Multiphonon Tunneling Conduction of Localized π Electrons in Amorphous Carbon Films

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The temperature dependence of the dc conductivity has been measured on sputtered amorphous carbon films. The conductivity is proportional to T^n with $n=15$–17 over a wide temperature range, suggesting for the first time that the multiphonon tunneling transition with weak electron-lattice coupling of localized π electrons is a probable mechanism for charge transport. This may be attributed to the delocalized nature of the π defect in amorphous carbon.

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It is believed that amorphous carbon (a-C) prepared by evaporation or sputtering is predominantly sp^2 bonded with an optical gap of 0.4–0.7 eV.[1-4] At a carbon sp^2 site, there are three strong σ bonds and one weak π bond lying normal to the σ bonding plane. The π states will form both valence- and conduction-band states.[3,4] The π defects (breaking π bonds) may have a lower creation energy than the σ defects and hence predominate in the gap states lying close to the Fermi level E_F.[3,4] These localized states may form a continuous distribution across the gap, and electronic conduction by variable-range hopping ($\ln\sigma_{dc} \propto T^{-1/4}$)[5,6] is anticipated to occur in a-C in the same manner as in tetrahedral a-Ge and a-Si.[7] Several authors[1,8-10] have reported that, in a-C films, variable-range hopping (VRH) dominates dc conduction at lower temperatures. However, the quality of the fitting seems to be poor for the complete temperature region measured. It is not clear whether or not the hopping of electrons between π defects is dominated by the single-phonon process as expected in impurity conduction.[11]

In this Letter, we examine the dc conductivity for sputtered a-C films. The conductivity is found to be well described by $\sigma_{dc}=\sigma_0(T/T_0)^n$ with $n=15$–17 for both the as-deposited and the annealed films. The origin of this temperature dependence is discussed in terms of the multiphonon tunneling of localized π electrons.

Thin films of a-C were prepared on Corning 7059 glass substrates with a bottom Au electrode by rf (13.56 MHz) sputtering of a 60-mm (diameter) graphite target (99.999%) in argon gas (0.18 Torr). The forward power applied to the target was 100 W and the substrate temperature was 20 °C. The deposition rate under these conditions is approximately 0.6 Å/s. Front contacts were made by thermal evaporation of Au.

The temperature dependence of the dc conductivities for as-deposited (Fig. 1, curve a) and annealed (Fig. 1, curve b) a-C films (0.6 μm) is shown by the open circles in Fig. 1. The data are plotted against $T^{-1/4}$. The conductivities are several orders smaller than those from the other reports.[1,8-10]. Annealing (400 °C, 1 h) results in an increase in σ_{dc}, as found by several authors.[8-10] The experimental data cannot be described by a single straight line. The fits to the data at higher temperatures are shown by the solid lines and those at lower temperatures are shown by the dashed lines. It is hard to distinguish from the figure which line (solid or dashed) correctly describes the behavior.

The variable-range hopping (VRH) theory predicts the temperature dependence of σ_{dc} for three-dimensional materials as[5]

$$\ln\sigma_{dc}=A-BT^{-1/4}, \quad (1)$$

where A and B are constants. While the theory reproduces many experimental features, particularly for σ-defect amorphous Ge and Si, some difficulties exist: The most serious is the discrepancy, by many orders of mag-

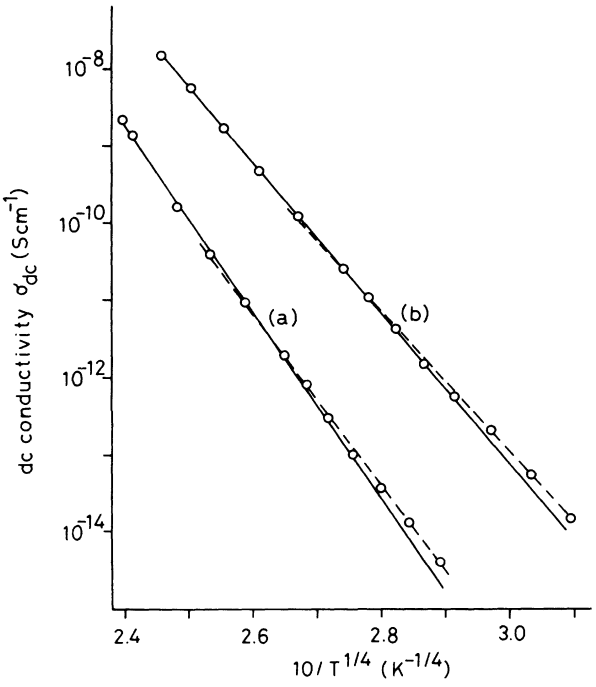

FIG. 1. Temperature dependence of dc conductivities for (curve a) as-deposited and (curve b) annealed (400 °C, 1 h) a-C films. The temperature scale is $T^{-1/4}$. The solid lines are high-temperature fits with the VRH theory and the dashed lines are low-temperature fits.

nitude, between experimental and theoretical values of the constant A.[12,13] The parameter B is used by many authors (see Refs. 12 and 13) to estimate the density of states $N(E_F)$. On the other hand, Pramanik and Islam[12] have pointed out that $N(E_F)$ estimated from the parameter A is a much more reasonable quantity. Note that discrepancies still remain. In spite of this, however, $N(E_F)$ can be estimated for our carbon films using Eq. (1). $N(E_F)$ here is estimated from $16\alpha^3/kB^4$, where α^{-1} is the Bohr radius of localized electrons and k the Boltzmann constant. With the assumption of $\alpha^{-1}=10$ Å, which seems to be smaller than the practical value in a-C because of its weak localization, $N(E_F)$ for the high-temperature fits (solid lines) is estimated to be 3×10^{16} and 7×10^{16} cm^{-3} eV^{-1} for as-deposited ($B=274$ K$^{1/4}$) and annealed ($B=224$ K$^{1/4}$) films. $N(E_F)$ for the low-temperature fits (dashed lines) is estimated to be 4×10^{16} and 1×10^{17} cm^{-3} eV^{-1} for as-deposited ($B=251$ K$^{1/4}$) and annealed ($B=204$ K$^{1/4}$) films. These values, perhaps upper limits, seem to be very much smaller than those ($1\times10^{18\text{-}20}$ cm^{-3} eV^{-1}) estimated from the VRH theory[7,12] for a-Ge and a-Si. The density of π defects could be much higher than that of σ defects.[3,4] It is hence suspected that the observed unactivated behavior cannot be explained by the VRH theory.

The same data (Fig. 1) are replotted on a logarithmic T scale and shown in Fig. 2. Data for as-deposited (Fig. 2, curve a) and for annealed (Fig. 2, curve b) films are fitted well by the straight lines for all measured temperatures, suggesting that the logarithmic T scale is better than a $T^{1/4}$ plot. This shows σ_{dc} is proportional to T^n. The values of n are 17.4 for the as-deposited film and 15.1 for the annealed one. Note that almost the same value of dc conductivity was obtained for the coplanar configuration (gap separation $=40$ μm), suggesting that the films obtained are isotropic. Evaporated a-C, sometimes, showed that σ_{dc} was anisotropic, being lower along the film (coplanar) than through it (sandwich).[8] Note also that a similar temperature dependence, with $n\simeq14$, has been found in one-dimensional polyacetylene $(CH)_x$ for which electron hopping in a soliton band has been discussed.[14]

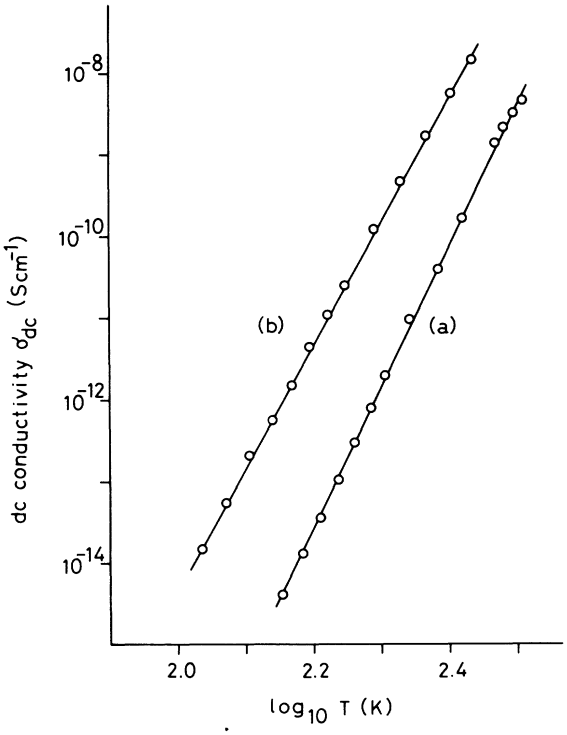

FIG. 2. Replotted (Fig. 1) temperature dependence of dc conductivities for (curve a) as-deposited and (curve b) annealed films in a-C. The temperature scale is $\log_{10}T$.

The dc hopping conductivity can generally be given by[7]

$$\sigma_{dc}=N(eR)^2\nu/6kT, \tag{2}$$

where N is the number of localized carriers, R is the hopping distance, and ν is the hopping rate. The single-phonon process (either nearest neighbor or variable-range hopping) is expected to occur when the site-energy difference Δ and the polarization energy (lattice deformation) are less than the maximum phonon energy $\hbar\omega_m$. However, when Δ is comparable with $\hbar\omega_m$ and the Bohr radius (α^{-1}) of localized electrons is much bigger than the lattice constant (a_0), the probability of single-phonon tunneling becomes very small.[7] Instead, the multiphonon process makes the major contribution to electronic conduction.[15]

The hopping rate due to a multiphonon tunneling of localized electrons with a weak electron-lattice interaction is given by[7,15,16]

$$\nu=C\exp(-\gamma p)\exp(-2aR)(T/T_0)^p, \tag{3}$$

where $C\simeq\omega_0/2\pi$, $p=\Delta/\hbar\omega_0$, and $T_0=\hbar\omega_0/k$. Here, $\hbar\omega_0/kT$ is required to be smaller than $\simeq0.1$. ω_0 is the frequency of the acoustic phonon which is most effectively coupled to localized electrons. The value of α^{-1} is expected to be much bigger than the average lattice separation (a_0) (weak localization of π defects). Since the large-radius localized electrons couple only to long-wavelength phonons,[17] ω_0 here is smaller than the maximum phonon (Debye) frequency ω_m and is given by $(a_0/\alpha^{-1})\omega_m$.[17] The parameter γ lies between 2 and 3 for the weak-coupling case.[7] As N must be $N(E_F)kT$, σ_{dc} is proportional to T^p. The value of p should be an integral number. However, if Δ or ω_0 is distributed around a certain value, p may have a finite distribution and its mean value will be nonintegral. Experimentally obtained p values are, in fact, nonintegral.

Rough estimates of the physical parameters which appear in Eqs. (2) and (3) should be made to check the validity of the present model. If we assume $N=1\times10^{18}$ cm^{-3}, which is derived from electron-spin resonance

(ESR) data,[3] then $R \simeq N^{-1/3} = 100$ Å. For the as-deposited film [$\sigma_{dc}(300\ K) = 2 \times 10^{-9}$ S cm^{-1}], the hopping rate $\nu \simeq 2000$ s^{-1} is obtained from Eq. (2), which seems very large for the multiphonon transition rate with weak electron-lattice coupling.[15] However, if we assume $\alpha^{-1} = 30$ Å (somewhat arbitrarily) and $T_0 = 10$ K ($\omega_0 = 1.3 \times 10^{12}$ s^{-1}), which is about an order smaller than the Debye temperature (390 K for graphite), and use $p = 17.4$, γ is estimated to be 4.1, which may satisfy the weak-coupling condition.[7,16]

σ_{dc} at 273 K for an annealed film is 1.5×10^{-8} S cm^{-1}. The same calculation using the same parameters (α, γ, T_0) gives $N = 2.5 \times 10^{18}$ cm^{-3}. The fractional increase in the carrier number [or $N(E_F)$] on annealing (400 °C) is very small. This is consistent with the ESR results[2,18] in which spin densities (10^{18}–10^{19} cm^{-3}) are relatively independent of annealing temperature. This is also consistent with the suggestion that the fraction of sp^2 clusters interconnected by sp^3 sites increases by annealing without significant change in the number of π defects.[3,4]

The small-polaron model (multiphonon process with a strong electron-lattice coupling)[15,17] is an interesting alternative model for interpreting transport in disordered materials. This model predicts a gradual weakening of the temperature dependence of conductivity as the temperature is lowered. However, as the π defect electrons in a-C cannot be severely localized,[3] the interaction with the lattice should be weak and hence the small polaron will not be formed in a-C. This argument will be elaborated on in a future publication.

Although it has not been shown that the empirical relation $\sigma_{dc} \propto T^n$ is definitely better than $\ln\sigma_{dc} \propto T^{-1/4}$, the multiphonon tunneling of localized π electrons (weak interaction with lattice) is a probable mechanism for a-C films. This may be attributed to the delocalized nature of the π defects. To obtain more detailed information, the measurement of the ac conductivity (σ_{ac}), from which can be deduced the jump rate, may be a useful technique and will be presented elsewhere.

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