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Magnetoresistance mechanisms in carbon-nanotube yarns

Reza Ghanbari[a], Shaban Reza Ghorbani[a,*], Hadi Arabi[a], Javad Foroughi[b]

[a] Renewable Energies, Magnetism and Nanotechnology Lab, Department of Physics, Faculty of Science, Ferdowsi University of Mashhad, Mashhad, Iran

[b] ARC Centre of Excellence for Electromaterials Science, Intelligent Polymer Research Institute, University of Wollongong, Wollongong, NSW, 2519, Australia

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ABSTRACT

Carbon nanotube (CNT) yarns are novel CNT-based materials that extend the advantages of CNT from the nanoscale to macroscale applications. Herein we have modeled the electrical properties of carbon nanotube yarn as a function of temperature and magnetic field. The conductivity was well explained by 3D Mott Variable Range Hopping (VRH) law at $T < 100$ K. The hopping effective dimension is reduced with increasing of magnetic field. Negative magnetoresistance (MR) was observed at different magnetic field range. A quadratic MR was found at small magnetic fields up to B_{D2}, where a deviation occurred from the quadratic magnetic field dependence of the MR. In the intermediate magnetic field region, the negative MR shows linear magnetic field dependence up to the magnetic crossover field of B_{D1}. It was found that physical parameters such as the localization length and the density of states at the Fermi level are temperature and magnetic field dependent. In addition, a general scaling behavior was found for the MR as a function of $(B/B^*)^{1/3}$, where B^* is a crossover magnetic field.

1. Introduction

Carbon nanotubes (CNTs) have been of considerable interest due to their good electrical, chemical and mechanical properties. The CNTs show high electrical conductivity, thermal conductivity, chemical stability and mechanical strength. These properties are suitable for a broad range of applications including electronic nano-devices, biosensors, chemical microsensors and energy storage [1–3]. Recently, yarn microstructures were prepared to make better use of the CNT features [4–7]. It was found that the conductivity of CNT yarns is around $\sim 10^4$ S/cm and 10^2–10^3 S/cm for single-walled carbon nanotube (SWCNT) yarns and multi-walled carbon nanotube (MWCNT) yarns, respectively [6,8].

Transport mechanisms in CNT are most important for their performance improvements [9–12]. However, the understanding of conduction mechanisms is still not yet completed even after years of research [13,14]. These materials are neither fully amorphous nor entirely crystalline [15], and therefore, the electrical transport in such disorder systems is described by a variety of phenomena such as quasi-one dimensional transport, localization effects, hopping and tunnelling transport [16,17] and percolation [18,19]. The conductivity of CNT yarn depends on the applied magnetic field. Magnetic field studies of the conductivity help investigators achieve a greater understanding of the electron and spin transport.

The mechanisms behind the MR phenomena in organic systems, including CNTs, are explained by different models such as the excitonic pair mechanism model [20], the electron-hole recombination model [21], the bipolaron model [22], the forward interference model (also called orbital magnetoconductivity theory), and the wave-function shrinkage model (WFSM) [23]. The forward interference model will be used to describe the magnetoresistance of the CNT yarns.

In this paper, CNT yarns were studied by measurements of the electrical conductivity as a function of temperature and magnetic field. The results showed that the temperature dependence of conductivity is well explained by 3D Mott-VRH model at $T < 100$ K. Also, the effect of magnetic field on the hopping effective dimension was investigated. Negative MR was observed, the absolute value of which increases with increasing magnetic fields and decreases with increasing temperature. Physical parameters such as the localization length, the density of states and the average hopping length were obtained from the magnetic field dependence of the magnetoresistance. In addition, a general scaling behavior for MR is demonstrated.

2. Experiment

CNT yarn was fabricated as described previously [4,7]. A spinnable-multi walled carbon nanotube forest was synthesized by catalytic chemical vapour deposition (CVD) using acetylene gas as the carbon source [6]. The CNTs typically had diameters of about 10 nm. The CNT yarns were drawn from the forest by pulling and twisting, as described by Zhang et al. [6]. The samples used in this work were single MWCNT yarns 6–10 μm in diameter and having 20,000 turns per meter (TPM)

* Corresponding author.
E-mail address: sh.ghorbani@um.ac.ir (S.R. Ghorbani).

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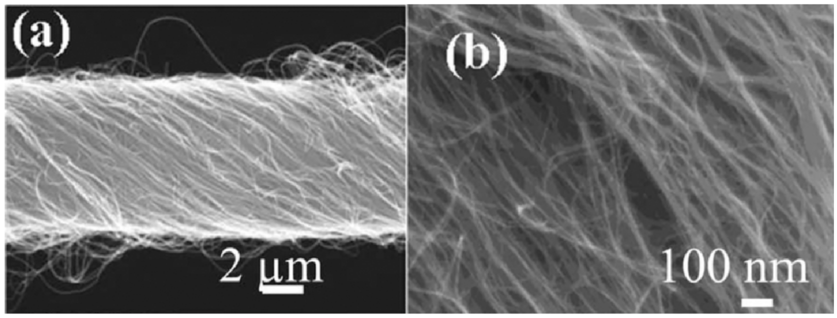

Fig. 1. SEM micrographs of pristine CNT yarn at (a) low and (b) higher magnification [7].

inserted twist. The details of the single MWCNT yarn are given in Ref. [24]. SEM micrographs of pristine CNT yarn are shown in Fig. 1 [7]. The resistivity was measured using a standard four-probe method over a wide range of temperatures from 10 to 300 K and magnetic filed up 10 T by using a physical properties measurement system (PPMS, Quantum Design). The distance between contacts was 0.97 mm. All measured yarns were placed on a Cu block substrate, which was isolated from the yarn by insulating varnish, and four Au wires were attached to the sample using silver paste.

3. Results and discussion

The temperature dependence of the resistivity, ρ(*T*), is shown in the inset of Fig. 2 (inset (a)) for the CNT yarn in the absence of a magnetic field. It can be seen that resistivity is 6 mΩ cm at room temperature and it increase to 10.5 mΩ cm at $T = 5$ K. These values are in agreement with values reported by Wells, et al. for CNT/epoxy composite [25]. But, the resistivity of CNT yarn is a little lower because of the pulling and twisting process.

In most heterogeneous systems, which are composed of partially crystalline regions and disordered regions, the conductivity occurs through tunnelling and hopping [16,26]. In these materials, the charge carriers, which form the polaron structure are localized in the gap region [27]. The conduction shows metallic behavior in the crystalline regions and it occurs in between two metallic domains through hopping [27] (i.e. phonon-assisted tunnelling between electronic localized states centred at different positions [16]). For these systems, the conductivity is well described by the variable-range hopping model [28]. The number of available energy states for hopping decreases with decreasing thermal energy k_BT and therefore, the average hopping length increases [16]. This leads to the following expression for the conductivity [28]

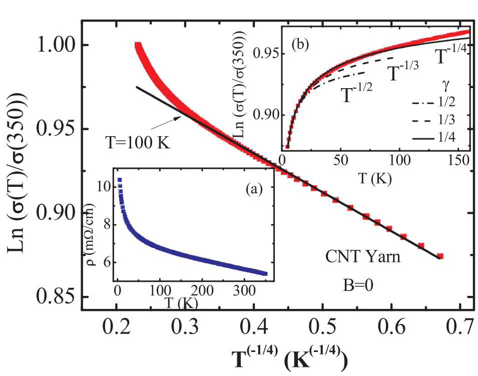

Fig. 2. Ln σ (*T*) / σ (350) *versus* $T^{-1/4}$, where the solid line shows the linear fitting for $T < 100$ K. Insets: (a) Temperature dependence of the resistivity, and (b) Ln σ(*T*)/σ(350) versus *T*, with the dashed lines showing the Mott law curves for γ = 1/2, 1/3, and 1/4 for CNT yarn in the absence of magnetic field.

$$\sigma(T) = \sigma_0 \exp[-(\frac{T_{Mott}}{T})^{\gamma}] \quad (1)$$

where $\gamma = 1/(1 + d)$ is called the effective hopping parameter and $d = 1, 2, 3$ is the hopping effective dimension. The pre-exponential σ_0 represents the conductivity at the high temperature limit and it is also temperature dependent although it is often neglected compared to the stronger temperature dependence on the exponential term [16,28]. *T* is the temperature and T_{Mott} is called the Mott characteristic temperature, which is related to the effective energy separations between localized states and can be expressed by the following equation [28,29]

$$T_{Mott} = \frac{24}{\pi k_B N(E_F)\xi^3} \quad (2)$$

where $N(E_F)$ is the density of states at the Fermi level and ξ is the localization length of the wave function for the localized charge carrier, and k_B is Boltzmann constant.

The logarithm of the conductivity was obtained based on Eq. (1), and it is plotted versus $T^{-1/(1+d)}$ in Fig. 2 (inset (b)). As can be seen, evaluation of Ln σ /σ(350) versus *T* with $d = 1$, 2 and 3 (γ = 1/2, 1/3, and 1/4) showed good fits to the experimental data only for $d = 3$ ($T^{-1/4}$) at temperatures lower than $T \approx 100$ K. Therefore, the conductivity results are supported by conductivity analysis in the framework of the three-dimensional (3D) variable range hopping (VRH) model at low temperature while increasing temperatures cause a deviation from the 3D-VRH model.

The Mott characterization temperature T_{Mott} and σ_0 were obtained from the best fit to the experimental data of Eq. (1) with $d = 3$. The values of 2.14 K and 215.10 S.cm were found for T_{Mott} and σ_0, respectively. These values will be used to calculate different parameters such as the localization length, the average hopping length, and density of states at Fermi level. Gu et al. [30] reported a T_{Mott} value of 17.75 *K* for MWCNT. As will be discussed later, the smaller T_{Mott} indicates a weaker localization of the charge carriers in CNT yarn. In fact, CNT yarn is made from a group of MWCNTs which are aligned, packed, and follow each other back to back using van der Waals interaction. Therefore, the 3D-VRH conduction mechanism is dominant by disordered MWCNT. In this case, electrons can switch direction at the ends of every piece of MWCNT in the yarn and move to another piece of nearby MWCNTs, which can explain 3D fitting model in the conduction mechanism [4].

The nature of low temperature conductivity (or resistivity) can be classified in terms of semiconductor (for $\sigma(T) \to 0$ as $T \to 0$) and metallic behavior (for $\sigma(T) \neq 0$ as $T \to 0$). These different types of behavior can exist because of the heterogeneous nature of crystalline and disordered regions in these systems. The behavior in a particular case is sometimes given by slope of "reduced activation energy", *W*, expressed by [16]

$$W(T) = \frac{\partial(Ln\,\sigma)}{\partial(Ln\,T)} = -\frac{\partial(Ln\,\rho)}{\partial(Ln\,T)} \quad (3)$$

For the VRH region explained by Eq. (1), the logarithm of the reduced activation energy is given by: