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Examining the structural contribution to the electrical character of single wall carbon nanotube forest by a height dependent study

Takayuki Watanabe [b], Hiroe Kimura [b, d], Shigeki Hano [b, d], Shunsuke Sakurai [a, b], Motoo Yumura [a, b], Kenji Hata [a, b, c, d, **], Don N. Futaba [a, b, *]

[a] CNT Application Research Center, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, 305-8565, Japan
[b] Technology Research Association for Single Wall Carbon Nanotubes (TASC), Tsukuba, 305-8565, Japan
[c] Japan Science and Technology Agency, c/o AIST, 34 Miyukigaoka, Tsukuba, Ibaraki 305-8501, Japan
[d] Tsukuba University, Department of Pure and Applied Sciences, Tsukuba University, Tsukuba, 305-8573, Japan

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A B S T R A C T

We report an electrical investigation of single-wall carbon nanotube (SWCNT) forests where we have succeeded in elucidating the electrical contributions of the forest surface (cap) and vertically aligned (body) structures of the assembly. We applied an electrical characterization method to SWCNT forests patterned into a Hall bar-like configuration to reliably evaluate the lateral (i.e. in-plane) resistance for a series of SWCNT forests spanning three orders of magnitude, 0.3–700 μm, in height while avoiding direct mechanical contact to the measurement region. A simple model based on treating the forests as two parallel resistors was used to explain the observed behavior of the lateral resistivity and forest height. Through this approach we showed that the forests could be described electrically by two structural features, the cap and body. In addition, our analysis found that the resistivity of the body was about 22–720 times higher than that of the cap.

1. Introduction

The electrical properties are an important aspect of carbon nanotubes (CNTs), and extensive research has been carried out investigating the electrical properties of CNTs from isolated CNTs [1–3] and macroscopic forms, such as buckypaper, sponges, fibers [4–11] etc. Among the various forms of CNTs, the forest is unique where the CNTs, when grown efficiently, self-assemble to vertically stand on the substrate. The as-grown forest is very sparse, anisotropic, and the majority of the volume (>90%) is open space [12]. The CNT forest has been extensively studied to possess various interesting properties and applications exemplified by strain sensors [13,14], temperature invariant viscoelastic material [15], aerogel muscles [16,17], strong adhesive tapes [18,19], stretchable conductors [20–22], optical light conversion to current [23] and so on. Moreover, CNT forests are envisioned a promising approach for the mass production of single-wall carbon nanotubes, and an industrial production plant for the continuous synthesis of SWCNT forests has recently been constructed and in operation.[1] In this sense, characterization of the CNT forest property is important. Yet, the fragile nature of the SWCNT forest structure makes reliable characterization of the electrical properties difficult. There have been several reports investigating the electrical characterization of CNT forests [24–27]. For example, Wang et al. demonstrated the increasing electrical anisotropy with decreasing temperature for a 5 μm-tall multi-walled carbon nanotube (MWCNT) forest using four and two probe method, respectively [24]. Okamoto et al. extended this anisotropy measurement to >1 mm tall MWCNT forests and observed that electrical conduction was dominated by 3D Mott variable range hopping [25]. Further, Lin et al. demonstrated height dependent electrical property for SWCNT forests showing that the out-of-plane conductivity was independent of thickness [26]. The scarcity of reports highlights, in part, the difficulty in reliably characterizing such a highly sparse and fragile

* Corresponding author. CNT Application Research Center, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, 305-8565, Japan.
** Corresponding author. CNT Application Research Center, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, 305-8565, Japan.
E-mail addresses: kenji-hata@aist.go.jp (K. Hata), d-futaba@aist.go.jp (D.N. Futaba).

[1] http://www.zeon.co.jp/press_e/151111.html.

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material without the need for deposited materials or direct mechanical contact to the measurement region.

From a structural standpoint, the CNT forest assembly has been extensively examined. Zhang et al. showed that the SWCNT forest is not a homogeneous unit [28]. It was shown that in the early stages of growth, a random mat of laterally entangled, non-aligned SWCNTs emerge followed by the self-assembly of SWCNTs into vertical alignment. As such, the SWCNT forest consists of this entangled network at the top (cap) seamlessly connected to the vertically aligned body (body). Therefore, the structure of the SWCNT forest is complex and inhomogeneous. Although the anisotropy of the forest resistivity and mechanisms of electron flow for intermittently contacting CNTs have been reported [24–27], there have been no reports to address the relative contributions of the well-known forest structures (cap and body) to the overall lateral electrical resistivity. We believe this may stem from the absence of an approach which affords reliable measurement across a wide range of resistances for forests spanning a wide height range.

In this paper, we report an electrical investigation of SWCNT forests where we have succeeded in elucidating the electrical contributions of the cap and body structures of the forest assembly. We propose an approach which combines a well-known electrical characterization technique, which is used to measure the Hall effect [29–31], with SWCNT forests patterned into a Hall bar-like configuration to allow the four-terminal measurement of the lateral (i.e. in-plane) resistance for the fragile material while not contacting the measurement region. We applied this to a series of SWCNT forests spanning three orders of magnitude in height, 0.3–700 μm. Most reports, to date, on the characterization of the SWCNT forest electrical properties rely either on two-probe method or direct contact to the measurement area, or both [26,32–34]. Without the effect of contact resistance and direct mechanical contact to the measurement region, we could characterize the electrical resistivity of the forest allowed accurately, reproducibly, and across a wide measureable range. By constructing a simple model based on treating the forests as two parallel resistors, each of which represented the two basic structures of the forest (cap, body), we could explain the observed sigmoidal relationship between the lateral resistivity and forest height. Further, our results revealed that both structures, cap and body, contribute to the overall forest resistance and dominate in short and tall height regimes, respectively.

2. Experimental

2.1. Sample preparation

SWCNT forests were synthesized in a 1 inch tube furnace by water-assisted chemical vapor deposition using a C_2H_4 carbon source on Si substrates with a sequentially sputtered Fe/Al2O3 catalyst (1.6 nm/40 nm) as described previously [35]. He and H_2 were used as carrier gases at a total flow of 1000 standard cubic centimeters per minute (sccm) at 1 atm with a controlled amount of water vapor (concentration 100–150 ppm). The heights of the SWCNT forests synthesized were controlled three orders of magnitude from 0.3 to 700 μm by controlling growth time length. No other growth conditions were changed to limit the structural changes to the forest height. Each forest within our series of SWCNT forests possessed an average diameter of ~3.0 nm, carbon purity over 99.99%, single-wall selectivity over 95% and carbon impurity level less than ~5%, based on the high specific surface area (>1100 m^2/g) [36]. It should be noted that previous evaluations of the SWCNT forest homogeneity by Raman line mapping along the length of the CNT have demonstrated nearly identical radial breathing mode (RBM) profiles indicating that no change in structure (e.g. diameter) has occurred [12]. We have not observed any increase diameter or wall number as reported previously [37].

For measurement, the ability to pattern the forest into a Hall bar configuration played a critical role in our ability to characterize resistivity. Each forest in the series was patterned into a Hall bar-like configuration as shown in Fig. 1 (a, b) using a commercial laser marker (Keyence MD-V). To cut the forest and minimize unwanted damage, the scanning speed was set to less than 10 mm/s and the cutting pattern was iterated up to 20 times. For each forest, the laser power was adjusted between 20% and 100%. The frequency of Q switch was fixed to 200 kHz for all samples. Shorter forest required higher laser power and iterations due to heat loss into the substrate. After the cutting process, the unnecessary sections were then removed from the substrate by a tweezer and adhesive tape (Supplementary information). The sample structure is similar to an "H" shape with its two additional extensions to serve as electrodes for voltage measurement while the left and right sections of "H" served as electrodes for the application of current as shown in Fig. 1(a). The area (3 × 4 mm) indicated by the dashed lines in Fig. 1(b) served as the measurement region. The homogeneous voltage distribution (green) in the measurement area confirmed, as determined by solving the Poisson equation, that the aspect ratio of the measurement region was sufficient to provide a uniform lateral voltage distribution as required for accurate measurement (Fig. 1(c)).

2.2. Electrical measurements

Electrical measurement of the forest in lateral orientation was performed using the four-terminal method with a commercial probe station (CASCADE microtech summit 1200) and a commercial semiconductor parameter analyzer (Agilent 4155C). Unless otherwise indicated, all resistance and resistivity data discussed in this paper refers to lateral (in-plane) resistance and resistivity. It should be noted that the ranges of applied current were adjusted based on forest height to avoid resistivity change through heat generation and to achieve a high signal to noise ratio (Fig. 1(d)). All electrical measurements were done in atmosphere and at room temperature (~298 K).

2.3. Merits of this approach

Our method possesses several advantages over previous methods to characterize the SWCNT forest electrical properties [32–34]. First, by patterning the forests into a Hall bar-like configuration (Fig. 1(a)), our approach separated the electrode contact region and the measurement region to avoid any structural change or the need for coatings in contrast to previous reports [24,26]. This point was confirmed experimentally by repeated contact/retract/re-contact cycles and found an exceptionally small variation (less than 1%) and was significant because, by volume, the SWCNTs occupy only ~3.6% of the forest [12]. Second, our method does not require specialized equipment, such as a vacuum chamber or AFM, and only requires a current meter and voltmeter. Third, our method utilizes the four-terminal method, which is not affected by contact resistance, and therefore, affords accuracy, reliability, and wide measurable range.

3. Experiment measurement results

To begin, the series of SWCNT forests were observed by scanning electron microscopy (SEM), to characterize the various height (Fig. 2(a)). As mentioned, the range of heights of our SWCNT forests spanned three orders of magnitude from 0.3 to 700 μm. One