Random stick network analysis of electronic transport in carbon nanotube thin films

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Electronic transport in metallic carbon nanotube (CNT) thin films is investigated theoretically using a random stick network analysis combined with circuit theory. To discuss the dependence of the sheet conductance on the CNT alignment in the films, an angle \( \varphi_{\text{max}} \) (0° ≤ \( \varphi_{\text{max}} \) ≤ 90°) is introduced as a new parameter to characterize the CNT alignment: \( \varphi_{\text{max}} = 0° \) and \( \varphi_{\text{max}} = 90° \) correspond to perfectly aligned and perfectly random network structures, respectively. The results indicate that the conductance exhibits a maximum around \( \varphi_{\text{max}} \) = 55°. In addition, the conductance shows a local minimum around \( \varphi_{\text{max}} = 30° \) because CNTs tend to intersect with incommensurate junctions that have a high contact resistance.

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T mplementation conducting films have a wide-range of applications, such as flat displays, solar panels, and touch sensors. Indium tin oxide (ITO) is the most widespread material for transparent conducting films, however, ITO has some problems with respect to flexibility and mechanical strength, which are essential to the realization of future flexible devices. As a potential candidate for flexible transparent conducting films, carbon nanotube (CNT) thin films have been attracting much attention, where both the length and the width of the film are equal. The (10,10) CNTs, of which the length \( l_{\text{CNT}} \) is 0.5 \( \mu \text{m} \), are randomly distributed in the film and a periodic boundary condition is imposed on the width direction (y-axis direction). The CNT areal density \( \sigma \), is defined as the number of CNTs per square micrometer (\( \mu \text{m}^2 \)).

The CNT alignment is characterized by the alignment angle \( \varphi_{\text{max}} \), because the angle between the axial direction of the CNT and the x-axis \( \varphi \), is assumed to vary randomly between \( -\varphi_{\text{max}} \) and \( +\varphi_{\text{max}} \). The range of \( \varphi_{\text{max}} \) is from 0° to 90°, as shown in Fig. 1(b). For instance, when \( \varphi_{\text{max}} = 20° \), most of the CNTs are aligned towards the x-axis direction, as shown in Fig. 1(c). On the other hand, when \( \varphi_{\text{max}} = 90° \), the CNTs are completely randomly distributed, as shown in Fig. 1(d). The positions of CNTs and \( \varphi \) are set randomly using the Mersenne Twister algorithm.

CNT networks are mapped on the RSN model to calculate the electrical conductivity of CNT thin films. Figure 2(a) represents a part of a RSN model consisting of three connected CNTs (CNT_{ab}) and Fig. 2(b) gives an equivalent circuit corresponding to the RSN model. The equivalent circuit is described as a combination of CNT resistance \( R_{\text{CNT}} \) and contact resistance \( R_{\text{cont}} \) as shown in Fig. 2(b). \( R_{\text{CNT}} \) is generally dependent on the CNT length \( l_{\text{CNT}} \) and \( R_{\text{cont}} \) is dependent on the contact angle \( \Theta \) between two CNTs. As for \( R_{\text{CNT}} \), the electrical resistance of a (10,10) CNT at room temperature (300 K) was calculated in our previous theoretical study as the length dependent actual resistance \( R_{\text{CNT}} \). In our previous article, we showed that \( R_{\text{CNT}} \) is proportional to \( l_{\text{CNT}} \) up to 0.5 \( \mu \text{m} \) because \( R_{\text{CNT}} = 9.6 l_{\text{CNT}} + R_{q} \) where \( R_{q} \) is the quantum resistance. For \( R_{\text{cont}} \), Ref. 30 investigated the contact resistance for two (10,10) CNTs as a function of the contact angle \( \Theta \), based on the tight-binding model. They found that \( R_{\text{cont}} \) with commensurate stacking of the lattice of two CNTs is lower than that for incommensurate stacking. In the case of (10,10)–(10,10) CNT contact, whereas \( R_{\text{cont}} \) exhibits local minimum values around \( \varphi = 0, 60, 120, \) and 180° (commensurate

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Fig. 1. (a) A schematic illustration of a CNT thin film showing the RSN model. The film length \( L \) and width \( W \) are both 5 \( \mu m \), and the CNT length \( l_{\text{CNT}} \) is 0.5 \( \mu m \). Here, the direction from Electrode 1 to Electrode 2 is defined as the \( x \)-axis and the vertical direction is defined as the \( y \)-axis. The film voltage \( V \) represents the voltage drop between Electrode 1 and Electrode 2. (b) Schematic illustration of a single CNT in the network. \( \varphi \) is the angle between the axial direction of the CNT and the \( x \)-axis, which is assumed to vary uniformly in the range \(-\varphi_{\text{max}} \leq \varphi \leq \varphi_{\text{max}} \). (c) Schematic illustrations of random CNT networks for \( \Theta = 30^\circ \). Fig. 1(b), where we obtain \( \varphi_{\text{max}} = 30^\circ \). (d) \( \varphi_{\text{max}} = 90^\circ \).

In our simulation, we adopt data from Ref. 31 for \( R_{\text{CNT}} \). For example, to estimate \( R_{\text{CNT}} \) of CNTs, we can obtain the averaged sheet conductance \( \sigma_{\text{CNT}} \) for various \( \sigma \). Here we consider the dependence of \( \sigma_{\text{CNT}} \) on \( \varphi_{\text{max}} \) for various \( \sigma \). For a fixed \( \sigma \), \( \sigma_{\text{CNT}} \) has a maximum near \( \varphi_{\text{max}} = 55^\circ \), while \( \sigma_{\text{CNT}} \) shows a dip near \( \varphi_{\text{max}} = 30^\circ \), as indicated by the red arrows. In the following, we describe the dependence of \( \sigma_{\text{CNT}} \) on \( \varphi_{\text{max}} \) for three distinct regimes: \( \varphi_{\text{max}} \approx 0^\circ \), \( \varphi_{\text{max}} \approx 90^\circ \), and \( \varphi_{\text{max}} \approx 30^\circ \).

Here we consider the \( \sigma_{\text{CNT}} \) behavior near \( \varphi_{\text{max}} = 0^\circ \). As shown in Fig. 3(b), \( \sigma_{\text{CNT}} \) is closely zero in the range of \( 0^\circ \leq \varphi_{\text{max}} < \varphi_c \), where \( \varphi_c \) is the percolation threshold. In this region, CNTs in the film are almost perfectly aligned along the \( x \)-axis and most of the CNTs do not intersect each other. As a result, there are few conduction paths that connect Electrode 1 and Electrode 2, so that \( \sigma_{\text{CNT}} \approx 0 \) (\( \varphi_{\text{max}} < \varphi_c \)). On the other hand, when \( \varphi_{\text{max}} \) exceeds \( \varphi_c \), \( \sigma_{\text{CNT}} \) increases steeply because the conduction paths begin to form. For a fixed \( \varphi_{\text{max}} \), \( \varphi_c \) decreases with increasing \( \sigma \) as detailed in our supplementary materials, available online at stacks.iop.org/APEX/12/055006/mmedia. This is because conduction paths can be formed with lower \( \varphi_c \) as \( \sigma \) increases.

Here, we consider the dependence of \( \sigma_{\text{CNT}} \) on \( \varphi_{\text{max}} \) based on percolation theory for the RSN model. According to the theory, the behavior of \( \sigma_{\text{CNT}} \) near \( \varphi_c \) can be described by:

\[
\sigma_{\text{CNT}}(\varphi_{\text{max}}) = a \varphi_c^{\tau_\varphi}(\varphi_{\text{max}} - \varphi_c)^{\tau_c} \quad (\varphi_{\text{max}} \geq \varphi_c),
\]

where \( \tau_\varphi \) is the critical exponent and \( a \) is a prefactor that is used as a fitting parameter for the numerical data in Fig. 3(b). The dashed curves for the best fit for \( \tau_\varphi \) and \( a \) are shown in Fig. 3(b), where we obtain \( \tau_\varphi = 1.33 \), which is in agreement with the universal value predicted by percolation theory. \( \Box \)
Therefore, the behavior of $G_s$ near $\varphi_c$ can be explained by percolation theory.

Here we focus on the behavior of $G_s$ near $\varphi_{\text{max}}=90^\circ$. Figure 3(a) shows that $G_s$ decreases with increasing $\varphi_{\text{max}}$ in the range of $55^\circ \lesssim \varphi_{\text{max}} \lesssim 90^\circ$. To show the decrease in $G_s$ quantitatively, we introduce a new quantity that represents the CNT alignment:

$$X_{\text{CNT}}(\varphi_{\text{max}}) = \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} X_{\text{CNT}}(\varphi) S(\varphi, \varphi_{\text{max}}) d\varphi,$$

where $S(\varphi, \varphi_{\text{max}})$ is the probability distribution for $\varphi$ and $X_{\text{CNT}}(\varphi)$ is an orthogonal projection of the CNT length $l_{\text{CNT}}$ along the $x$-axis for a certain CNT. $X_{\text{CNT}}(\varphi_{\text{max}})$ represents the average CNT length along the $x$-axis for a fixed $\varphi_{\text{max}}$, which is obtained by averaging $X_{\text{CNT}}(\varphi)$ weighted by $S(\varphi, \varphi_{\text{max}})$. $\varphi$ is distributed uniformly in the range of $-\varphi_{\text{max}} \leq \varphi \leq \varphi_{\text{max}}$; therefore, $X_{\text{CNT}}(\varphi_{\text{max}})$ can be calculated as:

$$X_{\text{CNT}}(\varphi_{\text{max}}) = l_{\text{CNT}} \int_{-\varphi_{\text{max}}}^{\varphi_{\text{max}}} \cos \varphi d\varphi = l_{\text{CNT}} \frac{2 \varphi_{\text{max}}}{2 \varphi_{\text{max}}} = l_{\text{CNT}} \frac{\sin \varphi_{\text{max}}}{\varphi_{\text{max}}}.$$

$X_{\text{CNT}}(\varphi_{\text{max}})$ represents the CNT alignment well. For instance, when $X_{\text{CNT}}$ is a maximum ($\varphi_{\text{max}} = 0^\circ$), all CNTs are perfectly aligned along the $x$-axis. On the other hand, when $X_{\text{CNT}}$ is a minimum ($\varphi_{\text{max}} = 90^\circ$), the CNTs are randomly oriented.

We now consider the effect of CNT alignment on $G_s$ in terms of $X_{\text{CNT}}(\varphi_{\text{max}})$. When $X_{\text{CNT}}$ is small, more CNTs forming a connection between Electrode 1 and Electrode 2 are required than aligned CNTs. In this case, CNTs form the conduction paths that contain more contact points than aligned CNTs, and $G_s$ decreases with $X_{\text{CNT}}$. Figure 3(a) shows that $G_s$ can be well fitted by $G_s(\varphi_{\text{max}}) = a_1 X_{\text{CNT}}(\varphi_{\text{max}}) + \beta_1$ near $\varphi_{\text{max}} = 90^\circ$ ($a_1$ and $\beta_1$ are fitting parameters) as shown by the solid curves. Thus, $G_s$ decreases monotonically with increasing $\varphi_{\text{max}}$ due to the effect of the decrease in $X_{\text{CNT}}$.

We next consider the physical origin of the dips indicated by the red arrows in Fig. 3(a) near $\varphi_{\text{max}} = 30^\circ$. The dips are due to the peaks in $R_{\text{cont}}$ around $\Theta = 30^\circ$ and $150^\circ$ in the case of $(10,10)-(10,10)$ CNT contact, which was not previously taken into account. To clarify this, we compare the dependence of $G_s$ on $\varphi_{\text{max}}$ for our model and the constant $R_{\text{cont}}$ model previously reported. In the constant model, $R_{\text{cont}}$ is independent of the contact angle and takes a fixed value. We also calculate the dependence of $G_s$ on $\varphi_{\text{max}}$ with the constant $R_{\text{cont}}$ model for the same range of $\sigma$ and show the result in our supplementary materials as shown in Fig. S3. The similarity between two models is that $G_s$ has the maximum by the adjustment of CNT alignment. On the other hand, no dips in $G_s$ are seen in the constant $R_{\text{cont}}$ model (see Fig. S3 in our supplementary materials). Near $\varphi_{\text{max}} = 30^\circ$, most of CNTs tend to intersect with incommensurate
incommensurate junction and form a high-resistance network. We therefore suggest that for the design of high-conductance CNT thin films, it is essential that CNTs do not intersect with the incommensurate junctions.

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