Preparation and transport properties of oriented buckypapers with single walled carbon nanotubes

Natalia P. Stepina¹, Mikhail S. Galkov², Mikhail R. Predtechenskiy², Alexander E. Bezrodny², Viktor V. Kirienko¹, Anatolii V. Dvurechenskii¹,³

¹ Institute of Semiconductor Physics, 13 Lavrent’ev ave., Novosibirsk 630090, Russia
² OCSiAl Group, 1804 Embarcadero Rd., Suite 202, Palo Alto, California, 94303, USA
³ Novosibirsk State University, 30 Pirogova Str., Novosibirsk 630090, Russia

Corresponding author: Natalia P. Stepina (nstepina@mail.ru)

Received 21 January 2019 ♦ Accepted 17 February 2019 ♦ Published 1 March 2019

Abstract

Buckypapers (BPs) with carbon nanotubes (CNTs) are very promising for a lot of applications, in which their high conductance, strength and small weight are required. In this work, isotropic BPs were prepared using the solution-based deposition that includes the single walled carbon nanotubes (SWCNTs) dispersion and the dispersion filtration from a solvent. To increase the BP conductivity, the orientation of the SWCNT bundles composing BPs and a following iodine doping were applied. The method of extrusion through the narrow (300 µm) gap was used for the SWCNT orientation. The temperature dependences of conductance for isotropic, oriented and doped BPs were studied to understand the effect of CNT alignment and the mechanism of transport through SWCNT BPs. It was shown that bundle orientation increases the BP conductivity from ~10⁴ S × cm⁻¹ to ~10⁵ S × cm⁻¹, and iodine doping of oriented samples additionally increase the conductivity by an order. The fluctuation – assisted tunneling between CNT bundles was used to describe the mechanism of low temperature conductivity.

Keywords

oriented buckypapers, single-walled carbon nanotubes, iodine doping

1. Introduction

Carbon nanotubes (CNTs), since the discovery of Iijima in 1991 [1], have been the object of numerous studies due to their unique properties. Depending on the production methods, there are single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) with open or closed ends. The high aspect ratio of CNTs (CNT diameter is changed from 1 to 100 nm, and their length can reach several micrometers) leads to a strong quantum confinement effect and quasi-one-dimensional conductance behavior.

SWCNTs are characterized by important electronic, thermal and mechanical properties. Thus, the SWCNT conductivity can exceed the copper conductivity more than 3 times [2–6], the tensile strength reaches 100 GPa,
the thermal conductivity of SWCNT (up to 5800 V/mK) [7] is almost 3 times higher than that of diamond. These physical properties make carbon nanotubes promising for the use as the components of micro- and nanodevices, carbon cells of lithium batteries, electrochemical catalysis electrodes and catalyst carriers, emerging materials for implantable and wearable biofuel cells, etc. [8–10].

Especially important applications are expected for the so-called buckypapers (BPs) – thin layers that consist of many SWCNTs interacting with each other by Van der Waals forces and forming a very lasting structure. Since BPs have sufficiently high electrical conductivity (\(10^7\)–\(10^9\) S/m) [8–14], they can be used in different applications, such as deicers [9], electrodes [15], actuators [16, 17], sensors [18], current collectors in lithium-ion batteries [8, 9], organic light-emitting diodes [19] and electromagnetic shielding [20], for effective lightning strike protection of aircrafts by facilitating the electrical current to the ground [21]. Thus, for the series of BP applications high electrical conductivity is required. The individual CNT conductivity can be as high as \(10^{-4}\)–\(10^3\) S/m [2–4]. However, it drops dramatically to only \(10^{-1}\)–\(10^5\) S/m for the array composed of many nanotubes [5, 6]. Currently, the preservation of electrical properties of an separate nanotube in carbon nanotube ensembles should be the important task. The conductivity of the CNT ensembles depends on the electrical properties of a single nanotube, contact resistance between nanotubes and an effective cross-sectional area [5, 6].

Typical methods of increasing the conductivity are the alignment of CNTs and their doping. There is a famous article on creating an oriented tape from MWCNTs [22]. The authors prepared the films from a CNT forest grown on a solid substrate and got a uniform sheet with oriented MWCNTs. The process is scalable, but the resistance is high enough even in oriented sheets. Moreover, the solid-state process can remain residual impurities within the structure [23].

The comparison of the conductance of the isotropic mate, formed from SWCNTs and a single rope, extracted from the mat using a sharpened Pt tip, shows the two order difference that is also a good confirmation of the orientation effect on the conductance value [24]. Doping with potassium additionally increases the single rope conductance [25]. The effect of doping on the SWCNT conductance was also examined in [26], but for fibers, not for BPs. The high fiber conductance after iodine doping (107 S/m) was shown.

In this work, we propose the scalable method of creating the oriented BPs composed of SWCNTs and analyze the transport behavior of BPs containing SWCNTs in dependence on their orientation and iodine doping.

2. Preparation of buckypapers

The SWCNTs (TUBALL® TM, OCSiAl production, Russia [27]) grown with the CVD method and chemically cleaned from the impurities up to ~99% of purity were used for the BP formation. Less than 1% weight of residual metals and other contaminations were detected using the energy-dispersive X-ray (EDX) analysis. The transmission electron microscopy (TEM) image of SWCNTs is shown in Fig. 1.

We used several steps for isotropic BP preparation. SWCNT agglomerates were ultrasonically dispersed in ethanol and the resulting suspension was filtered through the polyethylene membrane at porosity 60%. The uniform black deposit was left on the back side of the filter. To remove all possible residual solvents affecting the resistance, the obtained BPs with isotropic SWCNT bundles were additionally annealed at 110 °C overnight.

One of the main task in fabrication of the oriented films is the dissolution of CNTs in a solvent. The solution of this task is not too simple because of a high cohesive energy due to the van der Waals interaction between nanotubes. In accordance to a recent finding that CNTs are thermodynamically soluble in chlorosulfonic acid (CSA) [28, 29], we carried out the direct dispersion of functionalized CNTs in CSA. The CNT dispersion procedure, in our case, includes the SWCNT functionalization by carboxylic groups with a following SWCNT protonation. The functionalization was carried out by boiling the SWCNT functionalized CNTs in CSA for 20% nitric acid during 8 h. After washing in deionized water, for the complete removal of nitric acid, the samples were annealed at 80 °C overnight. The SWCNT protonation was carried out by dissolving SWCNTs with the functional groups in CSA [14, 28].

Figure 1. TEM image of TUBALL®, OCSiAl.

The authors prepared the films from a CNT forest grown on a solid substrate and got a uniform sheet with oriented MWCNTs. The process is scalable, but the resistance is high enough even in oriented sheets. Moreover, the solid-state process can remain residual impurities within the structure [23].

The comparison of the conductance of the isotropic mate, formed from SWCNTs and a single rope, extracted from the mat using a sharpened Pt tip, shows the two order difference that is also a good confirmation of the orientation effect on the conductance value [24]. Doping with potassium additionally increases the single rope conductance [25]. The effect of doping on the SWCNT conductance was also examined in [26], but for fibers, not for BPs. The high fiber conductance after iodine doping (107 S/m) was shown.

In this work, we propose the scalable method of creating the oriented BPs composed of SWCNTs and analyze the transport behavior of BPs containing SWCNTs in dependence on their orientation and iodine doping.
The measurement schemes testifying the considerable contact resistance behavior was observed for the two- and four-point potential drop. The film under investigation was placed onto an electrometer Keithley 6514 for measurements of the potential drop. The film was measured along wires exceeds the transverse conductivity and the contact resistance to iodine vapor at room temperature for various times.

3. Electrical properties of SWCNTs

To decrease the contact resistance, the Au deposition on the buckypaper surface was carried out followed by the Ag wire soldering by using indium. The measurements of electrical conductivity \( G \) and its temperature dependences \( G(T) \) for the buckypapers with SWCNTs were made by the four-point dc with the Keithley 6430 source, and electrometer Keithley 6514 for measurements of the potential drop. The film under investigation was placed onto a quartz substrate. A large difference between the conductance behavior was observed for the two- and four-point measurement schemes testifying the considerable contact resistance contribution to the system impedance. As a result, all experimental data represented in this work are presented for the four-point case.

To understand the transport mechanism, the temperature dependences of the conductivity \( G(T) \) for BPs with isotropic CNTs (random), with oriented CNTs and for BPs with oriented CNTs after additional iodine treatment were analyzed.

In Fig. 4 is the \( G(T) \) dependence of the structures with different CNT orientations. One can see that the bundle orientation (curve “oriented along”) increases the BP conductivity from about \(-10^4 \) S/cm\(^2\) to \(-10^0 \) S/cm\(^2\). Both isotropic and aligned samples exhibit their low resistance with a metallic-type temperature dependence above \( \sim 130 \) K, as shown in the inset to Fig. 4. Below this temperature we observe the conductivity drops with the decreasing temperature corresponding to the semiconductor behavior of \( G(T) \). Such behavior is usually observed in the nanotube systems with crossover temperature \( T_c \) being changed in a wide range of temperatures. Thus, \( T_c \) for CNT fibers was shown to vary between 40 K and above room temperature [31, 32].

The changes in the behavior of \( G(T) \) dependences should be affected by the structural properties of the CNT array. To get the curves close to the metallic behavior, one should obtain the structures with a higher part of metallic CNTs, larger level of purity, ordering of CNTs and their higher density [32–36]. Doping can increase the conductivity of semiconducting CNTs making the \( T_c \) lower and the \( R(T) \) dependence flatter. Any degradation of the structural properties and doping level decreasing should enhance the semiconductor behavior of \( R(T) \) dependences. Hence, the \( G(T) \) dependence measurements give a possibility to understand the quality of the CNT array and its capability for different applications in which high conductance of the structures is required.

Our samples demonstrate the enhancement of the semiconducting behavior of \( G(T) \) characteristics for the isotropic sample, whereas the oriented sample shows a flatter \( G(T) \) dependence. The conductivity of the oriented samples measured along wires exceeds the transverse conductivity and the conductivity of the isotropic sample by more than one order. We guess that the tubes alignment can lead to reducing the intertube density and decreasing the intertube contact resistance. To further increase the conductivity of the oriented structures, we carried out the iodine doping of these structures. The samples were loaded into the flask with iodine and kept there for the different times. It is known that iodine gives the p-type of conductance in CNTs [37]. In Fig. 5 are the temperature dependences \( G(T) \) for the oriented structure with iodine treatment. One can see that the iodine doping additionally increases the conductivity by an order. The dependence of conductance for the oriented sample on the iodine treatment time measured at room temperature is shown in the inset to Fig. 5. One can see that the saturation is reached already in 30–40 minutes of treatment.

There are two contributions to the conductance in the SWCNT system [38]. The first one is due to the fluctuation-assisted tunneling (FAT) described in Ref. [39] for the structures with metallic regions connected by the electronic tunneling through the insulator matrix. The authors demonstrate that the main part to the conductivity is due to the voltage fluctuations in the tunneling junctions connecting the metallic regions (in our case, the conducting bundles of CNT). The second contribution is due to the properties of conducting bundles itself. We will analyze only the FAT mechanism because namely the FAT is responsible for the semiconductor part of the \( G(T) \) curve. At
high temperatures, FAT is described by simple activation dependences and, at low temperatures, the temperature independent behavior is observed. At the intermediate temperatures, the conductivity is determined by the tunneling barrier properties. The low temperature behavior can be described by the electron tunneling between different conductive regions induced by thermal fluctuations [40]:

$$\ln \rho \propto \left( \frac{T_0}{T + T_1} \right).$$

The temperature $T_0$ is an analog of the activation energy and corresponds to the barrier energies $E_0 \sim k_B T_0$. At $T = T_0$, the fluctuations are large enough to overcome the barrier, the $T_0/T_1$ ratio is the probability of tunneling at low temperatures without fluctuations. In this case the tunneling between metallic regions with a small electrostatic charging energy ($<k_B T$) proceeds without the phonon assisted hopping, when the energy of states on the opposite sides of the barriers is the same.

Fitting the low temperature parts of the $G(T)$ data to this model shows (Table 1) that $T_0$, which is an analog of the activation energy, decreases strongly with the iodine doping of oriented samples.

4. Conclusion

Highly conductive oriented single walled carbon nanotube buckypapers were fabricated using the extrusion of the viscous suspension of protonated SWCNTs through the narrow (300 μm) slit. Two different regimes in the temperature dependence of conductance were observed: high temperature metallic-like behavior and low temperature semiconductor behavior. The low-temperature behavior is related to the inter-SWCNT hopping, which is determined by the barrier magnitude that depends on the degree of CNT packing and, correspondingly, on the alignment. Doping affects the semiconductor behavior and increases the intra-CNT conductance. As a result, the orientation results in the increase of buckypaper conductivity by more than one order of magnitude. In addition, one order conductance growth is observed after the iodine treatment at room temperature. The fluctuation-assisted tunneling mechanism was used for the explanation of the experimental transport data. The obtained conductivity value for SWCNT buckypapers is suitable for many applications.

**Acknowledgements**

This work was supported by the Russian State Program (Grant No. 0306-2019-2019).
31. Zhou W., Vavro J., Guthy C., Winey K.I., Fischer J.E. et al. Single
wall carbon nanotube fibers extruded from super-acid suspensions:
preferred orientation, electrical, and thermal transport, J. Appl. Phys.
95(2004) 649–655. https://doi.org/10.1063/1.1627457
32. Harutyunyan A.R., Chen G., Paronyan T.M., Pigos E.M., Kuznetsov
O.A., Hewaparakrama K., Kim S.M., Zakharov D., Stach E.A.,
Sumanasekera G.U. Preferential growth of single-walled carbon
nanotubes with metallic conductivity, Science 326(2009) 116–120.
https://doi.org/10.1126/science.1177599
33. Zhang X., Li Q., Tu Y., Li Y., Coulter J.Y. et al. Strong carbon-na-
notube fibers spun from long carbon-nanotube arrays, Small 3(2007)
244–248. https://doi.org/10.1002/smll.200600368
34. Kaiser A.B., Dusberg G., Roth S. Heterogeneous model for conduc-
tion in carbon nanotubes, Phys. Rev. B 57(1998) 1418–1421. https://
doi.org/10.1103/PhysRevB.57.1418
35. Steinmetz J., Glerup M., Paillot M., Bernier P., Holzinger M. Pro-
duction of pure nanotube fibers using a modified wet-spinning
method, Carbon 43(2005) 2397–2400. https://doi.org/10.1016/j.car-
bon.2005.03.047
36. Skákalová V., Kaiser A.B., Woo Y.S., Roth S. Electronic transport
in carbon nanotubes: from individual nanotubes to thin and thick
networks, Phys. Rev. B 74(2006) 085403–085412. https://doi.org/
10.1103/PhysRevB.74.085403
37. Cambedouzou J., Sauvajol J.L., Rahmani A., Flahaut E., Peigney
A., Laurent C. Raman spectroscopy of iodine-doped double-walled
carbon nanotubes, Phys. Rev. B 69(2004) 235422–235427. https://
doi.org/10.1103/PhysRevB.69.235422
38. Tsebro V.I., Tonkikh A.A., Rybkovskiy D.V., Obraztsova E.A.,
Kauppinen E.I. et al. Phonon contribution to electrical resistance
of acceptor-doped single-wall carbon nanotubes assembled into
transparent films, Phys. Rev. B 94(2016) 245438–24546. https://doi.
org/10.1103/PhysRevB.94.245438
39. Kivelson S., Heeger A.J. Intrinsic conductivity of conducting poly-
mers, Synth. Met. 22(1988) 371–375. https://doi.org/10.1016/0379-
6779(88)90108-7
40. Sheng P. Fluctuation-induced tunneling condition in disordered ma-
terials, Phys. Rev. B 21(1980) 2180–2195. https://doi.org/10.1103/
PhysRevB.21.2180