Chapter 10
Thermoelectric Properties of Carbon Nanotubes Layers

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Abstract Thermoelectric power (TEP) of the carbon nanotubes (CNTs) films, grown by radiofrequency plasma-enhanced chemical vapor technology onto silicon substrates, has been measured. Two different metal contacts of Cr–Al and Cr–Au have been fabricated for the CNTs-based thermocouples and preliminarily investigated. The CNTs-based thermocouples exhibit large values of TEP due to the Schottky barriers at semiconducting CNTs-metal junctions. The highest TEP of 40.7 μV/K has been achieved for the thermocouple CNTs/Cr–Al. This value is enhanced of about 2 times compared to single-walled CNTs bundles reported in literature (Collins et al. Science 287:1801–1804, 2000), and comparable to isolated suspended single-walled carbon nanotubes with Pt-electrodes reported in literature (Yu et al. Nano Lett 5(9):1842–1846, 2005) as well. The CNTs-thermocouples exhibit linear relationship for the output voltage versus temperature in the range from 20 to 70°C by providing an interesting nanomaterial for energy applications and temperature and/or radiation microsensors.

10.1 Introduction

Carbon nanotubes (CNTs) have been largely studied in the form of networked films for highly-sensitive gas detection applications [1–6]. Due to very high surface-to-volume ratio, hollow nanostructure, high electron mobility, great surface

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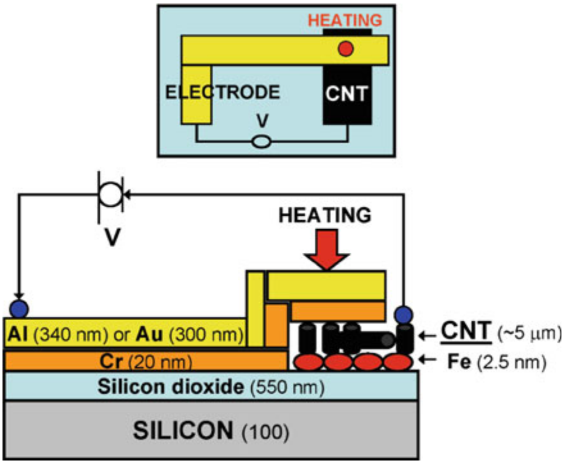

Fig. 10.1 Scheme of the fabricated thermoelectric device

reactivities and high capability of gas adsorption, CNTs have been investigated as building blocks for fabricating novel devices at nanoscale such as high-performance gas sensors and nano-platforms for biosensing.

The thermoelectric properties of the CNTs have been also investigated [7–12]. Thermoelectric experiments have been reported such as the modulation of the thermoelectric power (TEP) in the CNTs bundles by O_2 gas adsorption in vacuum cycles [7]. The thermoelectric transport in the CNTs bundles has been demonstrated to be modulated by doping with gas molecules adsorbed [11]. Doping of the multi-walled CNTs during their growth provides an increase in the Seebeck coefficient [10]. Moreover, at the temperature of 300 K, the observed TEP in the individual single-walled suspended CNT was measured as 42 μ/K, which is one order of magnitude higher than graphite or a typical metal [9].

Low-dimensional thermoelectric materials perform better than bulk materials due to the confinement to low dimensions with sizes comparable to the transport wavelength by producing sharp edges and peaks in the electronic density of states. The enhancement of the density of states near the Fermi energy caused by the reduction of dimensions leads to the enhancement of the Seebeck coefficient [10].

Here, we report on the preliminary experiments devoted to explore the thermoelectric properties of the thermocouples made by Cr–Au/CNT and Cr–Al/CNT thin film structures.

10.2 Experimental Details

The scheme of the fabricated device is shown in Fig. 10.1. CNTs films were grown by RF-PECVD technology onto SiO_2/Si substrates (1.5 × 1.5 cm). Fe (2.5 nm thick) catalyst was sputtered onto silicon substrates at a working pressure of

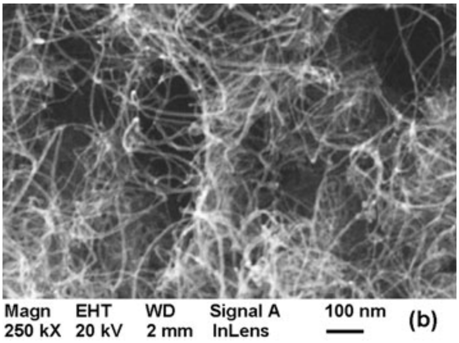

Fig. 10.2 FE-SEM image of the RF-PECVD Fe-grown CNTs layers

1.2×10^{-1} mbar, at room temperature and a supplied RF power of 150 W. Then, the Fe-coated substrates were placed in the RF-PECVD processing chamber to grow CNTs. The chamber was evacuated up to 1×10^{-2} Torr, then the substrates were heated at 600°C upon H_2 flow (100 sccm) at a pressure of 1.5 Torr. A RF discharge at 100 W for 5 min was supplied at the heated substrates (600°C) to promote the Fe clustering for CNTs growth. Finally, a carbon gaseous precursor of acetylene (C_2H_2) with a flow rate of 20 sccm was added to H_2 gas-plasma with a flow rate of 80 sccm. The working pressure was fixed at 1.5 Torr and RF power at 100 W with a deposition time of the CNTs layers for 20 min. After CNTs growth, the samples were equipped by vacuum thermally evaporated Cr–Au (20 nm/300 nm) or Cr–Al (20 nm/340 nm) contacts to serve for the electrical measurements.

The morphology and structure of the fabricated CNTs networks has been characterized by scanning electron microscopy (SEM), as shown in Fig. 10.2. A dense network of bundles of multiple tubes consisting of multi-walled carbon nanostructures appears with a maximum length up to 10 μm and single-tube diameter in the range of 5–35 nm.

The fabricated CNTs-based thermocouples have been located in an experimental setup for the thermoelectric measurements. The scheme of the experimental setup has been reported in Fig. 10.3. A thermo-controlled water-bath was used to generate a temperature gradient. The water was heated by a commercial heater by Joule-effect. The water temperature was measured by a commercial Pt100 thermocouple. The temperature range was from 18 to 70°C. The CNTs-based thermocouple to be characterized was held in air as cold junction ($T_{hot} = T_{cold}$) and immersed in water for the measurement as hot junction ($T_{hot} > T_{cold}$). Measurement time ($\sim$3 s) was as shorter as possible to maintain constant the cold junction temperature. The output voltage of the CNTs-based thermocouple under test was measured by a multimeter (Agilent, 34401A).

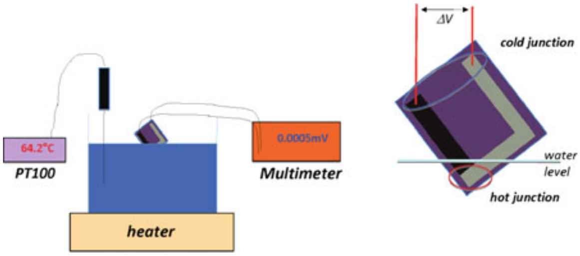

Fig. 10.3 Scheme of the experimental setup for measuring the CNTs-based thermocouples

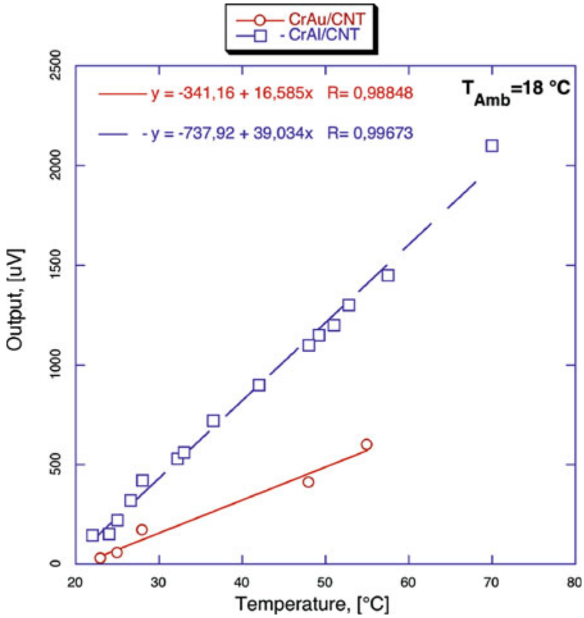

Fig. 10.4 Thermoelectric voltage value versus temperature for two types of thin film thermocouples

10.3 Results and Discussion

Two kinds of devices namely Cr–Au/CNT and Cr–Al/CNT thin film structures have been characterized as thermocouples that could be used as both temperature and radiation sensors. To this purpose this work aims at estimating, in a controlled experimental condition, their thermoelectric power. The hot junction was, for each measurement and for a short time (about 3 s), immersed into water whose temperature was controlled by a reference thermocouple and the other junction was left in air (about 18°C). This procedure was adopted in order to avoid the thermal diffusion effect from the hot to the cold junction that could have a negative effect on the measurement accuracy.

Figure 10.4 shows preliminary data relative to the two thermocouples thermal behaviours. A linear temperature-dependent thermoelectric power has been observed on CNTs-networks for both structures Cr–Al/CNT and Cr–Au/CNT in the measured range of temperature from 20 to 70°C. A voltage output for the Cr–Al/CNT thermocouple has been measured in the range from 50 to 2,200 μV with a related increasing temperature gradient. The two thermoelectric powers, expressed as slope of the voltage-versus-temperature relationships, are estimated to be as high as about 39 and 16.6 μV/°C respectively for Cr–Al/CNT and Cr–Au/CNT structures. The resistance of the two thermocouples are in the range of about 500 Ω, which does represent a negligible noise source.

The studied thermocouple is formed by three materials: CNT, Cr, Al or Au. According to the *homogeneous conductors* law, the active junction is based on top-layer of Al or Au and down-layer of CNT. Generally, the thermocouple voltage is given by the relationship:

$$V = \int_{T_1}^{T_2} (S_A - S_B)\, dT$$

where S_A and S_B are the Absolute Thermoelectric Power (ATP) of the thermoelements; ATP is temperature-dependent. In our case of maximum measured TEP for Al/CNT structure, the ATP of the Al, S_{Al}, has been reported in literature by Huebener et al. [13] as indicated as follows:

$$S_{\mathrm{Al}} = (-1.41 - 0.001 \cdot T)\, \frac{\mu\mathrm{V}}{\mathrm{K}}$$

By using this value of S_{Al}, the ATP of the CNT, S_{CNT}, has been calculated as follows as:

$$S_{\mathrm{CNT}} = (145.7 - 0.35 \cdot T)\, \frac{\mu\mathrm{V}}{\mathrm{K}}$$

At $T = 300$ K, $S_{\mathrm{CNT}} = 145.7 - 0.35.300 = 40.7$ μV/K.

Figure 10.5 shows temperature-dependent thermoelectric power calculated from data of Fig. 10.4 on CNTs-networks for Cr–Al/CNT structure in the measured range of temperature from 298 to 335 K. Table 10.1 reports the comparison of the TEP of the fabricated CNTs-based thermocouple with other thermocouples reported in literature. A high TEP of 40.7 μV/K has been achieved for the thermocouple CNTs/Cr–Al. This value is enhanced of about 2 times compared to single-walled CNTs bundles [7] and multi-walled CNTs bundles [10], and comparable to isolated suspended single-walled carbon nanotubes with Pt-electrodes [9] as well.

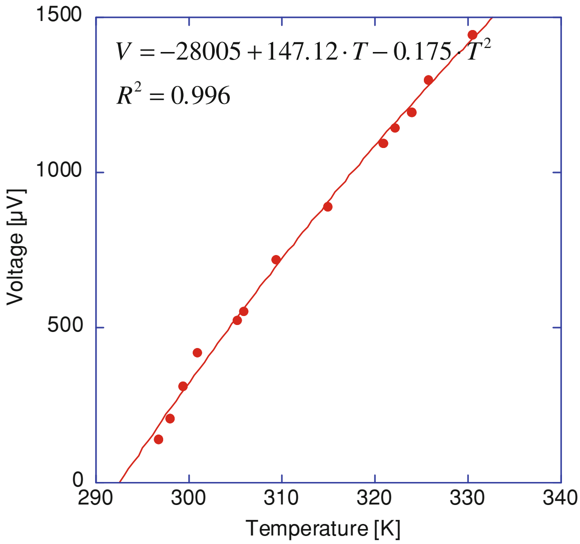

Fig. 10.5 Thermoelectric voltage versus temperature for Cr–Al/CNT thin film thermocouple

Table 10.1 Comparison of the thermoelectric power (TEP) for the CNT-based thermocouples

Thermocouple type	TEP (μV/K) at *T* (K)	Reference
SWCNTs bundles	24 μV/K (at 350 K)	Ref. [7]
Isolated suspended SWCNTs with Pt-electrodes	42 μV/K (at 300 K)	Ref. [9]
Doped MWCNTs bundles with metal contacts	22 μV/K (at 300 K)	Ref. [10]
CNTs bundles with Cr–Al electrodes	40.7 μV/K (at 300 K)	This work

10.4 Conclusions

The CNTs-based thermocouples are very promising sensors for measuring temperature and future applications (e.g., radiation). RF-PECVD technology has been used to grow networked layers of multi-walled CNTs. Metal contacts (Cr–Al, Cr–Au) have been used to fabricate the junction in the CNTs-based thermoelectric cells. High thermoelectric power of 39 and 16.6 μV/°C has been measured for Cr–Al/CNT and Cr–Au/CNT thermocouples, respectively. In particular, the high value of 40.7 μV/K measured for the fabricated Cr–Al/CNTs thermocouple is comparable to the suspended individual single-walled CNT with Pt-electrodes. Finally, CNTs-based thermocouples are very interesting for advanced nanosensors and energy harvesting applications.

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