

Dependence of Young's modulus of vertically aligned carbon nanotubes on their aspect ratio

M V Il'ina, O I Il'in, A A Konshin, A A Fedotov and O A Ageev

Southern Federal University, Institute of Nanotechnologies, Electronics and Electronic Equipment Engineering, Taganrog, 347922, Russia

mailina@sfedu.ru

Abstract. The experimental studies of the dependence of Young's modulus of vertically aligned carbon nanotubes (CNTs) on their aspect ratio were carried out. It was shown that the Young's modulus of the individual CNTs increased from 1.63 to 1.83 TPa with an increase in their aspect ratio from 8 to 15.8. This dependence is probably due to the fact that the relative number of the structure defects in the CNT decreases with increasing its aspect ratio. The Young's modulus of the CNT bundles also increased with the growth of the aspect ratio of CNTs. However, the calculated values of the Young's modulus of the CNT bundles with a large aspect ratio were smaller than ones of the individual CNTs with a smaller aspect ratio. It is due to the fact that CNTs that form the bundles are in strained state initially. A smaller strain is required to form a given deformation in CNT bundle than that of individual nanotube. The obtained results can be used to develop and create nanoelectronics devices based on vertically aligned CNTs, in particular adhesion coatings and nonvolatile memory elements.

1. Introduction

The rapid development of nanotechnology and the new opportunities in the field of nanoscale structures created a wide interest in the research of carbon nanotubes (CNTs) [1]. However, for the application of CNTs as a material for the elemental base of new generation electronics, it is necessary to study in detail their mechanical parameters, in particular, the Young's modulus [2,3]. Theoretical studies of the Young's modulus of CNTs are conducted mainly using models that are valid only for ideal (physically and chemically homogeneous over the entire length) nanotubes [4,5]. Experimental studies of the CNTs Young's modulus are not numerous [6-9], since the use of traditional research methods, such as direct tensile loading, is difficult due to the nanoscale material.

As a consequence, the conclusions about the dependence of the CNTs elastic properties on their geometric parameters are also not numerous and contradictory: some note the "insensitivity" of Young's modulus to the nanotube diameter [10], others demonstrate an increase in the Young's modulus with an increase in diameter for a fixed CNT length [11,12], and, conversely, its decrease [13,14]. Thus, there is a need for further studies of the Young's modulus of CNTs on their geometric parameters, the main of which is the aspect ratio – the ratio of the length to diameter.

The aim of this study is to investigate the dependence of the Young's modulus of vertically aligned CNTs on their aspect ratio using the previously developed measurement technique based on the nanoindentation method.



2. Experimental studies

As the studied samples there were CNT arrays grown by plasma enhanced chemical vapour deposition method on a silicon wafer with a Ni/Ti structure using NANOFAB NTC-9 (NT-MDT, Russia) [15-17]. Six samples of two types were selected for investigation: individual vertically aligned CNTs (Fig. 1a) and vertically aligned CNTs combined in bundles (Fig. 1b). The geometric parameters of the experimental samples were evaluated on the basis of scanning electron microscopy (SEM) images obtained using SEM Nova NanoLab 600 (FEI, the Netherlands).

Experimental studies of the Young's modulus of experimental samples were carried out using the previously developed technique based on the nanoindentation method [18,19]. The measurements were carried out at the Ntegra probe nanolaboratory (NT-MDT, Russia) using a scanning hardness nanotester integrated in it. The indenter was the diamond tree-sided Berkovich pyramid with the apex angle $\theta = 70^\circ$ between the edge and height.

The nanoindentation process was carried out with the application of loads of 100 μN at 20 different points of the CNT array on the distance about 10 μm from each other. The dependence of the indentation force P_{IND} on the corresponding penetration depth h of the indenter in the material was obtained during the measurement. The dependences $P_{IND}(h)$ for each experimental sample are shown in the Figure 2.

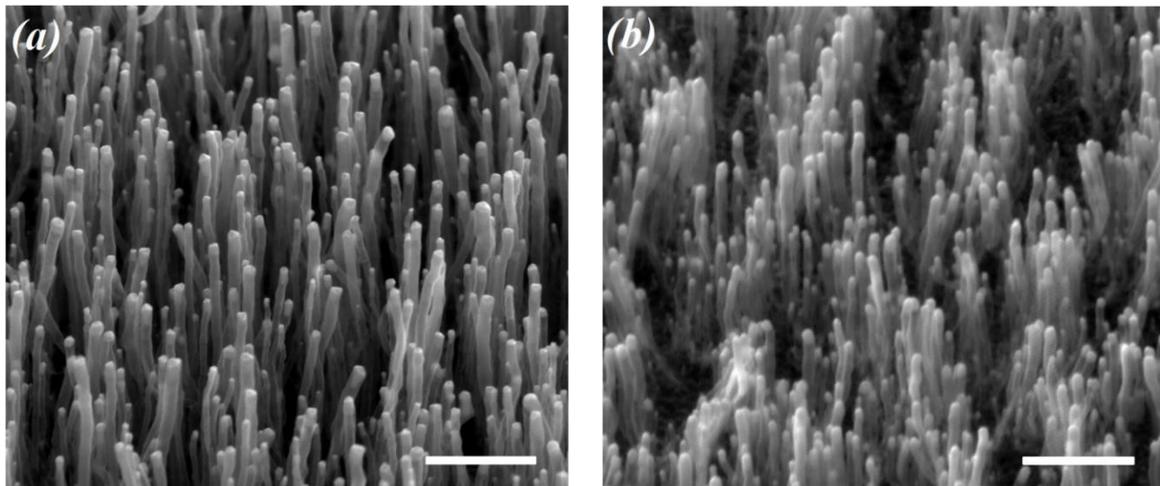


Figure 1. SEM images of experimental samples of CNT arrays: (a) type 1 and (b) type 2. Scale segment 500 nm.

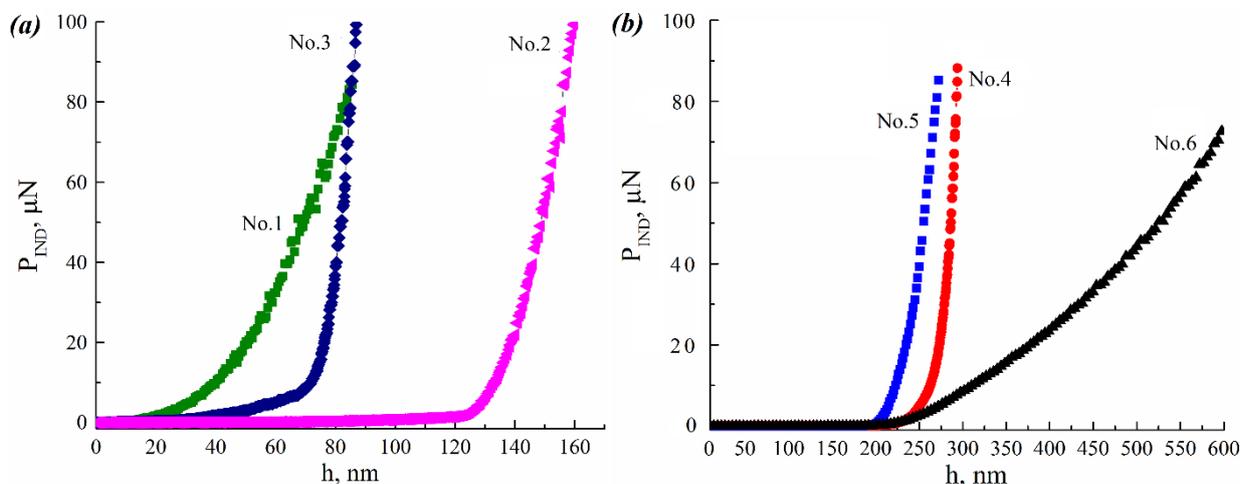


Figure 2. Averaged load curves of vertically aligned CNT for samples of (a) type 1 and (b) type 2.

On the basis of the obtained experimental dependences using the technique from Ref. [18], a Young's modulus of vertically aligned CNTs was calculated by the formula:

$$E = \frac{64(P_{IND} - P_i) \cos \theta}{\pi i D^4 k^2}, \quad (1)$$

where P_{IND} – indentation force, P_i – indentation force corresponding to the depth of the i -tube touch, i – amount of nanotubes interacting with the indenter at P_{IND} , D – a CNT diameter, $k = (P/(EI)_{eff})^{1/2}$ – the coefficient, $(EI)_{eff}$ – a effective bending stiffness of CNT.

Geometric parameters and calculated values of Young's modulus of vertically aligned CNTs are given in Table 1.

Table 1. The calculated values of the Young's modulus and geometric parameters of experimental samples.

Sample No.	Diameter, nm	Length, μm	Density of CNTs in array, μm^{-2}	Aspect ratio	Young's modulus, TPa
Type 1					
1	44.1	0.35	95	8	1.63
2	63.2	0.65	38	10.2	1.69
3	44.9	0.71	60	15.8	1.83
Type 2					
4	43.8	0.65	82	14.8	1.15
5	35.6	1.21	72	34	1.29
6	51	0.69	69	13.5	0.59

It should be noted that the $P_{IND}(h)$ dependence sections corresponding to the elastic interaction area of CNTs with an indenter were used in order to calculate the Young's modulus of the experimental samples.

3. Results

The results of experimental studies have shown that the Young's modulus of individual vertically aligned CNTs increases from 1.63 to 1.83 TPa with an increase in their aspect ratio from 8 to 15.8 (Fig. 3a). This dependence is probably due to the fact that the relative number of the structure defects in the CNT decreases with increasing its aspect ratio. Thus, the defects are concentrated near the base of the CNT during the growth of CNTs and their relative size number with increasing CNT length. In addition, the number of defects can increase with increasing diameter of the multi-walled CNT due to the increase in the number of layers in it.

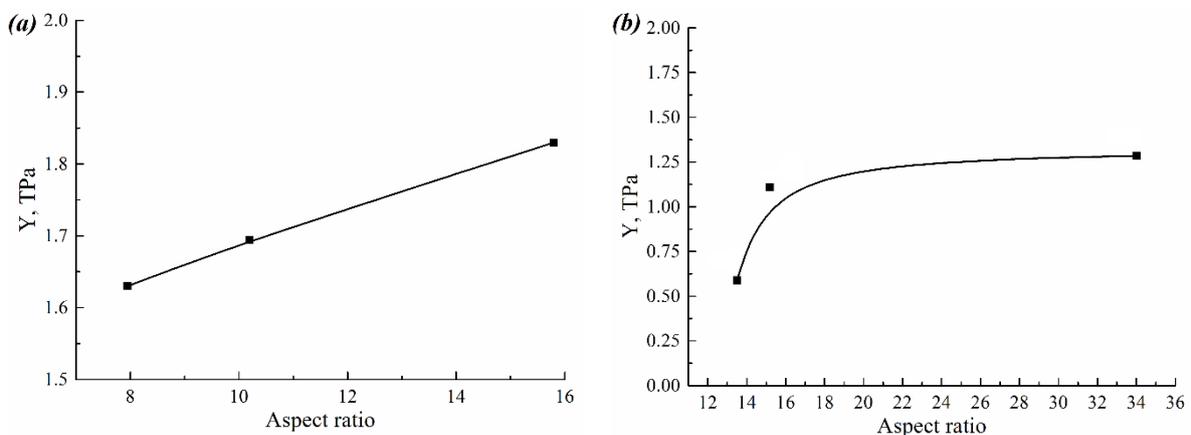


Figure 3. Dependences of Young's modulus of CNTs on their aspect ratio for (a) type 1, (b) type 2.

The Young's modulus of experimental samples of type 2, which are bundles of CNTs, also increases with an increase of the CNT aspect ratio (Fig. 3b). However, the calculated values of the Young's modulus for samples of type 2 with a large aspect ratio are smaller than ones for samples of type 1 with a smaller aspect ratio (Table 1). This may be due to the fact that CNTs forming the bundles are initially in a strained state. As a result, a smaller load is required to form a deformation in bundles than that for individual CNTs in the nanoindentation process. This fact must be taken into account when measuring the mechanical parameters of combined into bundles CNTs using by the nanoindentation method.

4. Conclusion

The dependence of Young's modulus of vertically aligned CNTs on their aspect ratio is established experimentally. It is shown that the Young's modulus of the individual CNTs increases from 1.63 to 1.83 TPa with an increase in their aspect ratio from 8 to 15.8. The Young's modulus of the CNT bundles also increases from 0.59 to 1.29 TPa with the growth of the aspect ratio of CNTs from 13.5 to 34. This is due to the fact that the relative number of the structure defects in the CNT decreases with increasing its aspect ratio. The obtained results are in good agreement with the literature data [6-9,18-20]. The obtained results can be used to develop and create nanoelectronics devices based on vertically aligned CNTs, in particular adhesion coatings and non-volatile memory elements [2,3,21,22].

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References

- [1] Ren Z, Lan Y and Wang Y *Aligned Carbon Nanotubes, NanoScience and Technology* (Springer-Verlag Berlin Heidelberg) (2013)
- [2] Il'ina M V, Il'in O I, Blinov Y F, Konshin A A, Konoplev B G and Ageev O A 2018 *Materials* **11** 638
- [3] Il'ina M V, Il'in O I, Blinov Yu F, Smirnov V A, Kolomiitsev A S, Fedotov A A, Konoplev B G and Ageev O A 2017 *Carbon* **123** 514-24
- [4] Zhou X, Zhou J J and Ou-Yang Z C 2000 *Phys. Rev.* **62** 13692-6
- [5] Batra R C and Sears A 2007 *Int. J. Solids Struct.* **44** 7577-96
- [6] Ding W, Calabri L, Kohlhaas K M, Chen X, Dikin D A and Ruoff R 2007 *Exp. Mech.* **47** 25-36
- [7] Lourie O and Wagner H D 1998 *J. Mater. Res.* **13** 2418-22
- [8] Wong E W, Wong E W, Sheehan P E and Lieber C M 1997 *Science* **277** 1971-5
- [9] Qi H J, Teo K B K, Lau K K S et al. 2003 *J. Mech. Phys. Solids* **51** 2213-37
- [10] Wang Q, Vara dan V K and Quek S T 2006 *Phys. Lett. A* **357** 130-5
- [11] Li C and Chou T 2003 *Int. J. Solids Struct.* **40** 2487-99
- [12] Chang T and Gao H 2003 *J. Mech. Phys. Solids* **51** 1059-74
- [13] Lei X, Natsuki T, Shi J and Ni Q Q 2011 *J. Nanomat.* **2011** 805313
- [14] Parvaneh V and Shariati M 2011 *Acta Mech.* **216** 281-9
- [15] Klimin V S, Il'ina M V, Il'in O I, Rudyk N N and Ageev O A 2017 *IOP J. Phys.: Conf. Ser.* **917** 092023
- [16] Il'in O I, Il'ina M V, Rudyk N N, Fedotov A A and Ageev O A 2018 *Nanosystems: Phys. Chem. Math.* **9** 92-4
- [17] Il'in O I, Il'ina M V, Rudyk N N, Fedotov A A, Levshov D I and Ageev O A 2018 *IOP J. Phys.: Conf. Ser.* **1038** 012062
- [18] Ageev O A, Il'in O I, Kolomiitsev A S, Konoplev B G, Rubashkina M V, Smirnov V A and Fedotov A A 2012 *Nanotechnologies in Russia* **7** 47-53

- [19] Ageev O A, Blinov Yu F, Il'ina M V, Konoplev B G and Smirnov V A 2016 *Intelligent Nanomaterials, 2nd Edition*. Eds. A Tiwari, Y K Mishra, H Kobayashi, A P F Turner (Wiley Scrivener Publishing LLC), chapter **11** 361-94
- [20] Ageev O A, Ilin O I, Kolomytsev A S, Rubashkina M V, Smirnov V A and Fedotov A A 2014 *Adv. Mat. Res.* **894** 355-8
- [21] Ageev O A, Blinov Yu F, Iilina M V, Ilin O I and Smirnov V A 2016 *IOP J. Phys.: Conf. Ser.* **741** 012168
- [22] Ageev O A, Blinov Yu F, Il'ina M V, Il'in O I, Smirnov V A and Tsukanova O G 2016 *Phys. Solid State* **58** 309-14