Frequency dependent ac transport of films of close-packed carbon nanotube arrays

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Abstract. We have measured low-temperature ac impedance of films of close-packed, highly-aligned carbon nanotubes prepared by thermal decomposition of silicon carbide wafers. The measurement was performed on films with the thickness (the length of the nanotubes) ranging from 6.5 to 65 nm. We found that the impedance rapidly decreases with the frequency. This can be interpreted as resulting from the electric transport via capacitive coupling between adjacent nanotubes. We also found numbers of sharp spikes superposed on frequency vs. impedance curves, which presumably represent resonant frequencies seen in the calculated conductivity of random capacitance networks. Capacitive coupling between the nanotubes was reduced by the magnetic field perpendicular to the films at 8.2 mK, resulting in the transition from negative to positive magnetoresistance with an increase of the frequency.

1. Introduction

A film composed of a highly-aligned, close-packed array of nanotubes (CNT) can be grown on the surface of a SiC(0001) substrate by thermal decomposition; in the film, multi-walled CNTs having the diameter ranging from 2 to 5 nm are distributed randomly, with their tube axes aligned perpendicular to the substrate surface [1, 2, 3]. Such films provide interesting subjects for transport studies, owing to the intricate combination of inter- and intra-CNT transport in the network of randomly arranged CNTs. In the present paper, we report the measurements of ac impedance, focusing on the frequency, the temperature, and the magnetic-field dependence.

2. Experimental

A schematic drawing of a CNT film is shown in Fig. 1. Details of the growth of the CNT films are given in [1, 2, 3]. We measured four samples with different thickness (CNT length) L tabulated in Fig. 1. Electrical contacts were made by balls of silver paste placed on the corners of a macroscopic (∼5 × 5 mm²) sample, as depicted in the insets of Figs. 2, 3, 4 (a). Measurements were performed by the standard ac lock-in technique. For measurements below 1 K, we used a dilution refrigerator (Oxford Kelvinox TLD) equipped with a superconducting magnet.
SiC substrate

Figure 1. Schematic drawing of a CNT-array film. Four samples with different thickness $L$ (the length of CNT), tabulated in the table, were examined.

| Sample | $L$ (nm) |
|--------|---------|
| A      | 6.5     |
| B      | 22.6    |
| C      | 25.0    |
| D      | 65      |

Figure 2. (a) Frequency dependence of the impedance $|Z|$ for sample A taken at RT and 4.2 K. Inset: schematic illustration of the contact geometry. $I_{j,k}$-$V_{l,m}$ designates the measurement configuration employing pairs of electrical contacts $j,k$ and $l,m$ as current and voltage probes, respectively. (b) Replot of the data in (a) as $|Z|^{-2}$ vs. $\omega^2$. The thin overlaid lines represent fitting to Eq. (2), using $R_0$ and $C$ as fitting parameters. Inset: equivalent circuit, represented by Eq. (1), modelling the conduction through the film. Shaded areas in both (a) and (b) indicate 50 Hz and its harmonics, where measurements are unreliable owing to the disturbance by the commercial power supply.

3. Results and discussion

3.1. Frequency dependence of the impedance at room temperature and 4.2 K

Figure 2 (a) shows the ac impedance $|Z|$ of sample A ($L = 6.5$ nm), measured by varying the ac frequency $f$ from 4 to 100 Hz with the interval of 0.1 Hz per step. The traces taken both at room temperature (RT) and at 4.2 K are shown. At 4.2 K, $|Z|$ exhibits a remarkably rapid decrease with the increase of $f$ in this rather low frequency range, and becomes smaller than $|Z|$ for RT at $\sim 72$ Hz, although the latter also slightly decreases with $f$. The rapid decrease of $|Z|$ with $f$ suggests that the capacitive coupling between adjacent CNTs plays a substantial role in the electric conduction. As the simplest possible model describing the conduction through the film, we consider an equivalent circuit containing the resistance $R_0$ and the capacitance $C$ in parallel, as depicted in the inset of Fig. 2 (b). In this model, the impedance $Z$ is given by

$$Z = \left( R_0^{-1} + i\omega C \right)^{-1}, \tag{1}$$

or, equivalently, by

$$|Z|^{-2} = R_0^{-2} + \omega^2 C^2, \tag{2}$$
with \( \omega = 2\pi f \). The excellent linearity of the data replotted in the form of \(|Z|^{-2} \) versus \( \omega^2 \) in Fig. 2 (b) demonstrates that the simple model actually describes the conduction of the film remarkably well. One can deduce the values of \( R_0 \) and \( C \) from the intercept and the slope of the line, respectively. The values thus obtained are plotted in Fig. 5. In Figs. 3 and 4, we present the measurement results for samples B (\( L = 22.6 \) nm) and D (\( L = 65 \) nm), respectively. The decrease of \(|Z| \) with \( f \) becomes less apparent with the increase of the film thickness \( L \). As can be seen in Figs. 3 (b) and 4 (b), the relation between \(|Z| \) and \( \omega \) can still basically be described by Eq. (2) for these samples (and also for sample C, not shown). The parameters \( C \) and \( R_0 \) obtained by the fittings are plotted in Fig. 5 against \( L \). At RT, \( C \) increases and \( R_0 \) decreases monotonically with increasing \( L \), as can be readily expected from the increase in the areas with which adjacent CNTs are facing. At 4.2 K, however, both \( C \) and \( R_0 \) exhibit non-monotonic behavior, suggesting that electric conduction at low temperatures is more sensitive to details of the films, such as impurities or fluctuations in inter-CNT distances. By reducing the temperature from RT to 4.2 K, \( R_0 \) increases in all samples, consistent with thermally assisted inter-CNT hopping. In fact, Matsuda et al. observed temperature dependence consistent with variable range hopping (VRH) at \( 20 \text{K} < T < 300 \text{K} \) by dc measurements [4]. The capacitance \( C \) decreases except for sample A with the smallest \( L \). The decrease is presumably caused by the increase in the inter-CNT

Figure 3. Similar to Fig. 2 for sample B. In (b), the right and left axes correspond to RT and 4.2 K traces, respectively.

Figure 4. The same as Fig. 3 for sample D.
Figure 5. Parameters obtained by fitting to Eq. (2), plotted as a function $L$: $C$ (a), $R_0$ (b), and their product $R_0C$ (c).

distance owing to the radial contraction of CNTs on cooling. Deviation from this trend in the thinnest film may possibly be resulting from the strong influence of the SiC substrate on the CNT’s elastic behavior. The product $R_0C$, which determines the rapidness of the decrease of $|Z|$ with $f$, monotonically decrease with increasing $L$.

In Fig. 4 (b), a number of sharp spikes are seen superposed on the linear background. Major peaks are observed at 42, 55, 60, 68, 73, 78, 84, 91, and 95 Hz in the trace taken at 4.2 K, and some of them (55, 60, 78 Hz) can be recognized even in the trace taken at RT. These spikes are reproducible. In fact, traces taken in three different $f$-sweeps are shown for 4.2 K in Fig. 4 (b) with slightly different grayscale tone, and all of them show the spikes at the same frequencies. Although much smaller in intensity, similar spikes are also observed in samples B (Fig. 3 (b)) and C. The spikes take place at the sample-specific random frequencies. The origin of these spikes is not clear at present, but is presumably related to resonant frequencies seen in the calculated conductivity of random capacitance networks [5, 6].

3.2. Frequency dependence of the impedance below 1 K
In this and the following subsection, we focus on sample D. Figure 6 shows the temperature dependence of $|Z|$ taken below 1 K with $f = 4$ Hz. As can be seen, $|Z|$ steadily increases with decreasing temperature and starts to steeply rise below $T_r \sim 46$ mK. The frequency dependence of $|Z|$ at fixed temperatures is presented in Fig. 8 (a). For temperatures well above $T_r$, the

Figure 6. Temperature dependence of the impedance $|Z|$ taken at $f = 4$ Hz for sample D. Inset: log-log plot of the data shown in the main panel.

Figure 7. Temperature dependence of $R_0$ (left axis) and $C$ (right axis) obtained by fitting to Eq. (2) in sample D. Inset: $R_0$ in log scale vs. $T^{-1/4}$. 
Figure 8. (a) Frequency dependence of the impedance $|Z|$ for sample D taken at temperatures ranging from 8.2 mK to 4.2 K. (b) Replot of the data in (a) as $|Z|^{-2}$ vs. $\omega^2$.

$|Z|^{-2}$ vs. $\omega^2$ plot shown in Fig. 8 (b) exhibits linearity above $\sim 70$ Hz, indicating that the simple equivalent circuit model, Eq. (1), is still valid in this temperature and frequency range. The parameters $C$ and $R_0$ deduced from the fittings to Eq. (2) are plotted in Fig. 7 along with those at 4.2 K and RT deduced above. $C$ and $R_0$ show monotonic increase and decrease with the temperature, respectively, revealing that the trend we saw in Fig. 5 continues down to lower temperatures. As shown in the inset of Fig. 7, $R_0$, corresponding to the resistance at $f \to 0$, is well described above $\sim 200$ mK by 3-dimensional VRH,

$$R_0 \propto \exp\left[\frac{T_0}{T}\right]^{1/(d+1)}, \quad (3)$$

with $d = 3$, in agreement with the behavior observed at higher temperatures $20 \, \text{K} < T < 300 \, \text{K}$ by dc measurements for films with $L = 65 \, \text{nm}$ [4]. Linearity in $|Z|^{-2}$ vs. $\omega^2$ is lost around $T_r$ but restored for the lowest temperature (8.2 mK), albeit within a limited frequency range $25 \leq f \leq 80 \, \text{Hz}$.

3.3. The effect of magnetic field

Finally, we examine the effect of the magnetic field applied perpendicular to the film. As can be seen in Fig. 9, negative magnetoresistance is observed, which becomes more prominent with decreasing temperature. At the lowest temperature (Fig. 9 (c)), $|Z|$ decreases more rapidly with $f$ around $B = 0 \, \text{T}$ than at higher magnetic fields. Thus, the magnetoresistance turns from negative to positive at around $f \approx 103$ Hz. The parameters $R_0$ and $C$ deduced by the same procedure as in the previous subsections are plotted as a function of the magnetic field in Figs. 10 and 11 for $T = 225$ and 8.2 mK, respectively. For both temperatures, $R_0$ exhibits negative magnetoresistance resembling those observed by dc measurements on samples composed of bundles of randomly arranged CNTs [7, 8, 9], which is interpreted in terms of theories that take into account the quantum interference effect in the VRH conduction [10, 11].

The effective capacitance $C$ slightly increases with $B$ for the higher temperature, but decreases with $B$ for the lowest temperature. The decrease is responsible for the smaller $f$ dependence hence the transition from negative to positive magnetoresistance with $f$ observed at the lowest temperature, although the mechanism through which the magnetic field affects $C$ is not well understood at present.
Figure 9. Frequency dependence of the impedance $|Z|$ for sample D taken at fixed magnetic fields ranging from $-1$ to $1$ T with the step of $0.02$ T. (a) $964$ mK. (b) $225$ mK. (c) $8.2$ mK.

Figure 10. Magnetic-field dependence of $R_0$ (left axis) and $C$ (right axis) obtained by fitting to Eq. (2) at $225$ mK in sample D.

Figure 11. Magnetic-field dependence of $R_0$ (left axis) and $C$ (right axis) obtained by fitting to Eq. (2) at $8.2$ mK in sample D.

4. Summary
We have measured the ac impedance $|Z|$ of films composed of closely-packed, highly-aligned carbon nanotubes. The observed decrease of $|Z|$ with the frequency $f$ was found to be described remarkably well by a simple equivalent circuit containing resistance $R_0$ and capacitance $C$ in parallel. The dependence of $R_0$ on the temperature and the magnetic field was consistent with those obtained by dc measurements. We also observed reproducible sharp spikes superposed on the $|Z|$ vs. $f$ traces.

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