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Electrical conductivity of carbon-nanotube/cellulose composite paper

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We fabricated multiwalled carbon-nanotube/cellulose composite papers and measured their temperature dependences of electrical conductivity. The dependences were described with the Sheng's fluctuation-induced tunneling (FIT) model. A possible mechanism of the electrical conduction in the composite paper was discussed in the context of the FIT model.

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I. INTRODUCTION

Carbon-nanotubes (CNTs) are considered to be a new class of material with reduced dimensionality. They have unique properties such as high mechanical strength, as well as high thermal and electrical conductivity. Much work has been done on CNT composites as well as on CNT sheets to fully utilize these properties for many kinds of applications.¹⁻³ To control their electrical conductance, the electrical conduction mechanism of CNT composites needs to be elucidated, and, to do this, the temperature dependences of electrical conductivities for CNT composites are very useful.^{4,5}

There are two major mechanisms of electrical conduction for composite materials: variable range hopping (VRH) (Ref. 6) and fluctuation-induced tunneling (FIT).⁷ The VRH model matches the electrical conductivities of single-walled (SW) CNT mats⁸ and networks,^{9,10} while the FIT model matches those of SWCNT mats,^{11,12} SWCNT bundles,¹³ and SWCNT/polymer composites.⁸ On the other hand, the FIT model matches the electrical conductivities of multiwalled (MW) CNT composites.¹⁴⁻²⁰ The electrical conduction through the CNT-CNT junctions dominates the conductivity of CNT network in the FIT model. The tunnel width w and barrier height V_0 can be estimated from two specific temperatures T_0 and T_1 obtained by fitting the FIT law to the measured temperature dependence of the conductivity. However, only a few papers reported w and V_0 . Kim *et al.*¹¹ estimated a w of 3.5 nm and a V_0 of 0.1 eV for a SWCNT network, while Mdarhri *et al.*¹⁹ estimated a w of 5 nm and a V_0 of 15 meV for MWCNT composites. These heights and widths seem to be too low and wide to be clearly explained. Salvato *et al.*¹³ reported the barrier height dependence on the current and temperature in SWCNT bundles. The physical reason of this phenomenon is still unclear.

We report the temperature dependence of electrical conductivities for recently fabricated MWCNT/cellulose composite paper, a new kind of CNT composite,²¹ and discuss the possible conduction mechanism obtained by using rigorous calculations of T_0 and T_1 in the FIT model.

II. FABRICATION AND MEASUREMENT METHODS

The CNTs used in this work were MWCNTs, the Nanocyl 7000, fabricated by Nanocyl SA. The average diameter of the CNTs was 10 nm, and the average length was 1.5 μm . A 1%-CNT water dispersion was provided by Daido Corporation. Anionic surfactant was used to disperse CNTs.²² Pulp fibers have negative charges because they generate carboxyl groups during the cooking and bleaching involved in making paper making.²³ The Coulomb repulsion prevents CNTs from fixing on pulp fibers. Therefore, a cationic fixer should be applied to fix the CNTs to the pulp.

Bleached hardwood Kraft pulp (50 wt %) and bleached softwood Kraft pulp (50 wt %) were dispersed in water and beat was obtained. A fixer of 2%-cationized starch water solution was then added to the pulp and mixed with the 1%-CNT dispersion. Hand-made CNT/cellulose composite paper was prepared using a $25 \times 25 \text{ cm}^2$ wire cloth. A scanning electron microscope (SEM) image is shown in Fig. 1. A CNT network was formed on the surface of cellulose fiber.

We prepared three samples of paper with different CNT contents of 1, 4, and 5 wt %. The CNT content was calculated by dividing the weight of CNTs by the total weight of CNTs and cellulose because it could not be determined by thermogravimetric analysis with sufficient accuracy. The thickness of the paper was 0.15 mm.

The electric conductivity was measured by a four-probe method with a source meter (Keithley 2636A). Small pieces of indium were bonded to the samples to ensure that there

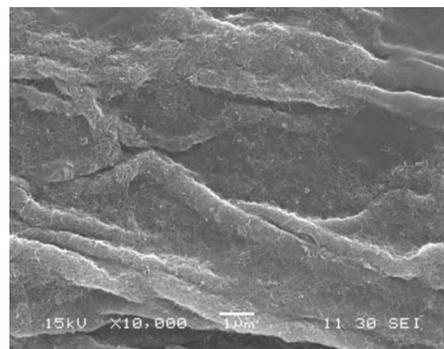


FIG. 1. SEM image of MWCNT/cellulose composite paper.

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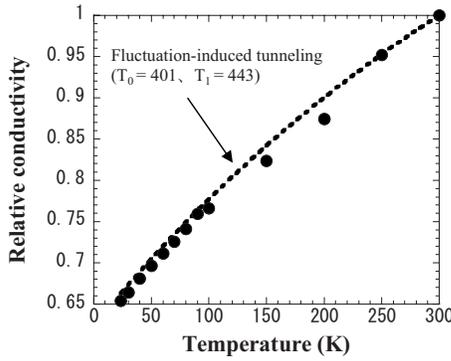


FIG. 2. Measured temperature dependence of electrical conductivity normalized with conductivity at 300 K.

was proper contact with the probe. The current was increased from 0 to 0.1 mA to check the linearity of current-voltage characteristics. The temperature was increased from 10 to 300 K.

III. RESULTS AND DISCUSSION

The temperature dependences of electrical conductivity normalized with the conductivity at 300 K for the composite paper with a CNT content of 1 wt % are shown in Fig. 2. According to the Sheng’s FIT model,⁷ the conductivity is expressed as

$$\sigma = \sigma_0 \exp\left(-\frac{T_1}{T + T_0}\right), \quad (1)$$

where T_0 and T_1 are the specific temperatures. The measured temperature dependence of electrical conductivity can be fitted to the FIT model with $T_0=401$ K and $T_1=443$ K as shown by the dotted line in Fig. 2. The same procedure revealed that $T_0=602$ K and $T_1=543$ K for 4 wt % and $T_0 = 105$ K and $T_1=192$ K for 5 wt % composite papers.

The T_0 and T_1 obtained from our measurements with those reported in Refs. 8, 11, 13–17, and 20 are shown in Fig. 3. The probability for tunneling at the Fermi energy through a junction between two CNTs is proportional to $\exp(-T_1/T_0)$. The dotted lines in Fig. 3 correspond to constant tunneling probabilities. Our T_0 and T_1 were close to those for SWCNT composites⁸ and MWCNT composites.^{14,16,20} As mentioned before, the tunnel width w

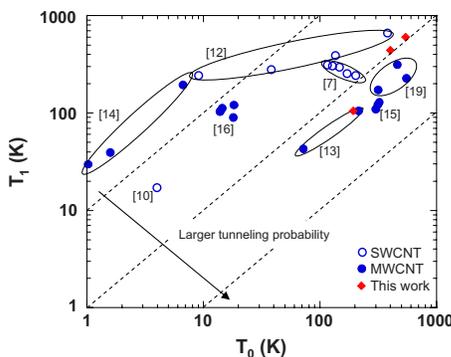


FIG. 3. (Color online) Comparison of our T_0 and T_1 with those reported in literature (Refs. 8, 11, 13–17, and 20) Dotted lines correspond to constant tunneling probabilities.

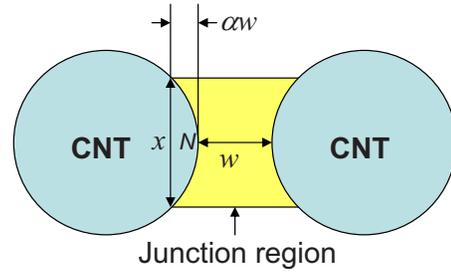


FIG. 4. (Color online) Cross section of junction model used for calculations.

and barrier height V_0 can be estimated from T_0 and T_1 . Kim *et al.*¹¹ and Mdarhri *et al.*¹⁹ used approximate expressions for T_0 and T_1 . Since there are three unknown parameters (w , V_0 , and the junction area A) in the two equations, we cannot determine these values uniquely. Applying the equations to our values of T_0 and T_1 leads to $wV_0^{1/2}=1.37 \times 10^{-10}$. When we assume V_0 to be 4.4 eV [the work function of MWCNT (Ref. 24)], w becomes 0.065 nm. This is an unrealistic value because it is smaller than the distance between two carbon atoms in the hexagonal cell.

We then estimate w , V_0 , and A on the basis of a junction model and rigorous calculations of Sheng’s model. According to the FIT model,⁷ the specific temperatures are

$$T_1 = a\varepsilon_0^2/k, \quad (2)$$

$$T_0 = T_1/2xw\xi(0), \quad (3)$$

where $a=wA/8\pi$ is the junction volume, w is the tunnel width, A is the junction area, k is the Boltzmann constant, and $x=(2mV_0/\hbar^2)^{1/2}$ is the tunneling constant. Here, $\xi(0)$ is defined as follows:

$$\xi(0) = \int_{u_3}^{u_4} \left[1 - \frac{\lambda}{u(1-u)}\right]^{1/2} du, \quad (4)$$

where $u_3, u_4 (>u_3)$ denotes the two zeros of potential $V(u, \varepsilon)$, and $\lambda=0.795e^2/4wKV_0$ with K being the dielectric constant of the barrier region. In (2), ε_0 is the electric field at which the potential maximum equals to 0. Refer to Sheng’s paper⁷ for more detail.

A crosssection of the junction region we used as a model is shown in Fig. 4. The CNT surface belonging to the junction region is defined as an arc whose ends are laterally apart from the point N by αw . The junction area A is defined as x^2 . The diameter of CNT was assumed to be 10 μm . The dielectric constant of the barrier region K was assumed to be 1.

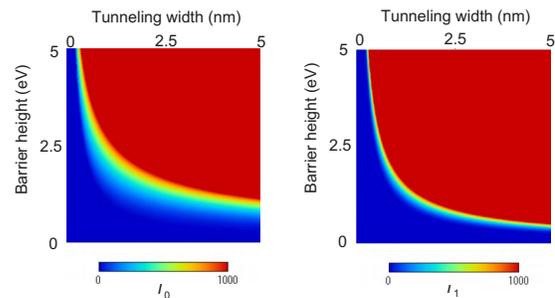


FIG. 5. (Color online) Example of calculated T_0 and T_1 in w - V_0 plane.

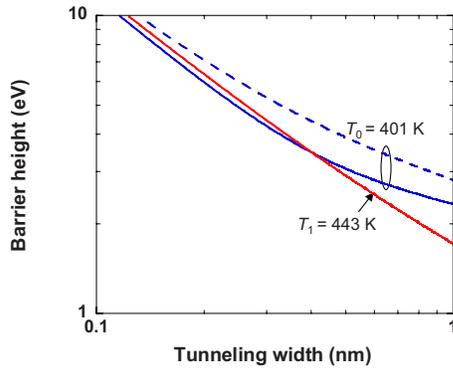


FIG. 6. (Color online) Magnified view of Fig. 5.

An example of calculated T_0 and T_1 in the w - V_0 plane Fig. 5. A magnified view of Fig. 5 is shown in Fig. 6. The intersection of the two contours for T_0 and T_1 gives a set of solution for w and V_0 . The dotted line for T_0 shown in Fig. 6 was calculated by assuming that $\xi(0)=1$. The contour for T_0 does not cross the contour for T_1 in the region shown in Fig. 6. This means that an exact numerical calculation is needed to obtain a set of solution for w and V_0 .

Estimated w and V_0 are summarized in Fig. 7, where the symbols denote w and V_0 calculated with T_0 and T_1 described above and the regions enclosed by the dotted line using $a=0.01$ correspond to w and V_0 that match the measured conductivity within 1% standard-deviation uncertainty. No distinct dependence of w and V_0 on the CNT fraction was observed. The w and V_0 were close to the interlayer distance of graphite (0.34 nm) and the work function of MWCNT (4.4 eV). The uncertainty ranges for w and V_0 are very narrow. Since almost all the surfactant had been removed in the paper making process and the sizes of cellulose fibers were much larger than the estimated w , two CNTs are thought to form a junction with no inclusion. The electrical conduction described in our composite paper was dominated by such CNT-CNT junctions. Although the junction model is simple, this is a reasonable consequence. Fuhrer *et al.*²⁵ used the first principles method to calculate the tunneling probability of CNT-CNT junction with a distance of 0.34 nm to be 2×10^{-4} . The narrow region between CNTs acts as a potential

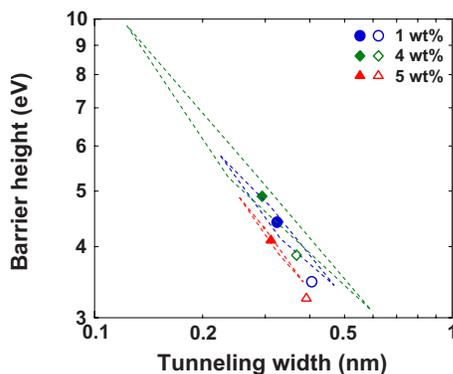
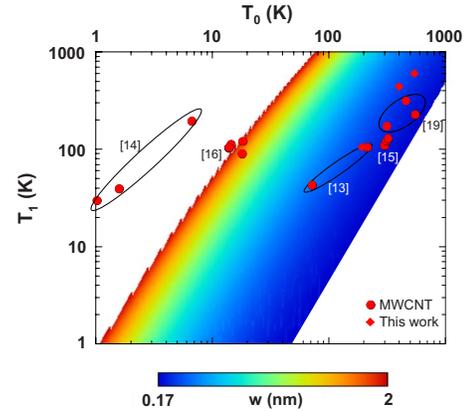


FIG. 7. (Color online) Estimated w and V_0 . Solid and open symbols are calculated with $\alpha=0.01$ and 0.02 , respectively, from T_0 and T_1 that optimally fit measured data to FIT model. Regions enclosed by dotted line for $\alpha=0.01$ correspond to w and V_0 that reproduce measured temperature dependence of the conductivity within 1% standard deviation.

FIG. 8. (Color online) Map of tunneling width w in T_0 - T_1 plane.

barrier. It is quite natural to think that V_0 equals the work function of MWCNT. The calculation with $\alpha=0.01$ suggests that w was around 0.3 nm smaller than the interlayer distance of graphite. Crossed MWCNTs might be deformed at the junction as calculated by the first principles method.^{25,26}

A map of the tunneling width w in the T_0 - T_1 plane is shown in Fig. 8. Here, the barrier height V_0 was decreased from 25 to 5 eV. $\alpha=0.01$ and $K=1$. The T_0 and T_1 reported in the literature^{14-17,20} also are plotted in Fig. 8. It is noted that the exact area of the junction should be calculated with the first principles method and the accuracy of the map should be improved in future work. However, the present map of the tunneling width w may be useful for qualitatively elucidating the properties of CNT networks.

IV. CONCLUSION

In summary, we fabricated MWCNT/cellulose composite papers and measured their temperature dependences of electrical conductivity. The dependences were described with the Sheng's FIT model. The tunneling widths and barrier heights were estimated from the specific temperatures T_0 and T_1 deduced from rigorous calculations with a simple junction model. The estimated widths and barrier heights were close to the interlayer distance of graphite and the work function of MWCNT. This suggested that the electrical conduction in MWCNT/cellulose composite paper was dominated by the FIT between the CNT-CNT junctions and there was no inclusion.

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