Average SWCNT bundle length estimated by resistance measurement

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Abstract. The length of single-walled carbon nanotubes (SWCNTs) affects the optoelectronic and mechanical properties of macroscopic SWCNT layers. Modern methods are capable to measure the length of short nanotubes, and also require complex sample preparation procedures. In this work we show that the average length of SWCNTs can be estimated by measuring the resistance of randomly oriented SWCNTs array. We observe the change in the slope of the resistance dependence on the distance between the contacts with the interval between 100 and 200 µm. The change of resistance slope indicates a change in the path of current flow through the SWCNT. The change in the conduction path can be associated with the “effective bundle length”, which should be related to the average nanotube length. Thus, we have demonstrated a simple and quick technique to measure SWCNT bundle length, which can be used in-situ and does not require special sample preparation.

1. Introduction

It is well known that the properties of transparent conducting electrodes (TCEs) and other devices consisting of single walled carbon nanotubes (SWCNTs) are highly dependent on the size of SWCNTs or of their bundles. For example, mechanical strengthening and the stress transfer efficiency in composites should be favoured with long and thin SWCNTs [1,2]. Length is also an important parameter for the functioning of electronic devices which define the density of nanotubes required to form a conductive network above the percolation threshold [3]. Developing methods to adapt the length distribution by controlled growth or subsequent proliferation obviously requires practical and efficient analytical methods that detect length values.

Different methods for measuring the average length of the CNT were reported. All of them have significant disadvantages, especially when it is needs to measure long CNTs [4]. The most widespread method is the atomic force microscopy (AFM), but preparation of samples for AFM always includes ultrasonic processing. In addition, this technique based on the individual measurement of a large amount of CNT to obtain statistically significant mean values, which requires much time for analysis. In the
same way, the length of the CNT can be measured by the dynamic light scattering (DLS) method, which is also requires the ultrasonic processing. Although, it is well known that ultrasound destroys the CNTs and reduces their average length [2,5–7]. Scanning electron microscopy (SEM) is another method to measure the CNT length. However, the use of SEM assumes that CNTs must be grown vertically (carpet-grown CNTs) and have the similar length [8]. These facts do not allow to use this method for CNTs grown by chemical vapor deposition with different densities along the height or for randomly oriented CNTs. Shear-aligned photoluminescence and shear rheology in solutions were used for characterization of CNT length distribution [9]. However, these techniques have limitation ~1 µm CNT length. Work by E. Amram Bengio and co-workers [10] has shown a method for measuring CNT length based on cryogenic transmission electron microscopy (cryo-TEM) of CNTs in chlorosulfonic acid. Cryo-TEM imaging appears to bias the length estimation towards longer CNTs, likely due to difficulties in identification of the shorter CNTs through imaging. Besides, this technique is also time-consuming.

In this work we present a new method for measuring CNT length over a wide range of lengths. Our approach allows to measure CNTs length in wide a range in a short time. Also, it can be used as an in-situ method during CNT deposition processes.

2. Materials and methods
Films of randomly oriented SWCNTs synthesized by the aerosol chemical vapor deposition (CVD) method were deposited on a nitrocellulose filter at the outlet of the reactor as reported previously [11,12].

Figure 1 shows the optical image of the studied sample, which is a SWCNT layer transferred to a quartz substrate with Cr/Au (2/300 nm thick) metal contacts deposited on SWCNT by vacuum evaporation. The SWCNT layer transmittance (T) estimated to 95%. The fabrication process was detailed in the work [13]. Contact gap patterns have been chosen to cover the entire range of widths 5-500 µm. The widths of the gap were: 5-40 µm with a step of 5 µm, 40-100 µm with a step of 10 µm, 100-200 µm with a step of 25 µm, 200-500 µm with a step of 50 µm.

![Figure 1. Optical image fragment of Cr/Au contacts (2 and 300 nm thick respectively) deposited on SWCNT layer with 9 nm thickness and 95% transmittance (T)](image)

A scanning ion helium microscope (HIM) was used to visualize SWCNTs bundles array by direct imaging.

To define the resistance of SWCNT the I-V characteristics of SWCNT films were measured using probe station in -1…+1 V range.

3. Results and discussion
A top view image of SWCNT layer on silicon substrate obtained by HIM microscope is shown in Figure 2. Despite we know a typical length of individual SWCNT estimated in work [14], it was found that the SWCNT layer is not an array of individual randomly oriented nanotubes, but so-called "bundles" consisting of bonded nanotubes with average diameter about 10 nm.
We consider the bundle as an effective medium through which the current can flow with lower losses than through the intersections of single nanotubes. Thus, the flow of the current through the SWCNT layer can be considered as the flow of current through the bundles or their intersections, while the actual length of the conducting channel may differ from the length of a single nanotube.

The current-voltage characteristics of a SWCNT layer under pairs of contacts located at different distances from each other (5-500 μm) were measured using a four-probe method. The dependence of the resistance on the distance between the contacts for the experimentally obtained data is shown in Figure 3. It can be seen that the resistance of SWCNTs grows with increase of distance between the contacts. We observe the change in the slope of the resistance as the function of distance between the contacts, presumably associated with the approach of the distance between the contacts to the average length of the SWCNT bundle.

We relate the change in the resistance to a change in the path of current flow. The change in the conduction path can be associated with the "effective bundle length", which should be related to the average nanotube length. In the case of narrow gap, (less than bundle length) current flows to an opposite contact without any bundle interconnections. In the case of wide gap, bundles length is less than distance between contacts therefore current flows through bundle interconnections.

It was observed that the characteristic length of the conducting channel formed by bundles at which the resistance changes is about ~ 190 μm (Figure 3).
4. Conclusions
In this study the new method of SWCNT bundle length measurement was proposed. The method consists of the sequential measurement of resistances between pairs of contacts deposited at different distances on top of a SWCNT layer. Based on the experimental data the dependence of the resistance on the distance between the contacts was plotted. It was found that at within the interval of distances between 100 and 200 \(\mu m\) the slope of the resistance changes. A change in the resistance indicates a change in the path of current flow through the array of SWCNT. The change in the conduction path can be associated with the "effective bundle length", which should be related to the average nanotube length. The effective conductive length of SWCNT bundle obtained by resistance measurement was \(\sim190\ \mu m\). The proposed technique can be used for a simple and quick definition of the average bundle length of randomly oriented SWCNTs array.

Acknowledgments
The reported study was funded by RFBR, project number 19-38-60008 (metal contacts deposition, sheet resistance measurement), the Ministry of Science and Higher Education of the Russian Federation (grant 0791-2020-0005).

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