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Short Communication

Hall effect in carbon nanotube thin films

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ABSTRACT

We have investigated Hall coefficient and magnetoresistance in thin films of single-walled carbon nanotubes, prepared in four different ways. Hall voltages are linear for all samples in magnetic fields up to 6 T, and the measured carrier density lies in $\sim 10^{21}$–10^{22} cm^{-3}. Whereas earlier Hall-effect experiments reported $\sim 10^{18}$–10^{19} cm^{-3} for the carrier density, our results are consistent with the theoretically predicted value of $\sim 10^{22}$ cm^{-3}, calculated for the aligned metallic CNTs. The signs of the Hall coefficients are positive in general, indicating that majority carriers are holes in these films. In a nanotube film with the lowest conductivity, however, we find the Hall coefficient reverses the sign at low temperature around $T = 15$ K. The origin of the sign change is not clear. In strongly localized regime, the Hall effect can be anomalous.

1. Introduction

Carbon nanotube (CNT) films and networks have been widely investigated for many applications, including flexible thin-film electronics, composite materials, and large-area coatings [1,2]. Whereas the carrier density of graphite is low with $\sim 10^{18}$ cm^{-3}, the carrier density of aligned metallic CNTs was predicted to be $\sim 10^{22}$–10^{23} cm^{-3} from the tight-binding model [3]. However, early Hall-effect experiments reported $\sim 10^{18}$–10^{19} cm^{-3} for the carrier density of a bundle [4] and films [5] of CNTs. The marked discrepancy between the theory and the experiments remained unclear. In this paper, we present Hall effect and magnetoresistance, measured in four differently prepared CNT films. With advances in CNT synthesis, purification and chemical modification, the measured carrier density exhibits $\sim 10^{22}$ cm^{-3}, consistent with the theoretical prediction.

2. Experimental

Experiments have been carried out on four different types of single-walled carbon nanotubes (SWNTs) prepared as films; purified SWNTs, synthesized either by high-pressure CO conversion process (denoted as HiPCO CNTs) or by laser ablation method (denoted as LA CNTs), and the HiPCO and the LA CNTs chemically treated by $SOCl_2$. CNT films were prepared by the filtration of the nanotube suspension in sodium dodecyl sulfate. The $SOCl_2$ treatment started from a suspension of SWNTs in $SOCl_2$. The suspension was stirred at 45 °C for 24 h and filtered and subsequently dried in air, as described in the literature [6]. Treatment by $SOCl_2$ improves tube alignment by the aggregation to thicker CNT bundles, and significantly increases conductivity by *p*-type doing of the pristine materials in addition to the tube alignment and enhanced tube overlap [6].

SWNT films were cut into rectangular bars, and Hall coefficient and magnetoresistance were measured by using standard five probe configuration in a Janis variable temperature cryogenic system for temperature down to $T = 1.4$ K. For the Hall measurements, magnetic field, H, was swept between −6 T and 6 T, and the Hall voltage at a certain $|H|$ was determined by taking the half of the difference between the values at positive and negative H.

3. Magnetoresistance of CNT films

Fig. 1 presents the temperature dependence of the conductivity, σ, measured in four different types of the CNT films. The $SOCl_2$-treated CNT films show overall higher conductivity compared to the pristine CNT films. At room temperature, the highest conductivity (710 S/cm) is observed in the $SOCl_2$-treated HiPCO

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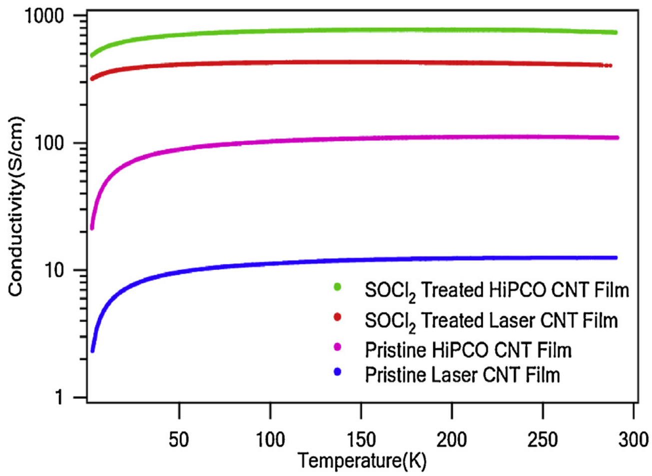

Fig. 1. Temperature dependence of the conductivity measured in four different types of CNT films. The temperature dependence of the conductivity is much weaker for the $SOCl_2$-treated CNT films.

film and the lowest (12 S/cm) in the pristine LA CNT film. The conductivities of the HiPCO films are larger than those of the LA CNT films irrespective of the $SOCl_2$-treatment. This could be due to the lower degree of disorder in the HiPCO CNTs, or the ratio of metallic to semiconducting CNTs might be lower in the LA CNT films. At low temperatures, the conductivity increases with temperature, exhibiting the semiconducting behavior, for all CNT films investigated. We observe a crossover to metallic behavior, i.e. decreasing conductivity with *T*, at higher temperatures above 150 K. The crossover temperature depends on the CNT samples. In addition, the temperature dependence of the conductivity is much weaker for the $SOCl_2$-treated CNT films. To compare conductivities at 290 K to at 2 K, we have $\sigma(290\,K)/\sigma(2\,K)$ of 1.5 and 1.27 for the $SOCl_2$-treated HiPCO and the $SOCl_2$-treated LA CNT film, respectively. The ratios are 4.77 and 5.4 for the pristine HiPCO and LA CNT film.

One can explain the temperature dependence of the conductivity by a heterogeneous model [7], which involves regions of highly conducting CNTs separated by barriers such as inter-tube junctions and intra-tube defects. At lower temperatures, the conduction through the barriers becomes dominant while metallic conduction at higher temperatures. The weak temperature dependence of the conductivity suggests less significance of the barriers in the $SOCl_2$-treated CNT films with improved tube alignment and enhanced tube overlap.

Turning our attention to the magnetoresistance (MR) of the CNT films, Fig. 2 displays the MR, measured in a magnetic field perpendicular to the pristine CNT films. The MR is defined as $[R(H) - R(0)]/R(0)$, where $R(0)$ is the zero-field resistance. For both the pristine HiPCO and LA CNT films, the MR's are negative at higher temperatures. However, positive term develops below 10 K and the MR's exhibit upturns at a certain magnetic field. The upturn, or the minimum of the MR, appears at a lower field with decreasing temperature. These observations are consistent with previous reports on similar films and networks of CNTs [8–10]. The MR at low temperatures has been explained by two different contributions, one positive and the other negative. The negative contribution to the MR is due to the interference effect, referred as weak localization. The magnetic field causes carriers to acquire an additional phase as they move around paths, which reduces coherent backscattering in a disordered medium such as our random networks of CNTs. This results in the negative MR. On the other hand, the positive contribution to the MR is generally considered as an effect of strong localization. The positive term is dominant at very low *T* and shows

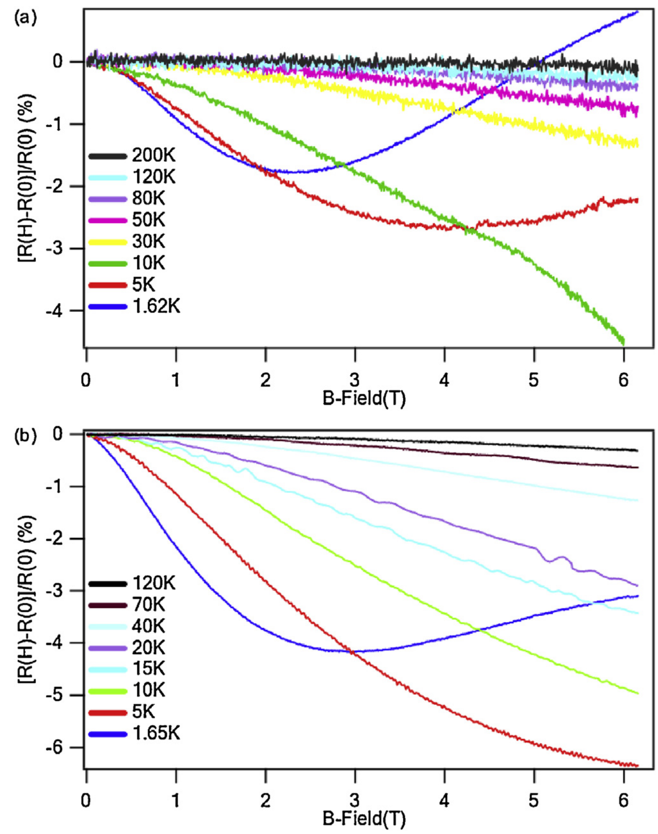

Fig. 2. Magnetoresistance of (a) HiPCO CNT film and (b) LA CNT film measured at various temperatures.

a quadratic H^2 dependence, consistent with the variable hopping mechanism. Both the Zeeman splitting of the localized states and the shrinkage of the wave functions can account for the positive MR [8–10]. The negative term due to the weak localization tends to saturate at high fields, and the upturn in the MR occurs at low temperatures with H^2-depending positive contribution.

The MR of the $SOCl_2$-treated CNT films, however, are distinguished from the MR of the pristine CNT films. As shown in Fig. 3, MR's are negative down to the lowest accessible temperature of 1.67 K without showing the positive upturn up to 6 T. This result is consistent with the temperature dependence of the conductivity observed in the $SOCl_2$-treated CNT films. With enhanced conductivity and the tube overlap, the $SOCl_2$ treatment leads to the absence of the strong localization in the CNT films and the positive term in the MR does not develop down to 1.67 K.

4. Hall effect in CNT films

Fig. 4 shows Hall voltage with respect to magnetic field, measured at different temperatures for the $SOCl_2$-treated HiPCO CNT film. For all temperatures, the Hall voltage is nearly proportional to the magnetic field, and similar linear dependencies are observed in all our CNT films investigated in this communication. From the linear slope, Hall coefficient, R_H, is deduced and plotted as a function of temperature in Fig. 5 for (a) the pristine HiPCO and (b) the $SOCl_2$-treated HiPCO CNT films. For both samples, Hall coefficients are decreasing with temperature, and show a tendency toward saturation at high temperatures. The signs of the Hall coefficients are positive in the whole temperature range, indicating that majority carriers are holes in these CNT films. Inserts in Fig. 5 present the hole carrier density, n_h, calculated from the R_H. At $T = 80$ K, carrier densities are estimated to be 1.7×10^{22} cm^{-3} and 2.8×10^{22} cm^{-3} for