Electrically Stable Carbon Nanotube Yarn Under Tensile Strain

Tuan-Khoa Nguyen, Toan Dinh, Hoang-Phuong Phan, Canh-Dung Tran, Abu Riduan Md. Foisal, Yong Zhu, and Dzung Viet Dao

***Abstract*—We report a highly stable electrical conductance of a compact and well-oriented carbon nanotube yarn under tensile strain. The gauge factor of the yarn was found to be extremely small of approximately 0.15 thanks to the improvements in the dry spinning process, including multi-web spinning and heat treatment. The threshold strain ε_s, below which the yarn retains its electrical conductance stability, has been also determined to be approximately 15×10^3 ppm. Owing to its highly stable resistance under mechanical strain, the yarn has a good potential as a wiring material for niche applications, where light weight and resistance stability are required.**

***Index Terms*—Carbon nanotube yarn, Dry spinning, Gauge factor, Piezoresistive effect**

I. INTRODUCTION

SINCE the first discovery by Iijima in 1991 [1], carbon nanotubes (CNT) have attracted a rapidly increasing attention owing to their unique properties including the ultra-high mechanical strength [2]–[4], high electrical and thermal conductivity, low mass density [5], and high current carrying capacity [6]. To date, a great number of studies have been carried out to integrate CNT films, sheets, and yarns to micro structures, utilizing the superb properties of CNTs into new functionalities. For instance, a CNT film can be utilized in MEMS (Micro Electro-Mechanical Systems) for mechanical sensing by a top-down fabrication [7], patterned by an electron beam lithography to form a flexible hinge of a mirror [8], or embedded in a micro-thermoelectric device, which can be deployed in self-powering low consumption portable devices [9]. Moreover, CNT yarns and sheets have also been tailored for a broad range of applications including high performance supercapacitors, actuators, and lightweight electromagnetic shields [10]. Nanocomposite CNT fibers was demonstrated with a chromatic response to electrical current, where its color change could be observed by naked eyes [11]. Additionally, CNT yarns are potentially exploited as electrical wiring thanks to significant improvements of their electrical conductivity, mechanical robustness, and light weight. There are several approaches to enhance the conductivity of CNT yarns, including doping metal particles [12], self-assemble in a tube reactor operated at high temperature and then condense in liquid [13], coating polymer [14], and diamond wire-drawing dies [15]. The production of CNT yarns could be greatly scaled up by using a multi-hole spinning process [5]. Owing to their superior properties, CNT yarns have a potential to become a wiring material that can replace metals in niche wiring applications, such as aviation and aerospace, microscopic wires in electronics, and data cables [6].

This letter reports an extremely small gauge factor (GF) of the as-made CNT yarn, exhibiting its excellent stability of the electrical conduction under tensile strain. The GF of our as-made CNT yarn, found approximately 0.15, is the smallest value among the CNT yarn GFs in the literature to date [16]–[20]. The improvements in the synthesis of the CNT yarn including the use of a capstan rods system and heat treatment are considered to be the decisive factors for the electrical stability of the CNT yarn. The mechanism of the electrical conduction in the as-made CNT yarn will also be discussed, using a model of tunneling and percolating conductions.

II. SYNTHESIS OF CNT YARN AND GAUGE FACTOR MEASUREMENT

The synthesis of the CNT yarn from a multi-walled carbon nanotubes (MWNTs) forest grown on silicon wafers by Chemical Vapor Deposition (CVD) process was shown in Fig.1 (a). CNT fibers in the forest were pulled out into continuous CNT webs which were then twisted into a highly compact CNT yarn. The CNT yarn was spun from two split webs through a capstan rods system which gradually transfers the tension and torque to the twisting yarn.

The webs connected at the first rod of the capstan rods systems, forming the 2-plied twisted yarn instead of a single-ply twisted yarn. That would yield a higher tensile strength of the yarn which is approximately 20% stronger than that of the single twisted yarn. This is attributed to the elimination of both snarling and unbalance twisting phenomena which occur in single highly twisted yarn as discussed in [21].

After being pulled out from the CNT forests, the CNT webs were heated in a furnace by ambient air where the temperature can be adjusted in the range of 200-600°C. The heat treatment was introduced in the web zone to control the Van der Waals force which dictates the web formation [22]–[24]. Raravikar *et at.* and Zhang *et at.* investigated the mechanism of the Van der Waals force acting on the inter-tubular CNT interactions, which controls the formation of CNT bundles and webs as well as the compaction of CNT yarns [23], [24]. Additionally, the magnitude of the Van der Waals force is strongly dependent on thermal load and temperature of CNT fibers. The Van der

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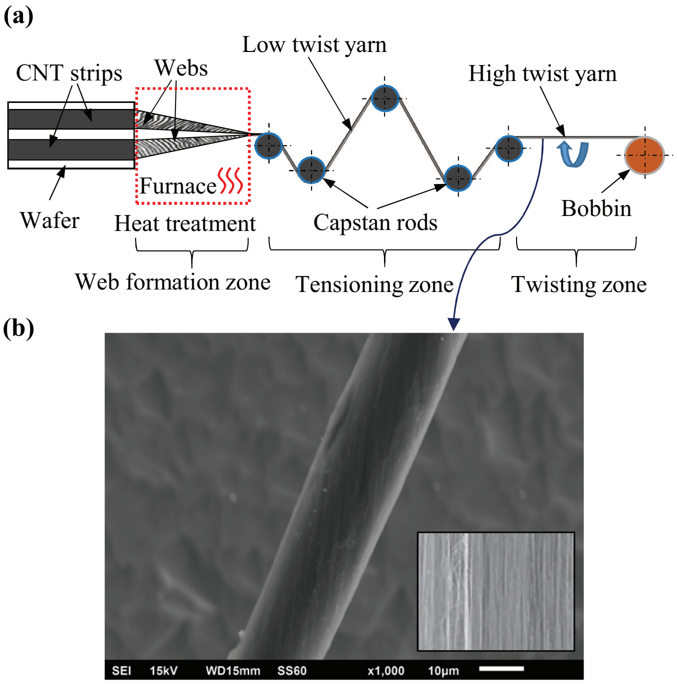

Fig. 1. a) CNT yarn formation by twisting CNT webs through the capstan rods system. b) Scanning electron microscope (SEM) image of the as-made CNT yarn. Inset: Highly aligned CNT web.

Waals interaction plays a role as the friction force between CNT fibers; therefore, reducing this force by heat treatment would facilitate the smooth drafting of each CNT fiber through the twisting system, making the yarn more compact and better-aligned under radial pressures from the tension (Fig.1 (b)). Evidently, the use of heat treatment has a significant impact on the yarn's conductivity, increasing the conductivity from $5{\times}10^4$ S/m to $3.1{\times}10^5$ S/m. The length of CNTs in the forest is in the range of 300-400 μm, and their diameter varies from 7.5 to 8.5 nm. The twist factor and the speed of twisting are 8,000 turns-per-meter (TPM) and 6 meter-per-hour (m/h), respectively. The twisted CNT yarn has an outer diameter of 12 μm (Fig.1) with the measured tensile strength in the range of 0.97-1.4 GPa, which is about three times higher than that of some conventional metals used in wiring applications. Additionally, the Young's modulus of the CNT yarn was found to be in the range of 15-17 GPa.

In the tensile experiment, two ends of a 20 mm-length CNT yarn were attached on to two separate pieces of paper by silver epoxy (Inset of Fig.2 (a)). The linear current-voltage characteristics indicates a good Ohmic contact of the electrodes to the CNT yarn at different applied strains (Fig.2 (a)). The tension was applied to the yarn via two pieces of paper instead of directly clamping the yarn, eliminating the stress concentration at two ends of the yarn. Aluminum wires of 20 μm diameter were used to electrically connect the two ends of the yarn to a multimeter, avoiding unexpected tension to the yarn.

III. RESULTS AND DISCUSSION

The resistance versus strain response of the CNT yarn was measured by the four-point probe measurement (Fig.2 (b)).

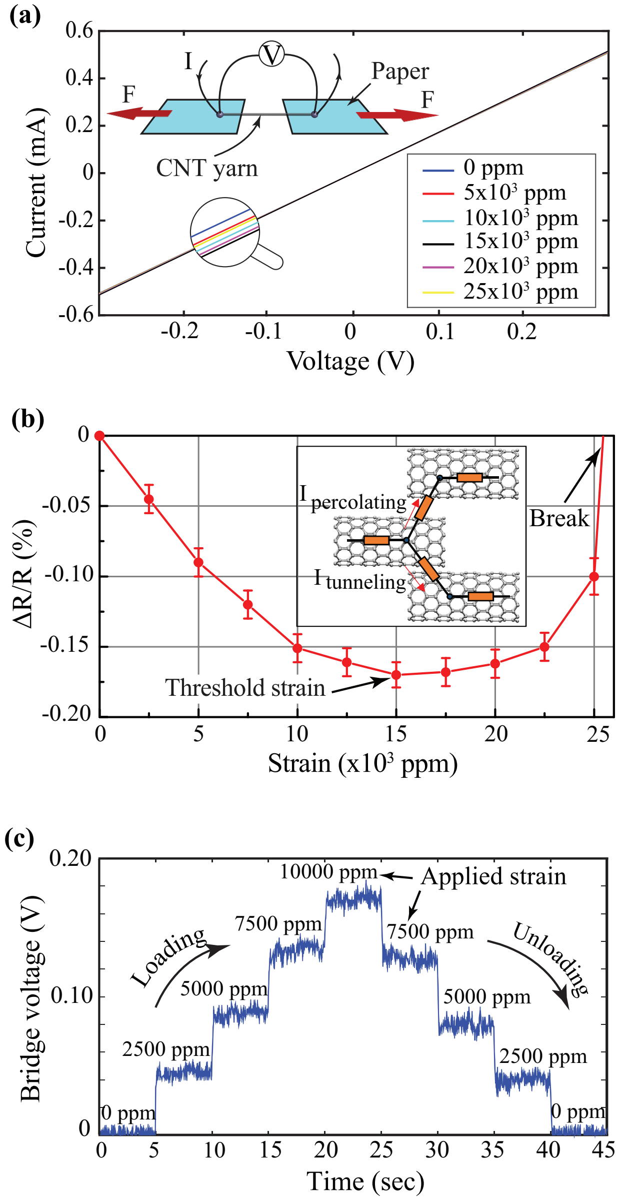

Fig. 2. a) I-V characteristics of the CNT yarn at different strains from 0 to 25 $\times 10^3$ ppm. Owing to the extremely small gauge factor of the yarn, the measured I-V lines are almost coincident. Inset: Configuration of the resistance versus strain measurement. b) Real time bridge voltage in tensile loading cycles of CNT yarn with different strains applied to the yarn. c) The resistance change of CNT yarn under tensile strain was measured by the four-point probe measurement using Agilent$^{\text{TM}}$344110A multimeter. The gauge length of the tested samples is 20 mm. Inset: Analysis model of the conductance through adjacent CNTs in the as-made CNT yarn.

Accordingly, the GF of the as-made yarn was found approximately 0.15, which is one order of magnitude smaller than that of most conventional metals used in wiring application and two orders of magnitude below that of some common semiconductor materials [25], [26]. The measured GF of the as-made yarn is in good agreement with a previous result [17]. This means that the as-made yarn could well retain its resistance under tensile strain. The extremely small GF in the as-made CNT yarn, comparing to other carbon-based materials [27], [28], also indicates its potential for wiring applications

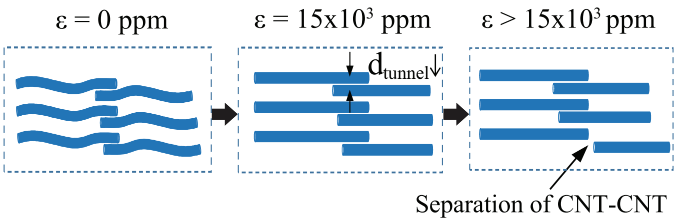

Fig. 3. A schema of the effect of tensile strain to the CNT-CNT fiber junctions.

where the effect of strain to electrical conductance is required to be negligible.

There are two main factors contributing to the extremely small GF of the as-made yarns. Firstly, the heat treatment at the web decreased the Van der Waals interaction between CNT fibers in the web before smoothly drafted through the twisting system, making the yarn more compact and well-oriented. It should be pointed out that the heat treatment also burned contaminants including amorphous carbon inside the CNT yarns, yielding higher homogeneous characteristics through the CNT yarn. The elimination of amorphous carbon also resulted in the stability of the electrical conductivity of the yarn. Secondly, by using the capstan rods system, the yarn was subjected to a gradually increasing tension and torque, improving the alignment of CNT fibers in bundles. Therefore, this would minimize changes in CNT-CNT junctions under strain, resulting in the highly stable resistance as well as the extremely small GF of the yarn.

In order to examine the repeatability and stability of the yarn's resistance, two ends of the CNT yarn were also connected to the Wheatstone circuit, amplifying the output voltage signal 110 times. The output voltage during the loading and unloading cycles (Fig.2 (c)) evidently indicates a good repeatability of the resistance of the yarn.

The mechanism of the electrical conduction in the CNT yarn under applied strain will be discussed as follows. In a CNT network the conduction occurs through either along individual CNT fibers and across CNT-CNT junctions [29]. Since the load transfer between individual CNT fibers is relatively weak due to their Van der Waals interaction force [30], it is expected that the contribution of piezoresistivity of CNTs themselves to the total piezoresistivity of CNT yarns is insignificant [31]. Therefore, the variation of conduction across CNTs junctions is considered as the dominant factor for the change of conductivity of CNT yarns [32].

The tunneling resistance in a CNT yarn is derived through Simmons's theory for tunneling resistance, given by [31]:

$$R_{tunnel} = \frac{V}{AJ} = \frac{h^2 d}{Ae^2\sqrt{2m\lambda}} exp(\frac{4\pi d}{h}\sqrt{2m\lambda}) \sim \frac{1}{\sigma_t}$$

where J is the tunneling current density, V is the electrical potential difference, h is the Planck's constant, d is the tunneling distance, A is the contact area of the junction between adjacent CNT fibers, e is the elementary charge, m is the mass of electron, λ is the height of barrier, λ=0.6 eV. From the tunneling resistance equation, it can be seen that R_{tunnel} is exponentially dependent on the tunneling distance d between adjacent CNTs. The effect of tensile strain to the resistance of the CNT yarn can be explained from the yarn mechanics as follows. When a force is applied to a twisted yarn, the axial tension radially compacts the yarn [3]. This radial compaction simultaneously lowers the distance between adjacent CNT fibers and increases the contact area of the CNT-CNT junctions [33]. Therefore, at a certain tensile strain range, the resistance of the yarn would decrease with the increasing applied strain. From Fig.2 (b), it can be clearly seen that the yarn's resistance initially decreases with the increase of tensile strain up to 15×10^3 ppm. At the induced strain of 15×10^3 ppm, the resistance reaches the smallest value before reversely increases. This strain is considered as the threshold strain of the as-made CNT yarn. The effect of tensile strain to the CNT-CNT junctions is hypothesized in Fig.3. Initially, when the CNT yarn is elongated in the range from 0 ppm to the threshold strain $\varepsilon_s = 15\times10^3$ ppm, individual CNTs are straightened by tension. As a result, the tunneling distance d between adjacent CNTs is decreased along with the increase of the contact area of CNT junctions A as aforementioned above. This yields a reduction in the tunneling resistance R_{tunnel}. On the other hand, the percolation resistance remains almost unchanged due to the fact that the CNT yarn was highly compact and there is an insignificant variation in the number of CNT-CNT contact points. The combination of these two resistance changes could explain the linear decrease of yarn's resistance under tensile strain despite the exponential relationship between R_{tunnel} and d. When the applied strain reaches 15×10^3 ppm, the tunneling distance d possibly reaches its minimum threshold, then R_{tunnel} stops decreasing. In the tensile strain range higher than the threshold strain, as the induced strain is not equally distributed among CNT fibers, there are a number of CNT-CNT junctions separating due to experiencing higher tensile strain (Fig.3 (c)), resulting in the increase of the yarn's resistance until it breaks.

IV. CONCLUSION

The use of capstan rods and heat treatment at the web improved the orientation and compactness of the as-made yarn. This results in the extremely small variation of resistance under tensile strain, showing the GF of approximately 0.15. For such applications requiring a highly stable resistance, the tensile strain applied to the yarn should not exceed the threshold strain of 15×10^3 ppm. In the future, improvements of the electrical conductivity are demanded to be carried out, enabling the yarn to be a wiring material for interconnecting electronic devices.

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