The electrical property of carbon nanocoils (CNCs) annealed from 300 to 2900 K has been studied by a four-probe technique. It was shown that the resistivity of the CNCs decreased with the increase of the annealing temperature owing to the improvement of crystallinity and the most notable change of resistivity occurred at the initial structure change of the CNCs. Besides the measurement of room-temperature resistivity of the annealed CNCs, temperature-dependent resistance of the annealed CNCs was also measured. According to the nearest neighboring hopping mechanism, the average activation energy for electron hopping in the annealed CNCs was calculated, which indicated that the average activation energy reduced with the structural improvement of CNCs. It was also found that the variation of average activation energy was also sensitive to the initial structural change of CNCs. Finally, through studying the electrical property of the CNCs under expansion, it was found that the resistance of the CNC was not changed with elongation.

1. Introduction

Carbon nanocoils (CNCs) were helical carbon nanotubes (nanofibers) and were synthesized by chemical vapor deposition (CVD) with transition metals as catalyst [1–4]. The line diameter and coil pitch of CNCs generally fell in the range from 200 to 500 nm and the length of CNCs could reach as long as several hundred micrometers [2]. Because CNCs had helical morphology and the structure of CNCs was a hybrid of sp² grains and sp³ amorphous structure [5,6], the physical properties of the CNCs may differ from both carbon nanotubes (CNTs) and amorphous carbon fibers (CNFs). For instance, due to the better crystallinity of CNCs, the electrical conductivity of CNCs was higher than that of amorphous CNFs [7]. Compared with CNFs and CNTs, CNCs performed better in field emission since the electrons could also emit from bodies of CNCs during field emission [8]. Moreover, CNCs showed spring-like behavior in mechanical properties [6], which was unique among carbon nanomaterial. With improvement of the synthesizing technique [1,2], exploration of CNC applications had also been conducted in the past ten years. It has been reported that CNCs could serve as field emitters [5,9], electromagnetic wave absorbers [10–12], nanosprings and templates for preparing helical materials [13,14]. Most recently, Ma et al. [15] reported that a single CNC was used as a bolometer-type infrared sensor, whose maximum conductance change could reach 22% and the response time was lower than 5 ms. Liu et al. [16] studied the photoresponse property of helical CNTs under 515 nm laser illumination, showing that the maximum photocurrent was 0.43 nA and the quantum efficiency was $2 \times 10^{-2}$. The optoelectronic applications of CNCs such as field-emission devices or...
infrared sensors depended strongly on electron transportation mechanism in the CNCs. Much effort has been devoted to this study. Chiu et al. [17] fabricated CNC devices by a lithography technique and measured their electrical properties from room temperature to 64 mK. They explained the electron transportation mechanism of the CNCs by an Efros-Shklovskii variable range hopping (VRH) model with a hopping length of 5 nm. Tang et al. [18] also studied electron transportation mechanism of individual CNCs. They found that the transportation mechanism in the CNCs changed from Mott-David VRH mode to Efros-Shklovskii VRH mode when the temperature was lower than 20 K. However, in previous studies, the pristine CNCs, whose structure was highly disordered, were used in experiments. Therefore, there is no knowledge about the influence of the structural change of a CNC on its electrical property. In this paper, the structure of CNCs was changed by annealing and the corresponding electrical property was studied by a four probe technique.

2. Experiment

2.1. CNC preparation and annealing treatment

CNCs used in this work were synthesized by CVD with Fe-In-Sn-O catalyst. [19]. The as-grown CNCs were annealed from 873 to 2873 K in an argon atmosphere for 20 min in the super-high temperature furnace (Marusho Denki-SPS1210-25G). The annealed samples were characterized by scanning electron microscopy (SEM, Hitachi S4500), Raman spectrometer (Renishaw inVia plus) and transmission electron microscopy (TEM, FEI TF30 and Joel JEM2500-SE).

2.2. Measuring room-temperature resistivity of the CNCs

Fig. 1(a) shows the optical microscope image of the four-probe measurement for an individual CNC, showing that a CNC was suspended by four CNT-tungsten probes. In Fig. 1(a), probes 1 and 4 were served for applying a current and probes 2 and 3 were used to perform a voltage measurement. The contact points between the CNC and probes 2 and 3 were marked by two short lines. Fig. 1(b) is the representative SEM image of a CNC used in this study.

CNT-tungsten probes were used for measuring the electrical property of the CNCs. The CNT-tungsten probes were prepared by using a tungsten probe to draw a CNT bundle from vertically aligned CNTs synthesized by CVD [20]. During the measurement, the CNC was attached to the CNT bundle due to the strong Van der Waals force. Moreover, compared with tungsten probes, CNT-tungsten probes showed better electrical contact with the CNC, which was shown in Fig. S1. The electrical measurement was performed by a Keithley 2400 source meter.

2.3. Measuring the resistance change of a single CNC with temperature

A microscopic four point probe (M4PP) [21] with four CNT arms was used for measuring the temperature-dependent resistance of annealed CNCs. Four CNT bundles were connected to four Au electrodes on the substrate. An optical microscope image of a CNT-M4PP probe was shown in Fig. 2.

For preparing the CNT-M4PP probe, a CNT bundle was also drawn from the vertically aligned CNTs by a tungsten probe. A part of the CNT bundle was attached to an Au electrode by manipulating the tungsten probe and after applying a large voltage, the suspended CNT bundle was broken near its center due to the Joule heat. The residual CNT bundle on the Au electrode served as a probe for the electrical measurement. After the CNT-M4PP probe was fabricated, a CNC was put on the four CNT arms, which was shown in Fig. 3(a). Fig. 3(b) is the enlarged image of contact area between the CNC and the CNT bundle, showing that the CNC was attached closely to the CNT bundle. The CNT-M4PP probe with the CNC was heated from 295 to 370 K by a hot plate in the air and the resistance of the CNC was measured by the source meter simultaneously.

2.4. Measuring the resistance of the CNCs under expansion

As shown in Fig. 4, an individual CNC without annealing was suspended between two Cu probes. The contacts between the CNC and Cu probes were enhanced by silver paste. A current was applied on the CNC and the voltage drop along the CNC was measured by two CNT-tungsten probes. Then the CNC was stretched by moving one Cu probe and the resistance of the CNC between two CNT-tungsten probes under expansion was measured. Due to strong Van der Waals force, the tip of the CNT bundle attached closely to the CNC in the whole pro-

Fig. 1 – (a) Optical microscope image of a CNC suspended by four CNT-tungsten probes, where the CNT probes and the CNC are marked by arrows and the contact points between the CNC and probes 2 and 3 are marked by two short lines. (b) SEM image of an individual CNC. (A color version of this figure can be viewed online.)
cess of the elongation, which ensured the four probe measurement during the expansion. In previous studies on electrical property of CNCs under expansion by a two-probe technique [22,23], two ends of CNCs were fixed on two electrodes by silver paste and the resistance change was monitored with elongation of the CNC by moving one electrode. Consequently, the anchoring points of the CNCs on the electrodes may be varied by stretching, which could change contact resistance and thus affected the measured resistance of expanded CNCs. However, by using the four-probe technique basing on CNT-tungsten probes, though the contact state between the CNC and Cu probe may also vary during expansion, the measured voltage between two CNT-tungsten probes was not affected so that the calculated resistance between two CNT-tungsten probes was also accurate.

3. Results and discussion

Fig. 5(a) is the TEM image of a pristine CNC. It is observed from Fig. 5(a) that the crystallinity of the pristine CNCs is poor because the crystalline size is very small and the orientation of the crystallite is disordered. The evolution of the crystallinity of CNCs with annealing temperature is shown in Fig. 5(c) by the ratio of D band intensity ($I_D$) to G band intensity ($I_G$) calculated from the Raman spectra of the CNCs (Fig. S2). The ratio of $I_D$ to $I_G$ is inversely proportional to the average crystalline size according to the empirical formula of $I_D/I_G = C(\lambda)/L_a$, where $C(\lambda)$ is a constant at the certain laser wavelength ($\lambda$) and $L_a$ indicates the size of sp² grains [24–26]. For the exciting laser of 632.8 nm used in our Raman system, $C(632.8)$ can be calculated by the formula of $C(\lambda) = -12.6 + 0.033\lambda^2$ [24], which is equal to 8.28 nm. In Fig. 5(c), the ratio of $I_D$ to $I_G$ is decreased from 1.9 to 0.58 as annealing temperature increases from 300 to 2873 K. Therefore, the average crystalline size in the CNCs is quickly increased from 4.3 to 14 nm with the increase of annealing temperature. Fig. 5(b) is the TEM image of a CNC annealed at 2873 K. It is observed that the crystalline size is much larger than that of the pristine CNC shown in Fig. 5(a). However, it is noted that even though the crystallinity is improved by annealing, there are still many defects and strains in the CNCs, which is a requirement for maintaining the helical structures of CNCs. Further evidence of the structural evolution of annealed CNCs was also provided by electron diffraction analysis [27]. From electron diffraction patterns, average interlayer spaces of (002) plane of CNCs were calculated to be 0.374 nm (300 K), 0.361 nm (1273 K), 0.351 nm (1673 K), 0.34 nm (2073 K), 0.341 nm (2473 K), 0.34 nm (2873 K). The average interlayer spaces of CNCs when the annealing temperature is lower than 1673 K is significantly larger than that of crystalline graphite (0.335 nm), which is caused by the existence of the turbostratic structure in the CNCs [28]. The improvement of crystallinity of the CNCs indicated by the average interlayer space is coincident with that of ratio of $I_D$ to $I_G$.

Fig. 3 – (a) SEM image of a CNT-M4PF probe with a suspended CNC. (b) Enlarged SEM image of area marked by a red circle in Fig. 3(a). (A color version of this figure can be viewed online.)

Fig. 4 – Optical microscope image of a four-probe measurement for an expanded CNC. (A color version of this figure can be viewed online.)
The room-temperature resistivity of the annealed CNCs is shown in Fig. 6. It is observed that the electrical property of the CNCs is very sensitive to the initial structure change of the CNCs. By annealing at 1073 K, the resistivity of the CNCs decreases sharply from $1.9 \times 10^{-4}$ to $7.7 \times 10^{-5}$ Ω m. The structure of CNCs is thermally stable in the temperature lower than synthesizing temperature (973 K). When the annealing temperature is higher than 973 K, the size of sp² grains in the CNCs begins to increase and the orientation of sp² grains is also rearranged to be aligned \[5,29\], which improve the electrical conductance of the CNCs significantly. From the annealing temperature of 1273 to 2473 K, the resistivity of the CNCs fluctuates around $7.1 \times 10^{-5}$ Ω m. When the annealing temperature of the CNCs exceeds 2473 K, the resistivity of the CNCs further reduces to approximately $3.5 \times 10^{-5}$ Ω m. On one hand, the improvement of the conductivity originates from the increase of the crystallinity. On the other hand, under such high temperature, it can be observed from Fig. 5(b) that many loops form at the graphene edges. These loops connect graphene planes, leading to the formation of new conductive channels and enhancement of conductivity of CNCs \[30\]. Based on the above measurement, the electrical property of CNCs can be compared with other carbon nanomaterials such as CNFs and MWCNTs. The room-temperature resistivity of CNCs is smaller than that of CNFs due to better crystallinity of CNCs. However, even though the CNCs were annealed at the temperature up to 2873 K, the resistivity of the CNCs was still higher than that of some MWCNTs which have relatively perfect structures \[31\]. This is probably because the electrical conductance mechanisms for the CNCs and CNTs are different and a great number of unrepaird defects in the annealed CNC, resulting in the strong carrier scattering, prevent the decrease of the room-temperature resistivity of the CNCs.

The resistance of the pristine CNC is measured by the CNT-M4PP probe when the temperature of the probe is changed from 295 to 370 K, which is plotted in Fig. 7(a). Because of the highly disordered structure of the CNCs, the electron transportation in the CNC is explained by an electron hopping mechanism. In the low temperature range from room temperature to about 20 K, electron transportation in the CNCs agrees with Mott-David VRH mode \[18,32\]. Briefly, electrons would prefer to hop between non-nearest-neighboring localized states which have lower energy difference. The localized states correspond to the sp² grains in CNCs. However, with increasing temperature, electrons obtain enough energy from phonons so that the electron hopping mechanism transfers from Mott-David VRH mode to nearest neighboring hopping mode which is described by $R = R_0 \exp(E/kT)$, where $E$ is the activation energy for electron hopping between nearest sp² grains. Because Tang et al. \[18\] reported that the characteristic temperature of the CNC for Mott-David VRH was 227 K and the temperature range in our experiment is higher than this temperature, the electrical transportation of the CNC in this work should be explained by the nearest neighboring hopping mechanism. From the linear fit for ln ($R$) vs. $1/T$ in Fig. 7(b), the average activation energy for electron hopping between the nearest neighboring localized states can be calculated.

The average activation energy of CNCs annealed at various temperatures is shown in Fig. 8(a). The average activation energy of CNCs without annealing is about 11 meV, which is the
same magnitude with that of carbon microcoils [23]. Being similar to the room-temperature resistivity of the CNC, the average activation energy of the CNC also decreases greatly from 11 to 4.2 meV when the CNCs are annealed near 1273 K, indicating again that the initial structure change of the CNCs has great influence on the electrical property of the CNCs. The average activation energy as a function of average interlayer space is drawn in Fig. 8(b). The average activation energy reduces rapidly as the average interlayer space decreases from 0.375 to 0.37 nm and does not change when the average interlayer space is smaller than 0.365 nm. The reduction of average interlayer space in the CNCs reflects the growth of sp² grains in the CNC and the reduction of the amorphous structure between sp² grains. Therefore, considering that electrons can transport free in the sp² grain, the graphitization of the CNCs after annealing causes that less activation energy is needed for overcoming the barrier of electron hopping from one sp² grain to another one.

Fig. 7 – (a) Temperature-dependent resistance of a pristine CNC. (b) ln (R) vs. 1/T and the linear fitting curve. (A color version of this figure can be viewed online.)

Fig. 8 – (a) Average activation energy of the CNCs annealed from 300 to 1650 K. (b) Change of the average activation energy of the CNC with the average interlayer space. (A color version of this figure can be viewed online.)

Fig. 9 shows a typical resistance change of a pristine CNC with expansion. It is noted that the expansion of the CNCs in the electrical measurement was much smaller than their

Fig. 9 – The measured resistance of a CNC under expansion and the inset is the optical microscope image of the CNC. (A color version of this figure can be viewed online.)
maximum deformations. In the case of the CNC 58 μm, 460 nm, 2.3 μm and 55 in Fig. 9, the maximum deformation of the CNC can reach approximately 340% according to its SEM image. It can be observed that the resistance of the CNC almost does not change with the expansion. The distance between the sp² grains in the CNC does not change by stretching when the deformation of the CNC is relatively small so that the electron transport in the CNC is not changed.

4. Conclusions

In this work, it was found that the electrical property of the CNCs was sensitive to the initial structure change of the CNCs. At the annealing temperature of 1073 K, the resistivity of the CNCs decreased to 3.5 × 10⁻⁴ Ω m. With further increase of the annealing temperature to 2873 K, the resistivity of the CNCs decreased to 3.5 × 10⁻⁵ Ω m. The decrease of the resistivity of the CNCs was attributed to the graphitization in CNCs and the formation of the loops at the graphene edge. The temperature-dependent resistances of the annealed CNCs were also measured. The electron transportation in CNCs was described by a nearest neighboring hopping mechanism and the activation energy was calculated. It was found that the activation energy decreased quickly when crystalline size in the CNCs increased and the amorphous structure between sp² grains reduced. Moreover, the resistance of the CNC under a small expansion was also measured, showing that the resistance of the CNC hardly changed with the expansion of the CNC.

Acknowledgements

We thank Mr. Ito in Nano Solution Company for providing the M4PP probes. This work was supported by the National Natural Science Foundation of China (Nos. 51072027, 11274055 and 61137005) the Fundamental Research Funds for the Central Universities (No. DUT12ZD204).

Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.carbon.2014.02.038.

REFERENCES


