place because the photoconductivity decreases with the increased ordering of the structure[17] and is totally absent in single-crystal graphite. The defects in disordered carbons are believed to be mainly dangling bonds. At least 10^{19}/g, more than that in a-Si:H,[18,19] is expected from electron-spin-resonance (ESR) measurements in carbon materials.[20–23] These analogies to a-Si:H in terms of the long decay time and the microstructure should be kept in mind in discussing the photoconductivity in disordered carbon materials.

In this paper, we show that a long decay time for the photoconductivity is observed even in carbon materials. Activated carbon fibers (ACF) characterized by their huge specific surface area (SSA) are used to observe the effect. The dependences of the decay time on temperature and on the illumination power, and the recombination kinetics are investigated. The results show that the decay time is thermally activated as in other materials. From the recombination kinetics and the magnitude of the photoconductivity relative to the dark conductivity, the carrier mobility is found to decrease during the illumination. Despite the analogies to other materials, there exist some distinctive differences. For example, the induced photocarriers are supposed to exist in localized states. No built-in electric field is probable in the ACF, taking into account the rather high conductivity (1–10 S/cm at 290 K). Finally, we propose a relaxation of dangling bonds as the mechanism for the long decay time of the photoconductivity in disordered carbon materials.

II. EXPERIMENTAL DETAILS

The detailed properties of the ACFs were reported elsewhere.[16] The ACF used in this study are derived from cellulose, polyacryonitrile (PAN), and phenol and contain some H ($<1\%$) and O (2–9 %). All fibers in this study have the same nominal SSA, 1000 m^2/g. The structure is rather amorphouslike with the c-axis crystallite size $L_c \simeq 11$ Å and the in-plane crystallite size $L_a \simeq 25$ Å.[17] The room-temperature conductivity is 1–10 S/cm for all the ACF. In general, one important feature of disordered carbons is their high density of localized spins,[20–24] usually more than 10^{19}/g. The g factor of disordered carbons is very close to that of free electrons. Although de-

tailed ESR properties are still under investigation for the ACF,[24] the magnetic susceptibility follows Curie's law in the temperature range from 4 to 300 K and a high density of dangling bonds is expected to exist in the ACF at room temperature.

The photoconductivity is measured in the temperature range 30–290 K under an Ar^{+} laser (0.488 nm, 10 mW/cm^{2}) illumination in vacuum (10^{-3} Torr). The laser illumination is continued for a few seconds until a steady photocurrent is obtained. Unlike the case of a-Si:H or GaAs, the fast decay of the photoconductivity preceding the PPC is not observed for the ACF when the light is turned off. Thus note that the photoconductivity in this study is well defined as the steady-state excess conductivity during the illumination over the dark conductivity. To determine the recombination kinetics, the dependence of the photoconductivity on the laser power is measured at 40 and 290 K, by changing the incident laser power from 1 to 40 mW/cm^{2}. The temperature dependence of the decay time is also measured in the above temperature range and its dependence on the laser power is measured at 40 and 290 K.

III. RESULTS AND DISCUSSION

The absence of the fast decay preceding the PPC is one difference from a-Si:H and GaAs where the initial fast decay is understood to be a fast recombination among the photocarriers in extended states. Our result gives no evidence for extended states in the ACF, though they may exist.

The temperature dependence of the photoconductivity is shown in Fig. 1, where the photoconductivity $\Delta\sigma(T)$ is normalized to the room-temperature value $\Delta\sigma$ (290 K). Starting at 30 K, the photoconductivity first increases with increasing temperature, but beyond $\simeq 100$ K it decreases. This decrease in $\Delta\sigma(T)$ above $\simeq 100$ K can be attributed to a decrease in the photocarrier density due to the fast recombination of the photocarriers with thermal-
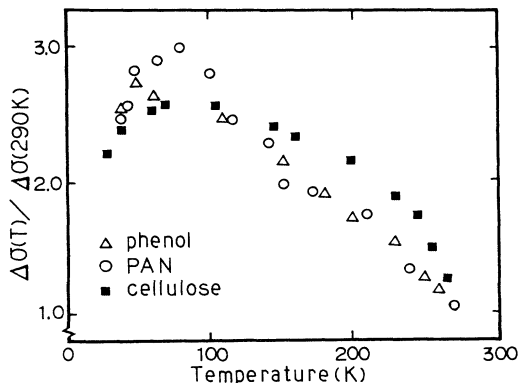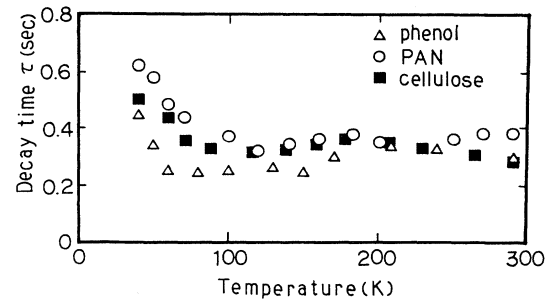

FIG. 2. The temperature dependence of the decay time in the ACF. At low temperatures, the decay time is activated (see Fig. 3).

ly activated dark carriers. On the other hand, the increase in $\Delta\sigma(T)$ with increasing temperature below $\simeq 100$ K implies that the photocarriers are in localized states and that their mobility is thermally activated. This is consistent with the thermally activated decay time shown in Fig. 2. At low temperatures, the decay time decreases with increasing temperature. The associated activation energy is estimated to be in the range 3–5 meV from Fig. 3, where the decay time is plotted versus $1/T$. This activated and rather long decay time for the ACF is one similarity to the decay-time behavior for the PPC in other materials, although the magnitudes of the decay time and of the activation energy are much smaller than reported values for a-Si:H [e.g., where the decay time is seconds to weeks and the activation energy is 0.2–0.5 eV (Refs. 5, 9, and 25)]. This activation energy can be regarded as the barrier height for the recombination as well as the barrier height for the hopping conduction since this barrier must be overcome by the hopping photocarriers both for the conduction and the recombination.

FIG. 1. The temperature dependence of the photoconductivity for phenol, PAN, and cellulose derived ACT with SSA of 1000 m[2]/g.
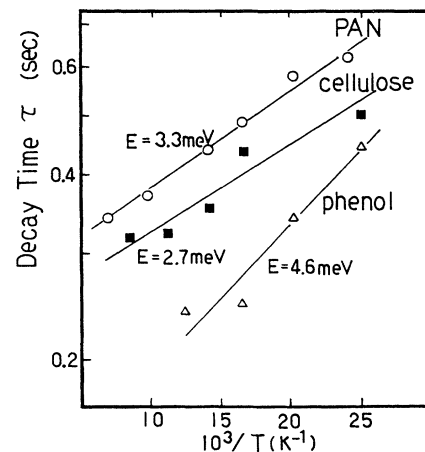

FIG. 3. The activation energy of the decay time in the ACF. The values of the activation energy E are rather small.

Another interesting feature of the decay time is its dependence on the illumination power, as shown in Fig. 4. Usually, an increase in the illumination power leads to a faster recombination because the distance between the photocarriers becomes shorter due to their enhanced population. The implication of the increased decay time in Fig. 4 with increasing illumination power is probably that the barrier height for the recombination and the mobility increases with increasing photocarrier population. It follows that the mobility decreases with increasing illumination power. The above result indicates that the charge separation mechanism,[6,26] one proposed mechanism for the PPC, is unlikely in the AFC since it yields a shorter decay time with higher illumination power that reduces the built-in fields. In terms of the mechanism of the long decay time, although a structural relaxation involving motion of hydrogen is pointed out,[27-29] the hydrogen concentration in the ACF is far smaller than that in a-Si:H.

The decrease in the mobility can also be inferred from the recombination kinetics. Information on the recombination kinetics is provided in Fig. 5 showing a log-log plot of the photoconductivity versus the illumination power, with the gradients of the curves indicated in the figure. Before discussing the decreased mobility, the relation between the kinetics and the density of photocarriers is clarified.

The value of 0.5 for the gradient in Fig. 5 implies a bimolecular recombination process, while the value of 1.0 for the gradient implies a monomolecular recombination process. Monomolecular recombination is generally observed when the density of photocarriers is much smaller than that of the dark carriers.[30] In Fig. 5, monomolecular recombination is observed at 290 K (denoted by the solid line) and this result is consistent with Fig. 6, where the magnitude of the photoconductivity is shown to be a few percent of the corresponding dark conductivity. In contrast, at low temperatures the slow recombination re-
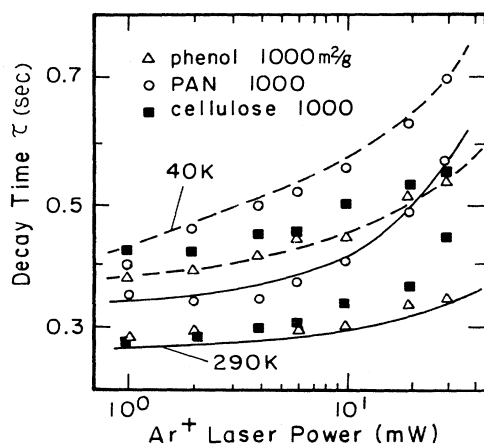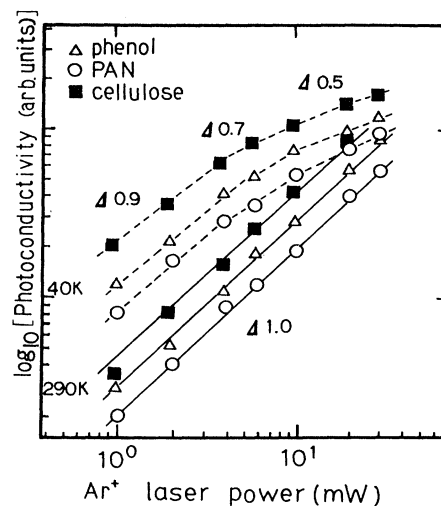

FIG. 5. The recombination kinetics of the photoconductivity in the ACF.

stricted by the energy barrier results in a high photocarrier density. When the photocarrier density is high enough to neglect the dark carrier density, the recombination takes place among the photocarriers independently of the dark carrier density. Thus the bimolecular recombination process appears at 40 K (denoted by the dotted line) and at high laser powers in Fig. 5. In other regimes, a mixture of the bimolecular and monomolecular recombination processes is observed.

Following the above description, a photoconductivity much higher than the corresponding dark conductivity must be observed in the bimolecular regime where the photocarrier density is dominant over the dark carrier density. However, the magnitude of the photoconductivity at low temperatures where the bimolecular process

FIG. 4. The dependence of the decay time on the illumination power.
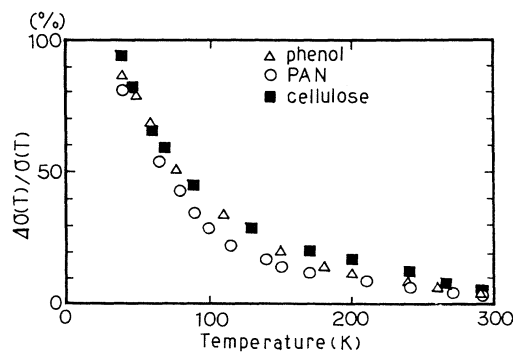

FIG. 6. The magnitude of the photoconductivity relative to the corresponding dark conductivity. Note that the photoconductivity is at best comparable to the dark conductivity even at low temperatures where bimolecular recombination is observed in Fig. 5.

is observed in Fig. 5 is at most comparable to that of the dark conductivity, as shown in Fig. 6, where the photoconductivity is normalized against the dark conductivity. This discrepancy from the expected behavior can be explained by assuming a decrease in the mobility during the illumination. Thus, although the photocarrier density is dominant over the dark carrier density, the reduced mobility yields a photoconductivity smaller than expected. This explains both the bimolecular recombination at 40 K in Fig. 5 and the magnitude of the photoconductivity smaller than expected at low temperatures in Fig. 6.

Note that our photoconductivity is not likely caused by a heating effect. Otherwise, the photoconductivity in Fig. 1 would show a monotonic increase with decreasing temperature. A heating effect, however, may contribute to the photoconductivity to some extent.

We propose a polaronic state of the photocarriers hopping between the dangling bonds on the surface. The hopping yields charged dangling bonds but they are screened by the surrounding bond relaxations facilitated by the flexible surface microstructure of the ACF. The screened photocarriers behave like neutral particles and their recombination is thus remarkably reduced. For example, the capture cross section of recombination centers is known to decrease by several orders of magnitude when the recombination centers change from being Coulomb attractive to neutral.[31] Then the lifetime of the photocarriers is prolonged by the same magnitude. Therefore our model is that the screened photocarriers hop between the dangling bonds on the surface of the ACF. Moreover, the thermally activated hopping motion of the photocarriers should also contribute to the long decay time since their motion is quite limited compared to

that of free carriers. In short, our polaron model can account for the long decay time based on the decrease in the capture cross section and on the limited motion of the carriers during the recombination. This mechanism may be applied to the photoconductivity in other disordered carbons because the high density of localized spins is one of the universal features in highly disordered carbons.

IV. CONCLUSIONS

We have described the long decay time of the photoconductivity in highly disordered carbon fibers (ACF). In analogy to the behavior in inhomogeneous semiconductors where the PPC is observed, the defects in carbon-based materials do not operate as recombination centers but are necessary structures to yield the long decay time of the photoconductivity. A decrease in the carrier mobility in the ACF by illumination is strongly suggested. The thermally activated decay time indicates the existence of an energy barrier for the recombination. To explain the long decay time, a relaxation of the dangling bonds screening the Coulomb attraction between the photoelectrons and photoholes is proposed. The hopping motion of the photocarriers is also considered to contribute to the long lifetime of the photocarriers. This mechanism is consistent with a high density of localized spins in disordered carbon materials.

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