Asian Journal of Chemistry; Vol. 25, Supplementary Issue (2013), S27-S29

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Tuning of Thermoelectric Property in the Flexible MWCNT Buckypaper†

JIH-HSIN LIU[1,3], HSIN-YUAN MIAO[1,3*], L. SARAVANAN[3], LI-CHIH WANG[2,3] and REN-HUI TSAI[1]

[1]Department of Electrical Engineering, Tunghai University, Taichung 40704, Taiwan
[2]Department of Industrial Engineering and Enterprise Information, Tunghai University, Taichung 40704, Taiwan
[3]Tunghai Green Energy Development and Management Institute, Tunghai University, Taichung 40704, Taiwan

*Corresponding author: Fax: +886 943203943; Tel: +886 4 23590121; E-mail: kenymiao@thu.edu.tw

AJC-12783

In this work, we report the preparation of flexible carbon nanotube buckypaper for thermoelectric applications. Different thermoelectric semimetal deposited multiwalled carbon nanotube buckypaper was prepared by the thermal evaporation method. Low temperature resistivity measurement was performed to confirm the semi-conducting nature of the synthesized carbon nanotube networks. We also demonstrated the significant increase in the S(T) value by connecting 3 layers of buckypaper in series. We studied here on increasing the Seebeck coefficient and the electrical conductivity to enhance the thermoelectric power factor ($S^2\sigma$) thereby improving the thermoelectric efficiency of the multiwalled carbon nanotube buckypaper.

Key Words: Multiwalled carbon nanotube, Buckypaper, Thermoelectric, Resistivity, Seebeck coefficient.

INTRODUCTION

Thermoelectric energy conversion, which can achieve the direct conversion between heat and electricity, is expected to play a progressively more important role as an alternative energy technology[1]. Thermoelectric materials have been widely used in solid-state electronic cooling and power generation cooling and power generation with many advantages such as long life, low maintenance and high reliability[2]. The efficiency of a thermoelectric material is related to the dimensionless figure of merit ZT, which is expressed as $ZT = S^2T/\rho k$, where S, ρ, T and k are the Seebeck coefficient, electrical resistivity, absolute temperature and thermal conductivity respectively. Tuning these properties somewhat allows for significant improvement in the materials thermoelectric performance[3].

Carbon nanotubes (CNTs) are promising building blocks for future nanoelectronics. Buckypaper is a macroscopic sheet assembly of carbon nanotubes formed by filtration from their dispersion in organic solvent. Buckypaper a free-standing porous sheet of entangled CNTs appears to be very attractive for thermal transport applications[4]. There is an enormous interest in developing buckypaper based composite materials with improved mechanical and electrical properties for a number of potential applications. Doping is another way to modify the electrical conductivity of CNTs, *i.e.*, incorporation of foreign atoms directly into lattice sites[5]. Several researchers have attempted to fabricate CNT-reinforced metal- or ceramic-matrix composite materials by means of traditional powder-metallurgy process[6]. However these attempts have failed to fabricate the composite with homogenously dispersed metal/CNTs in the matrix. Semimetals and its alloys like bismuth, antimony and tellurium[7,8] are the existing thermoelectric for these three semi-poor metals are known to have accentuated thermoelectric activity. This work focused on the deposition of these semi-metal Bi, Sb and Te nano particles on the surface of buckypaperby the thermal evaporation method to study the ρ(T) and S(T) called as thermo power($S^2\sigma$), which plays a vital role in improving the thermoelectric properties of MWCNT buckypaper.

EXPERIMENTAL

MWCNT buckypaper: The buckypaper used in this study is made from MWCNTs (supplied by UChees, Taiwan) by the method of vacuum filtration. In order to prepare buckypaper, CNTs must be dispersed in an appropriate solvent. This was done by dispersing the MWCNTs in the distilled water and stabilizing with a non-ionic surfactant Triton X-100 *via* ultrasonication (Misonic, 20 KHz, 63 W). The suspension vacuum filtrated through a nylon filter membrane, to form a buckypaper. The sample was then placed in the bath of isopropyl alcohol to wash off the surfactant completely to get pure CNT buckypaper. After the filtering

†International Conference on Nanoscience & Nanotechnology, (ICONN 2013), 18-20 March 2013, SRM University, Kattankulathur, Chennai, India

and drying process, the paper was peeled carefully from the filter membrane, resulting in a thin sheet of MWCNT network random buckypaper with *ca*. 110 µm thickness. The flexible buckypaper made was shown in Fig. 1(a).

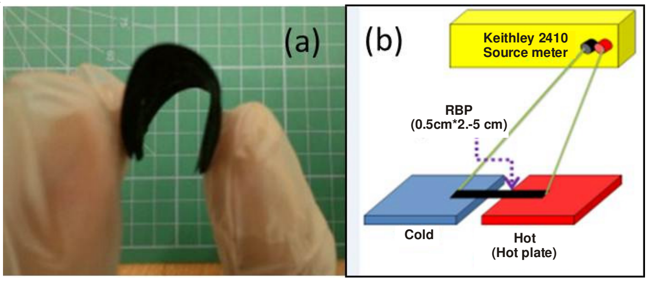

Fig. 1. (a) Flexible buckypaper and (b) Schematic of the thermoelectric measurement

Deposition of metal on the buckypaper: The deposition of the thermoelectric metal on the random buckypaper surface was carried out by thermal evaporation method. Bismuth (Bi), antimony (Sb) and tellurium (Te) granules (99.99 %, ADMAT Inc.) was used as a vapour source. The buckypaper substrate is holding on a ceramic holder and inserted inside the deposition chamber which was then evacuated under a relative pressure of 10^{-5} torr and distance from the source is 30 cm. The total deposition time is *ca.* 2 min under complete vacuum. The samples after deposition of Bi, Sb and Te on the surface of random buckypaper (RBP) were referred as Bi-RBP, Sb-RBP and Te-RBP respectively.

The surface morphology of the buckypapers was examined using field emission scanning electron microscope, FESEM JEOL JSM-7000F. The temperature dependent electrical resistivity (ρ) measurements for all the samples of the buckypaper were done by the standard programmable DC voltage/current detector four-point probe method in the temperature range from 30-300 K. The Seebeck coefficient (S) was extracted by applying a temperature gradient along the sample and measuring the thermoelectric voltage and the schematic is shown in Fig. 1(b). We also measured the Seebeck coefficient (S) for 3 sheets of buckypaper connected in series for all the samples.

RESULTS AND DISCUSSION

Fig. 2(a-c) shows the FESEM images of metal deposited buckypapers, Bi-RBP, Sb-RBP and Te-RBP respectively. FESEM image in the inset of Fig. 1(a), shows the random entanglement of MWCNTs network structures of pure random buckypaper. An increase in the diameter of nanotube observed from the Fig. 2(a-c) indicates the deposition of metal nanoparticles on the surface of nanotubes and decreases the porosity of buckypaper.

The low temperature resistivity (ρ) measurement in Fig. 3 reveals the semi-conducting behaviour of buckypaper[9]. It was observed that, the ρ(T) for all the samples rapidly increase at low temperature and decreases when temperature increases. The resistivity value reaches the range of 0.96-1.6 W-cm at 30 K, indicating the insulating properties of the semi-network at low temperature. When a carrier is transported within the CNT network structure under a temperature gradient, a hopping

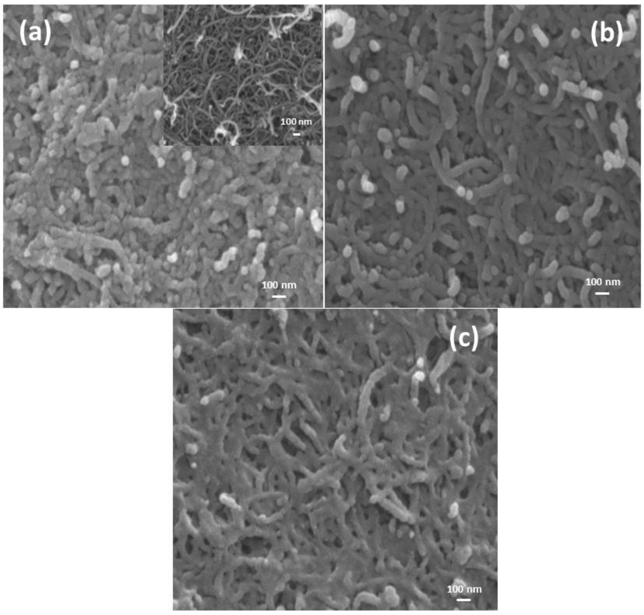

Fig. 2. FESEM images of metal deposited RBP. Inset in (a) FESEM image of pure RBP

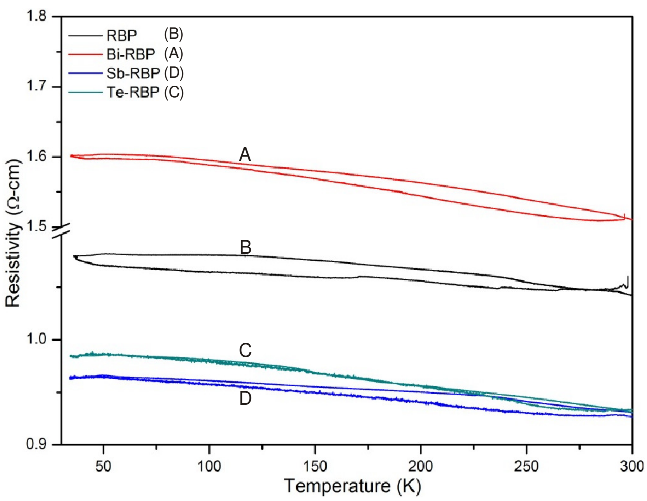

Fig. 3. Low temperature electrical resistivity for RBP and metal deposited RBP samples

mechanism for a heterogeneous model may be appropriate[10]. It has been reported that the electrical conductivity of a CNT thin films is dependent on CNT fabricating process, film thickness, doped chemicals and the functional groups on CNTs[11,12]. It was stated that the electric conductivity of the macroscopic assemblies of CNTs, such as buckypaper, pellet, thin films and fibers, are dependent on inter-CNT transport of charge carriers[13]. The thermally activated tunneling of charge carriers at inter-CNT contacts is considered as one of possible explanation for the electrical conduction[12]. Fuhrer *et al.*[14] stated the activation energy is very low for the conduction through semiconductor-semiconductor or metal-metal contacts, which transport the charge carrier easily and for semiconductor-metal contacts, requires relatively larger activation energy to transport the charge carrier. It supports our data, that the small eractivation energy is enough for semi-metal deposited semiconducting network of CNT for the enhancement of its electrical conductivity.

The Seebeck coefficient (S) is related to the transport of energetic charges, whereas the electrical conductivity is related to the transport of all mobile charges[15]. The Seebeck measurement results are plotted in Fig. 4, indicating that all measured samples were *n*-type with negative Seebeck coefficients. The measured S(T) for a single layer of metal deposited random buckypaper samples are shown in Fig. 4(a). The quantum confinement effect of charge carriers within low-dimensional structures that possess physical dimensions comparable to the electronic wavelength can potentially increase the Seebeck coefficient. The observed values are -13.5, -18, -17 and -20.5 (μV/K) for single layer of random buckypaper, Bi-RBP, Sb-RBP and Te-RBP respectively. The observed variation in the Seebeck coefficient may originates from the change in metal doping and the charges transferred in MWCNT/metal composite films. We also measured the Seebeck coefficient value for the 3 sheets of buckypaper connected in series, for all the samples is shown in Fig. 4(b). The values are -31, -36, -40 and -51 (μV/K)for 3-layers of random buckypaper, Bi-RBP, Sb-RBP and Te-RBP respectively. Here we found that, increase the number of layers/surface area of the buckypaper, thereby increasing the thermoelectric power factor for enhancing the efficiency of the MWCNT buckypaper.

The surrounding metal coated layer results in the enhancement in electron energy filtering effects of semi metal/BP composite films by blocking or scattering the transport of some carriers along the carbon nanotubes chain, which is similar to the screening of electrons by potential wells in inorganic materials, thus enhancing the Seebeck coefficient[16]. Enhanced power factors and reduced thermal conductivities are both beneficial to thermoelectric performance. Therefore, in all respects the method reported here is of great potential to enhance the performance of thermoelectric materials.

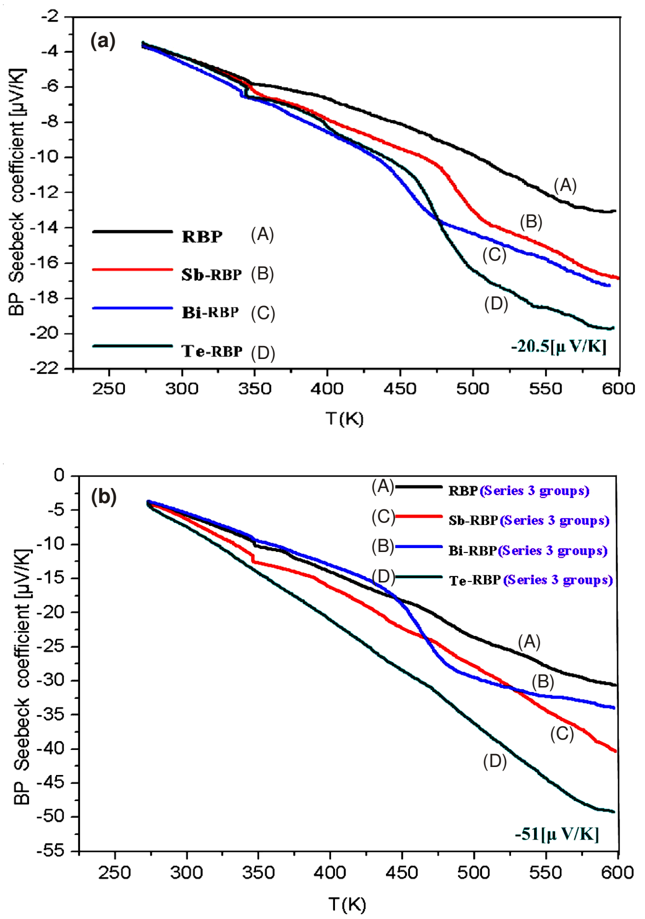

Fig. 4. Seebeck coefficient for all samples (a) single layer and (b) 3-layers in series

Conclusion

In summary, flexible films of various semimetal/MWNT composite with enhanced thermoelectric performance were prepared *via* thermal evaporation method. We found that the improved thermoelectric properties are mainly owing to the greatly increased Seebeck coefficient and increase in the electrical conductivity. This approach can also be used to deposit various metals onto nanotube composites and to prepare a variety of buckypaper-metal composites for a broad range of potential thermoelectric applications. We reported here the process of preparing flexible CNT buckypaper to make it a new type of thermoelectric material for some practical applications with an acceptable ZT value.

ACKNOWLEDGEMENTS

This work is supported by the program of Global Research and Education on Environment and Society (GREEnS), Tunghai University, Taiwan and by the National Science Council, Republic of China (NSC101-2221-E-029-006 and NSC101-2221-E-029-010).

REFERENCES

1. T.M. Tritt, H. Böttner and L. Chen, Thermoelectrics: Direct Solar Thermal Energy Conversion, MRS Bull., Special issue, Edited, vol. 33 (2008).
2. Y.C. Lan, A.J. Minnich, G. Chen and Z.F. Ren, *Adv. Funct. Mater.*, **20**, 357 (2010).
3. G.J. Snyder and E.S. Toberer, *Nat. Mater.*, **7**, 105 (2008).
4. M. Zhang, S. Fang, A.A. Zakhidov, S.B. Lee, A.E. Aliev, C.D. Williams, K.R. Atkinson and R.H. Baughman, *Science*, **309**, 1215 (2005).
5. B. Wei, R. Spolenak, P.K. Redlich, M. Ruhle and E. Arzt, *Appl. Phys. Lett.*, **74**, 3149 (1999).
6. G.D. Zhan, J.D. Kuntz, J. Wan and A.K. Mukherjee, *Nat. Mater.*, **2**, 38 (2003).
7. Y.W. Wang, H.H. Byung and S.K. Kwang, *J. Phys. Chem.*, **109**, 7067 (2005).
8. D. Mott, N.T. Mai, N.T.B. Thuy, Y. Maeda, T.P.T. Linh, M. Koyano and S. Maenosono, *Phys. Status Solidii A*, **208**, 52 (2011).
9. W. Primak and L.H. Ruchs, *Phys. Rev.*, **95**, 22 (1954).
10. A.B. Kaiser, *Phys. Rev. B*, **40**, 2806 (1989).
11. E. Artukovic, M. Kaempgen, D.S. Hecht, S. Roth and G. Gruner, *Nano Lett.*, **5**, 757 (2005).
12. E. Bekyarova, M.E. Itkis, N. Cabrera, B. Zhao, A. Yu, J. Gao and R.C. Haddon, *J. Am. Chem. Soc.*, **127**, 5990 (2005).
13. M.E. Itkis, F. Borondics, A. Yu and R.C. Haddon, *Science*, **312**, 413 (2006).
14. M.S. Fuhrer, J. Nygird, L. Shih, M. Forero, Y.G. Yoon, M.S.C. Mazzoni, H.J. Choi, J. Ihm, S.G. Louie, A. Zettl and P.L. McEuen, *Science*, **288**, 494 (2000).
15. C. Yu, Y.S. Kim, D. Kim and J.C. Grunlan, *Nano Lett.*, **8**, 4428 (2008).
16. C.Z. Meng, C.H. Liu and S.S. Fan, *Adv. Mater.*, **22**, 535 (2010).