St. Petersburg Polytechnic University Journal. Physics and Mathematics. 2024. Vol. 17. No. 3.1
Научно-технические ведомости СПбГПУ. Физико-математические науки. 17 (3.1) 2024

Conference materials
UDC 546.26; 537.226.86
DOI: https://doi.org/10.18721/JPM.173.142

Influence of ambient humidity on the magnitude of the piezoelectric strain coefficient of nitrogen-doped carbon nanotubes for the creation of strain sensors

O.I. Soboleva [1] ✉, M.V. Il`ina [1], M.R. Polyvianova [1], A.A. Chefranov [1], O.I. Il`in [1]

[1] Institute of Nanotechnologies, Electronics and Equipment Engineering,
Southern Federal University, Taganrog, Russia
✉ osotova@sfedu.ru

Abstract. This paper establishes patterns of influence of ambient humidity on the piezoelectric strain coefficient and the magnitude of the current generated by nitrogen-doped carbon nanotubes (N-CNTs) during their deformation. It is shown that at humidity up to 60%, stable current generation is observed during the deformation of N-CNTs; at higher humidity, the instability of measurements increases and the spread of the generated current grows significantly, which is associated with a decrease in the N-CNTs piezoelectric strain coefficient.

Keywords: carbon nanotubes, nanopiezotronics, piezoelectric response, piezoelectric force microscopy, atomic force microscopy

Funding: This research was supported by the Ministry of Science and Higher Education of the Russian Federation in the framework of the state task in the field of scientific activity, grant number FENW-2022-0001.

Citation: Soboleva O.I., Il`ina M.V., Polyvianova M.R., Chefranov A.A., Il`in O.I., Influence of ambient humidity on the magnitude of the piezoelectric strain coefficient of nitrogen-doped carbon nanotubes for the creation of strain sensors, St. Petersburg State Polytechnical University Journal. Physics and Mathematics. 17 (3.1) (2024) 210–214. DOI: https://doi.org/10.18721/JPM.173.142

Материалы конференции
УДК 546.26; 537.226.86
DOI: https://doi.org/10.18721/JPM.173.142

Влияние влажности окружающей среды на величину пьезоэлектрического модуля легированных азотом углеродных нанотрубок для создания сенсоров деформации

О.И. Соболева [1] ✉, М.В. Ильина [1], М.Р. Полывянова [1],
А.А. Чефранов [1], О.И. Ильин [1]

[1] Южный федеральный университет,
Институт нанотехнологий, электроники и приборостроения, г. Таганрог, Россия
✉ osotova@sfedu.ru

Аннотация. В данной работе установлены закономерности влияния окружающей среды на пьезоэлектрический коэффициент деформации и величину тока, генерируемого углеродными нанотрубками, легированными азотом (N-УНТ), в процессе их деформации. Показано, что при влажности до 60% наблюдается стабильное генерирование тока при деформации N-УНТ, при более высокой влажности возрастает нестабильность измерений и значительно увеличивается разброс генерируемого тока, что связано со снижением пьезоэлектрического модуля N-УНТ.

Ключевые слова: углеродные нанотрубки, нанопьезотроника, пьезоэлектрический отклик, метод силовой микроскопии пьезоотклика атомно-силовой микроскопии

Финансирование: Данное исследование выполнено при поддержке Министерства науки и высшего образования Российской Федерации в рамках государственного задания в области научной деятельности, грант № FENW-2022-0001.

Ссылка при цитировании: Соболева О.И., Ильина М.В., Полывянова М.Р., Чефранов А.А., Ильин О.И. Влияние влажности окружающей среды на величину пьезоэлектрического модуля легированных азотом углеродных нанотрубок для создания сенсоров деформации // Научно-технические ведомости СПбГПУ. Физико-математические науки. 2024. Т. 17. № 3.1. С. 210–214. DOI: https://doi.org/10.18721/JPM.173.142

Introduction

At present, implantable electronics is an actively developing field of science. Basically, various types of materials with piezoelectric effect are used to transmit “tactile” sensations, effectively converting mechanical impact into an electrical signal [1]. At the same time, the efficiency of energy conversion in such sensors is mainly determined by two factors: the electromechanical properties of the piezoelectric material and the design of the sensor itself. In addition, such designs can be used to create highly sensitive strain gauges or microphones [2,3]. Piezoelectric materials can become electrically polarized when an external voltage is applied or deformed in response to electrical stimuli. Thus, sensors based on the piezoelectric effect can be used as versatile sensors. Compared to other sensors or monitoring methods, piezoelectric sensors have numerous advantages such as small size, light weight, low cost, availability in various formats, and high sensitivity [4]. Nitrogen-doped vertically aligned carbon nanotubes (N-CNTs) with anomalous piezoelectric properties can be one of the promising functional materials with high piezoelectric strain coefficient and mechanical strength [5]. However, for an instrument N-CNTs, it is important to understand how environmental parameters can affect the characteristics of the device and limit its scope of application. In particular, changes in atmospheric humidity can not only increase the parasitic capacitance, for example in pressure sensors, but also “glue” CNTs together, as well as affect the piezoelectric strain coefficient of the array. At the same time, many works have been devoted to studies of the influence of growth parameters on the properties of N-CNT [6, 7] However, there are no studies on the effect of environmental humidity on the piezoelectric strain coefficient N-CNTs in the literature. In view of this, this paper presents the results of a study of the influence of ambient humidity on the magnitude of the piezoelectric strain coefficient of nitrogen-doped carbon nanotubes to create strain sensors.

Materials and Methods

The experimental sample was an array of vertically aligned carbon nanotubes grown by plasma enhanced chemical vapor deposition method (C_2H_2 + NH_3). In this case, ammonia added during the growth process acts as a source of nitrogen defects. The growth was carried out at a temperature of 550 °C for 30 min and a pressure of 600 Pa. The plasma power was 40 W. Nickel (15 nm) deposited on a molybdenum sublayer was used as a catalyst. The piezoelectric properties of vertically aligned N-CNTs were studied by piezoelectric force microscopy (PFM) method of atomic force microscopy (AFM). The main difficulty in such experimental research is that the PFM method is a contact AFM technique, which leads to the CNTs detaching from the substrate near its base. The piezoelectric response of N-CNTs was measured by AFM piezoelectric force microscopy. A commercial NSG10 cantilever with a conductive TiN coating was used as an AFM probe.

Air humidity was changed by creating a confined ambient using a hermetic box. A container with hot water was placed under the hermetic box, as a result of hot water evaporation humidity increased and was controlled by a humidity sensor. The air humidity varied from 25 to 90%.

In the process of air humidity change, the probe was withdrawn from the N-CNT array to prevent sticking in the “N-CNT/probe” system. After reaching a certain humidity level, the container with water was removed.

The crystalline perfection of the grown N-CNTs was assessed by Raman spectroscopy on a Renishaw InVia Reflex (Renishaw plc, UK) with a wavelength of 532 nm. It was found that for the obtained N-CNT samples the positions of D-, G-peaks correspond to frequencies ~1365 and ~1593 cm^{-1}, which is characteristic of multilayer carbon nanotubes (Fig. 1). The ratio of I_D/I_G peaks intensity = 1.06 shows high defectivity of N-CNTs, which is associated with the introduction of nitrogen atoms into the CNT structure and the graphite lattice disordering, as well as with the peculiarity of the spectra acquisition technique, in which the laser beam is incident along the normal to the sample surface (i.e., parallel to the N-CNTs). The formation of bamboo-like bridge in the N-CNT structure causes symmetry violations of the graphite layer with sp2 hybridization of carbon atoms and leads to an increase in the intensity of the D-peak. There is also a 2D band (2550–2700 cm^{-1}) on the spectrum, which is characteristic of multi-wall CNTs and is associated with the occurrence of a second-order double resonance of two iTO phonons [8, 9]. In pure graphene, this band consists of a single narrow peak, while in multi-walled N-CNTs, the shape of the line is deformed due to the presence of defects in the lattice and the influence of many layers in the CNT structure. In this connection, the band broadening is observed in the range of 2250–3500 cm^{-1}. Additionally, the contribution of luminescence is visible, which does not allow us to unambiguously identify the position of the 2D band at the used laser irradiation frequency. Indirectly, for multi-wall CNTs, the displacement of the 2D band can carry information about the change in the value of the Young's modulus of CNTs.

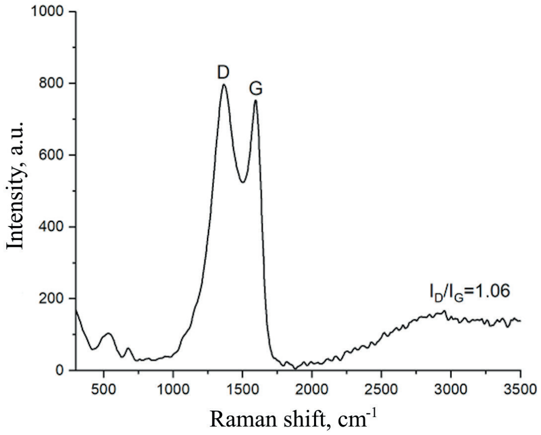

Fig. 1 Raman spectra of a N-CNT sample

Results and Discussion

The results of experimental studies showed that when the humidity increases from 30 to 60%, the value of the generated N-CNT current does not change significantly and is 7 ± 4 nA. With further increase in humidity up to 80%, the magnitude of the generated current increases to 12 ± 4 nA, and at 90% it decreases again to 5 ± 3 nA (Fig. 2, *a* and Fig. 3, *a*). This dependence is probably related to the change in the magnitude of the piezoelectric response of N-CNTs (Fig. 2, *b* and Fig. 3, *b*).

Thus, at a humidity of 30–55 %, the value of the piezoelectric strain coefficient of N-CNTs (Fig. 3, *b*) was 33 ± 14 pm/V, and then, when the humidity increased to 90%, it decreased to 0.5 pm/V. This pattern is probably due to the formation of an adsorption layer of water on the surface of N-CNTs, leading to a decrease in the magnitude of its polarization.

It is worth noting that the piezoelectric effect in N-CNTs differs from the classical volume effect and is surface [10, 11], which significantly affects the dependence of the piezoelectric strain coefficient of an N-CNT on the quality of its surface.

Thus, from Figure 3, it is found that at humidity above 60 %, unstable current generation with high spread of values is observed in the process of deformation of N-CNTs, as well as a significant decrease in the piezoelectric properties of N-CNTs.

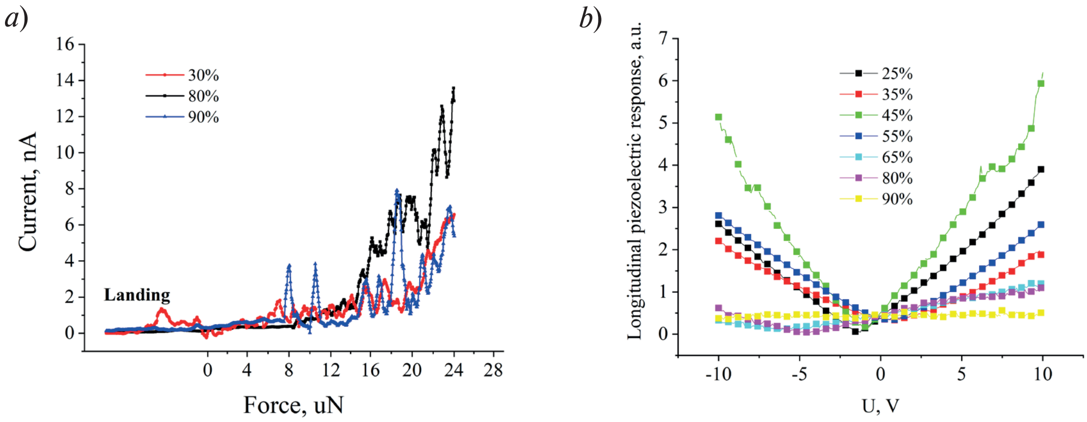

Fig. 2. The results of experimental studies of the influence of ambient humidity on the magnitude of the current generated by the N-CNT from the pressure force of the AFM probe (*a*) and the magnitude of the longitudinal piezoelectric response (*b*)

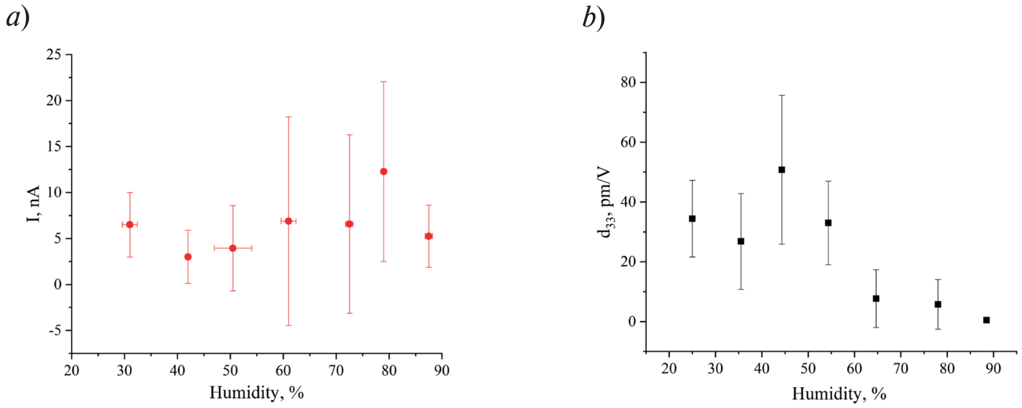

Fig. 3. Patterns of the influence of ambient humidity on the magnitude of the N-CNT-generated current at an AFM probe clamping force of 25 μN (*a*) and the magnitude of the N-CNT piezoelectric strain coefficient (*b*)

Conclusion

The paper establishes patterns of influence of ambient humidity on the piezoelectric strain coefficient and the magnitude of the current generated by N-CNTs during their deformation. It is shown that at humidity up to 60%, stable current generation is observed during the deformation of N-CNTs; at higher humidity, the instability of measurements increases, and the spread of the generated current grows significantly, which is associated with a decrease in the N-CNTs piezoelectric strain coefficient.

The research outcomes can be used in the development of mechanical energy converters: strain sensors or highly sensitive microphones.

REFERENCES

1. **Sawane M., Prasad M.,** MEMS piezoelectric sensor for self-powered devices: A review, Mater. Sci. Semicond. Process. 158 (2023) 107324.

2. **Ju M., Dou Z., Li J.W., Qiu X., Shen B., Zhang D., Yao F.Z., Gong W., Wang K.,** Piezoelectric Materials and Sensors for Structural Health Monitoring: Fundamental Aspects, Current Status, and Future Perspectives, Sensor. 23 (2023).

3. **Kwon S. ryung, Huang W., Zhang S., Yuan F.-G., Jiang X.,** A new type of microphone using flexoelectric barium strontium titnate, in: W. Ecke, K.J. Peters, N.G. Meyendorf, T.E. Matikas Eds. (2014) 90620Y.

4. **Sha F., Xu D., Cheng X., Huang S.,** Mechanical Sensing Properties of Embedded Smart Piezoelectric Sensor for Structural Health Monitoring of Concrete, Res. Nondestruct. Eval. 32 (2021) 88–112.

5. **Il'ina M.V., Il'in O.I., Guryanov A.V., Osotova O.I., Blinov Y.F., Fedotov A.A., Ageev O.A.,** Anomalous piezoelectricity and conductivity in aligned carbon nanotubes, J. Mater. Chem. C. 9 (2021) 6014–6021.

6. **Il'ina M.V., Soboleva O.I., Polyvianova M.R.,. Khubezhov S.A, Il'in O.I.,** Study of the Piezoelectric Properties of Nitrogen-Doped Carbon Nanotubes for the Development of Energy-Efficient Nanogenerators, Nanobiotechnology Reports. 18 (2023) 858–864.

7. **Il`ina M.V., Rudyk N.N., Soboleva O.I., Polyvianova M.R., Khubezhov S.A., Il`in O.I.,** Study of the Effect of Growth Temperature on the Properties of Nitrogen-Doped Carbon Nanotubes for Designing Nanopiezotronic Devices, Tech. Phys. 68 (2023) 871–877.

8. **Ferrari A.C., Robertson J.,** Interpretation of Raman spectra of disordered and amorphous carbon, Phys. Rev. B. 61 (2000) 14095–14107.

9. **Ferrari A.C., Meyer J.C., Scardaci V., Casiraghi C., Lazzeri M., Mauri F., Piscanec S., Jiang D., Novoselov K.S., Roth S., Geim A.K.,** Raman Spectrum of Graphene and Graphene Layers, Phys. Rev. Lett. 97 (2006) 187401.

10. **Kundalwal S.I., Meguid S.A., Weng G.J.,** Strain gradient polarization in graphene, Carbon N. Y. 117 (2017) 462–472.

11. **Il'ina M., Il'in O., Osotova O., Khubezhov S., Rudyk N., Pankov I., Fedotov A., Ageev O.,** Pyrrole-like defects as origin of piezoelectric effect in nitrogen-doped carbon nanotubes, Carbon N. Y. 190 (2022) 348–358.

THE AUTHORS

SOBOLEVA Olga I.
osotova@sfedu.ru
ORCID: 0000-0002-0487-7542

IL'INA Marina V.
mailina@sfedu.ru
ORCID: 0000-0002-8023-8283

POLYVIANOVA Maria R.
polyvianova@sfedu.ru
ORCID: 0009-0005-0152-1486

CHEFRANOV Alexander A.
chefranov@sfedu.ru

IL'IN Oleg I.
oiilin@sfedu.ru
ORCID: 0000-0002-1456-5139

Received 22.07.2024. Approved after reviewing 26.08.2024. Accepted 27.08.2024.