Transport phenomena in an anisotropically aligned single-wall carbon nanotube film

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Thin films of aligned carbon nanotubes were prepared by a simple mechanical rubbing from a singlewalled carbon nanotube powder, which was synthesized by the catalytic arc discharge. The measured electrical resistivity shows high anisotropy (ρ_N/ρ_P) ranging from 5 to 15. The annealed samples show a monotonic decrease in the resistivity with increasing temperature. Carbon nanotubes in the mat act as strong Luttinger liquids with g values ranging from 0.18 to 0.26, similar to an isolated nanotube. We propose that the transport is dominantly governed by the formation of metal-metal crossed junctions of nanotubes in the mat.

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Carbon nanotubes (CNT's) have peculiar quantum one-dimensional physical properties. For instance, the achiral armchair (n,n) (CNT) (Refs. 1 and 2) shows a metallic behavior, whereas the achiral zigzag $(n,0)$ CNT is a semiconductor with a finite size of band gap, when $n=3k$, and zero band gap (finite with strain energy), when $n=3k$, where n is an integer. In general, for chiral (n,m), all CNT's are semiconducting except $n\text{-}m=3k$, which show a metallic behavior.[1–3] These properties are manifested in the $I\text{-}V$ characteristics with gating effects, where the semiconducting CNT shows the gate-modulation effect, whereas the metallic CNT does not.[4,5]

One of the most intriguing phenomena is the effect of long-range Coulomb interactions which appears in one dimensional systems, i.e., an isolated metallic carbon nanotube behaves as a Luttinger liquid with an anomalous power-law dependence of the resistivity at moderate temperature range, unlike noninteracting Fermi liquids.[6] The measured Luttinger parameter g which expresses the strength of electron interactions, varies from different groups but mostly ranges from 0.2 to 0.3,[5,7] clearly well below the Fermi liquids value $g=1$. The g value is correlated to the ratio of the charging energy of the tube to the single particle level spacing. The conductance is in general expressed by using the power law of the temperature with an exponent α, although the exponent is correlated with different forms of the Luttinger parameter. For instance, for long-range Coulomb one-dimensional (1D) Luttinger liquids, the exponent $\alpha=(g+g^{-1}-2)/8$ for bulk contact and $\alpha=(g^{-1}-1)/4$ for end contact. For the inclusion of short-range interactions, $\alpha=1-2g$ for umklapp scattering, and $\alpha=(1-g)/2$ for disorder from Kane's model.[6] The applications of these models are strongly dependent on the systems.

The CNT films can be easily prepared in a mat form by simply coating the CNT slurry on the substrate. Transport phenomena from such mats exhibit neither normal semiconducting nor metallic behaviors.[8] Resistivity of the mat shows a monotonic decrease with increasing temperature and shows typically an upturn near room temperature from the pristine samples and this upturn disappears after degassing by annealing.[9,10] The upturn at high temperature (>400 K) remains unchanged in some cases even after the degassing, indicating the evidence of metallic contribution.[11] No analysis for 1D liquid behavior has yet been reported from the CNT films. Recently magnetically aligned CNT film in a high magnetic field (25 T) has been prepared, showing the anisotropy (ρ_N/ρ_P) of the resistivity of about 6.[9,10] However, the approach with high magnetic field is not easily accessible and thus some other practical approaches for aligned CNT films are always demanding.

The purpose of this Letter is twofold. We first provide a simple way of preparing the aligned CNT thin films by a mechanical rubbing. The anisotropy of the aligned CNT films ranges from 5 to 15, depending on the film thickness and the pristine CNT conditions. From nonlinear temperature dependence of the resistivity, we obtain the power law indices of temperature with relatively low Luttinger parameters of 0.18–0.26. This yet fails to reproduce the observed resistivity. The inclusion of the linear temperature dependence in the resistivity suggests that the CNT's in the mat are composed of metals revealing Luttinger liquids behavior and normal metals with Fermi liquids particularly at higher temperature. We propose that the transport is dominantly carried through the metal-metal junctions between CNT's in the mat.

Singlewalled carbon nanotubes were prepared using catalytic arc discharge at low pressure.[12] The pristine samples collected from the collar part contained mostly carbon nanotubes with 20 wt. % of transition metals. In order to dissolve the transition metals, this sample was further refluxed for 6 h in 2.8 M HNO_3 acids. The sonication in DI water for 10 min and the filtering were repeated until the pH of the suspension was equal to that of the DI water. The remaining transition metals were less than 1 wt. %. The slurry left on top of the filter was coated on glass and mechanically squeezed by a bar coater with a pattern width of 50 μm in order to align CNT's of thin film to a preferred plane direction. The samples were dried in a vacuum oven at 80 °C for a day. The thickness of the aligned CNT films was about 7 μm. The

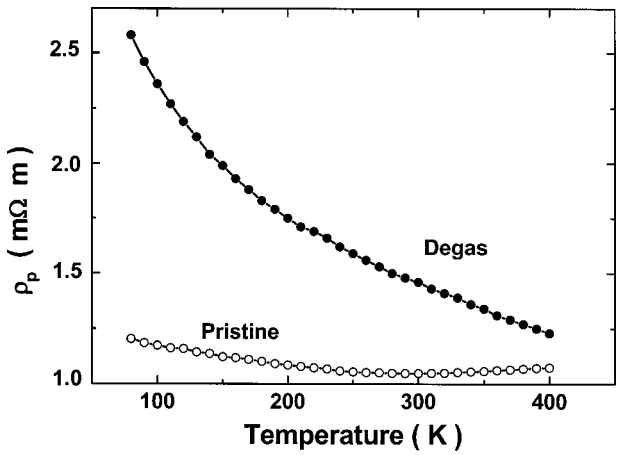

FIG. 1. Resistivity ρ_p vs temperature T, for a pristine (open circle) and degassed SWNT's film (filled circle), was measured in the parallel direction to the tube axis.

resistivity was measured by using the four-probe method in a vacuum chamber pressure 6×10^{-6} Torr, where the contact was formed by the Ag epoxy.

The pristine sample shows two resistivities: resistivity parallel to the tube axis, $\rho_P=15\,\mu\Omega\,\mathrm{m}$, and that normal to the tube axis, $\rho_N=146\,\mu\Omega\,\mathrm{m}$. The average of these is 80 $\mu\Omega\,\mathrm{m}$, which is comparable to 60 $\mu\Omega\,\mathrm{m}$ of the previously reported as-grown mat.[8] Figure 1 shows ρ_P of the pristine and degassed samples, where the degassed sample was first annealed in air at 350 °C for an hour and degassed in vacuum at 420 K for 12 h. The pristine resistivity shows a minimum near the room temperature, where nonmetallic behavior is shown at low temperature. However, the degassed sample shows a monotonic decrease with increasing temperature and thus nonmetallic behavior over the whole temperature range.[13] This is also observed from the previous report,[10] although the resistivity may give rise to a linear power law at high temperature, as observed in the recent report.[11] The issue whether this upturn at low temperature results from the adsorbates[10,11] or Kondo effect[14,15] is not clear at this moment. A possibility of Kondo effect may be excluded due to the disappearance of the minimum or at least shifting of the minimum resistivity point. This monotonic decrease of the resistivity with increasing temperature cannot be simply explained as the behavior of the semiconducting tubes. Long-range Coulomb interactions in 1D system play an important role in the transport, which will be discussed in the later paragraph.

Figure 2(a) clearly shows the anisotropic resistivities in the aligned mat sample after degassing. The anisotropy is almost constant at six over the entire temperature range and ranges from 5 to 15, depending on the thickness and sample treatment conditions. The inset shows a degree of alignment of the pristine mat surface of mechanically rubbed sample. Some carbonaceous particles and thick ropes are formed during the acid treatment that often causes to damage the CNT walls. Carbonaceous particles will be selectively etched away with high reaction rate during the oxidation in air,[16] resulting in an enhancement of the anisotropy of the sample. Although the resistivities of both parallel and perpendicular

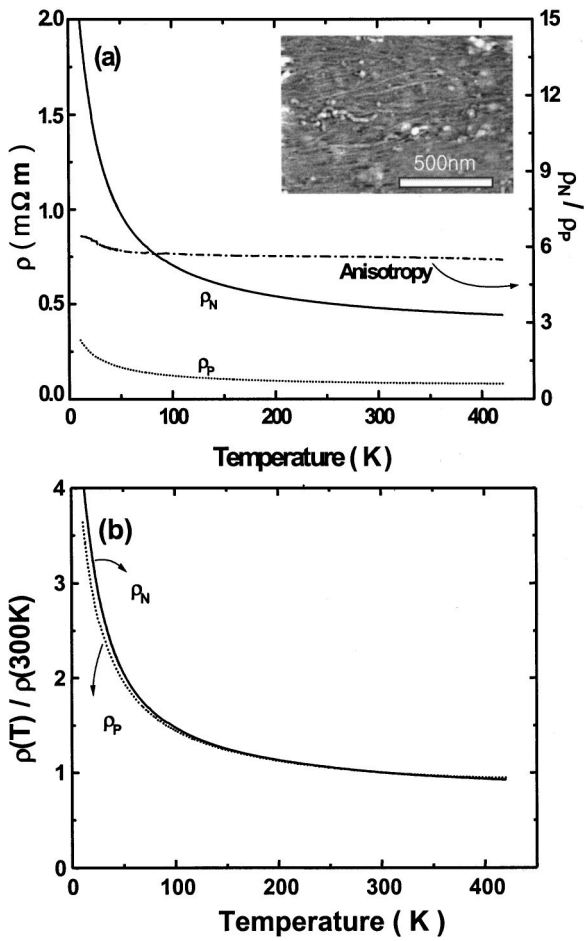

FIG. 2. (a) Resistivities (left axis) of both parallel (dotted line) and perpendicular (solid line) directions to the tube axis and anisotropy (dash-dotted line, right axis) ρ_N/ρ_P. (b) Scaled resistivity data $\rho(T)/\rho(300\,\mathrm{K})$ of both directions.

directions show different values and are expected to have different temperature dependence, the scaled resistivities of both directions are essentially identical to each other, as shown in Fig. 2(b). This strongly suggests that the transport mechanism of both directions is equivalent, independent of the aligned directions. The origin of the anisotropy in the aligned SWNT's film will be explained later.

We now address transport mechanism of the aligned CNT films. The scaled resistivity shows a nonlinear power law with temperature. Although our metal electrodes are formed for the four-point probe measurement, the distance between the electrodes is far apart for Luttinger liquids such that most CNT's cannot feel the contact. However, effective contacts between CNT's are formed randomly through the CNT-CNT crossed junctions. We assume that the resistivity of our sample is composed of two terms

$$\rho_{\mathrm{film}}=\rho_{\mathrm{junction}}+\rho_{\mathrm{CNT}}, \tag{1}$$

where ρ_{junction} is the junction resistivity which may be composed of metal-metal, metal-semiconductor, and semiconductor-semiconductor junctions and ρ_{CNT} is the resistivity of the metal and semiconductor CNT's. We first fit

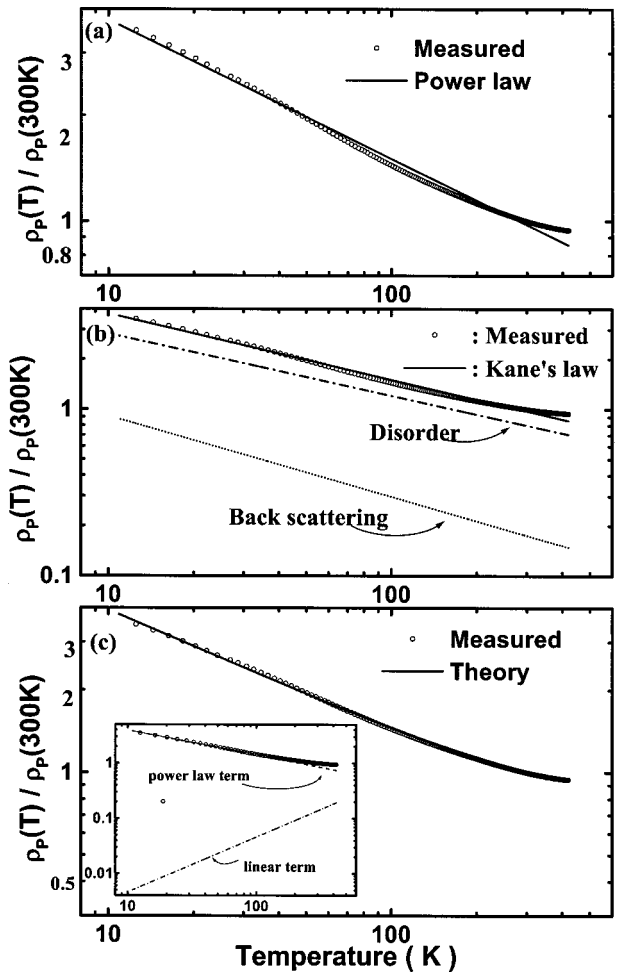

FIG. 3. Scaled resistivity data $\rho_P(T)/\rho_P(300\,\mathrm{K})$ (open circle) are roughly reproduced by (a) the power law fit (line) $\rho = aT^{-\alpha}$, (b) the Kane's theory with $\rho = aT^{2g-1} + bT^{-(g-1)/2}$ including the contributions from the backscattering (dot) and disorder (dash-dot), respectively, (c) our trial equation (line) with $\rho = aT^{-\alpha} + bT$, which is combined by a power law term of T (dash) and a linear dependent term (dash-dot), respectively.

our data by considering only the long-range Coulomb interactions, where the conductance $G(T) = T^{\alpha}$. If we assume a complete 1D Luttinger liquids and bulk contacts,[17] $g = 0.202$ is obtained from the fitting with $\alpha = 0.394$. This value is similar to the predicted value from Kane's theory.[6] However, the fitted curve deviates at intermediate and high-temperature regions, as shown in Fig. 3(a), indicating that other contributions should be incorporated in the mat sample.

We next try to fit the data by following the Kane's theory,[6] where short-range interactions of disorder and umklapp scattering are included, in addition to the long-range Coulomb repulsions. At temperatures above the energy gap, the power-law resistivity is

$$\rho(T) = u^2 T^{2g-1} + n_0 T^{-(1-g)/2}, \tag{2}$$

where the first term describes backscattering caused by the umklapp interactions and the second term describes disorder with respective constant terms u^2 and n_0. The Luttinger parameter g is implemented in the index of the power. With $g = 1$, the system becomes noninteracting Fermi liquid. For $g < 1$, the resistivity shows nonlinear power law with interacting Luttinger liquids. Figure 3(b) shows the fitting with inclusion of two terms of backscattering and disorder in Kane's approach. The obtained g value is 0.257, representing strong Luttinger liquids. The contribution from the backscattering is relatively weaker than that from the disorder. The fitting fails to reproduce the measured values at mid range and high temperature. The difficulty arises from the fitting of nonlinear power law by a single Luttinger parameter.

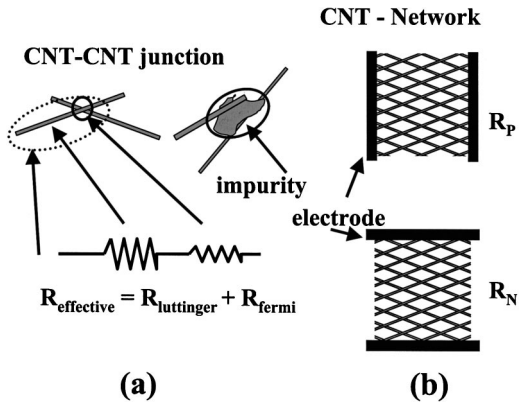

FIG. 4. (a) A schematic diagram of effective series resistor. (b) A simplified network model of the aligned CNT's thin film.

Since the tube-tube interactions that deviate from one-dimensional system and represent additional three-dimensional effects, may play as noninteracting Fermi liquids, we separate the linear term from Luttinger liquids. In this approach, the resistivity is expressed by adding of both linear and nonlinear power laws

$$\rho(T) = aT^{-\alpha} + bT, \tag{3}$$

where $\alpha \neq -1$. This prediction gives an excellent agreement with the measured value, as shown in Fig. 3(c). The power index $\alpha = 0.446$ gives the Luttinger parameter, $g = 0.186$ with bulk contact. This value is smaller than those measured from an isolated singlewalled carbon nanotube,[4,5] indicating stronger Luttinger liquids. The inclusion of the linear term, although the coefficient $b(=4.60\times10^{-4})$ is smaller than the coefficient $a(=11.0)$, particularly gives better fitting at higher temperatures. This further implies an upturn at high temperature, where our fitting provides an upturn at 600 K, which is beyond our temperature range of the measurements and not shown in Fig. 3(c). This may reflect the existence of the upturn at high temperature, as can be seen in the previous report,[11] although whether the existence of such an upturn originates from the gas adsorbates or not, is not clear at this moment. Although the transport in the mat of the thin films is governed by the Luttinger liquids, the effect from the noninteracting Fermi liquids cannot be excluded particularly at temperature >100 K.

The transport phenomena from the mat of the thin films can be understood in the following model. The original mat of the CNT's can be viewed as in Fig. 4(a). The random network of CNT's is connected with CNT/rope-CNT/rope

junctions. The crossed junctions between CNT's or ropes act importantly as a gate for carriers to move in the mat. These may be connected via amorphous carbons and/or metal impurities, in which represent normal Fermi liquids. Therefore the mat of the CNT film can be represented by the network of effective resistors, in which the effective series resistor is formed by the Luttinger liquids (CNT) and Fermi liquids (junction); $R_{\text{effective}}=R_{\text{Luttinger}}+R_{\text{Fermi}}$. From the simplified network model of resistors as in Fig. 4(b), we can extract $R_P=N_P R_{\text{effective}}/N_N=nR_{\text{effective}}/\gamma n=R_{\text{effective}}/\gamma$ or $R_N=N_N R_{\text{effective}}/N_P=\gamma n R_{\text{effective}}/n=\gamma R_{\text{effective}}$ and also explain anisotropy $A=R_N/R_P=\gamma^2$, where R_P or R_N are the resistances measured between two electrodes with the parallel direction or perpendicular direction to the axis of tube respectively and γ is a ratio of effective path lengths or number of junctions of perpendicular direction ($N_N=\gamma n$) to those of parallel direction ($N_P=n$). Therefore the alignment $\gamma=\sqrt{A}$. In our samples, the alignment is relatively poor, ranging from 2 to 4.

In summary, the singlewalled carbon nanotubes have been anisotropically aligned by the simple mechanical rubbing on film as a form of mat. High anisotropy of 5 to 15 in the resistivity was obtained depending on the sample thickness and sample preparation conditions. The monotonic decrease of the resistivity with increasing temperature cannot be explained by either the long-range Coulomb interactions or the inclusion of short-range interactions, which is different from an isolated singlewalled carbon nanotube. The measured data were well fitted by including a small contribution of the linear power term. The mat of the CNT film with a mean field approximation can be modeled as a network of the effective resistors, in which each resistor is represented by a series resistance of Luttinger liquids with $g=0.186$ and Fermi liquids.

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