# Analysis and optimization of photonics devices manufacturing technologies based on carbon nanotubes

**N. Tripathi[1], V.S. But[1], S.A. Lebedev[1], M.A. Sovetkina[1], S. Kumar[1]**

[1]Samara National Research University, Moskovskoye Shosse 34, Samara, Russia, 443086

**Abstract.** The analysis and optimization of optical devices manufacturing technologies based on carbon nanotubes intended for work in the terahertz range were carried out. These processes studied in the work have practical application for the deposition of carbon nanotubes and their subsequent use as materials for prototypes of the waveguide and sensor of the terahertz range. To obtain a layer of carbon nanotubes, a chemical vapor deposition chamber was used. Various aspects of the synthesis and growth of the mechanism of CNT are considered in this article. Carbon nanotubes (CNTs) were grown on a sandwich structure based on a silicon wafer, where a layer of aluminum and copper 100 nm thick was deposited, then an iron catalyst was applied about 5 nm thick, and then copper and aluminum were deposited again, but with a thickness of 10 nm layer is also using magnetron sputtering. The growth was carried out with two variable parameters: flow rate and flow duration.

## 1. Introduction

Carbon nanotubes (CNTs) have been of great interest since their discovery in 1991 because of their unique properties. The high mechanical strength of carbon nanotubes in combination with their electrical conductivity makes it possible to use them as a probe in scanning probe microscopes, which increases the resolution of devices of this kind by several orders of magnitude and puts them on a par with such a unique device as a field ion microscope. Also, nanotubes have high emission characteristics [3]. The current of autoelectron emission at a voltage of about 500 V reaches, at room temperature, values of the order of 0.1 Volts on $cm^{-2}$. This opens up the possibility of creating a new generation of displays on their basis. The use of nanotubes in chemical technology seems very promising, which is due, on the one hand, to their high specific surface and chemical stability, and on the other hand, to the possibility of attaching various radicals to the surface of nanotubes, which can later serve as either catalytic centers or nuclei for the implementation of various chemical transformations. Due to all these properties, carbon nanotubes have a large number of other potential applications in the field of electronics, medical sciences and many other areas. Thanks to these facts, CNT has been considered as one of the best candidates for future applications in the field of nanotechnology [3].

All these advantages encourage researchers to look for new possibilities of using carbon nanotubes. Potential optical devices based on them are waveguides and sensors of the terrahertz range [2]. But for their high-quality manufacturing, in order for them to function, certain properties of carbon nanotubes are needed. To do this, you need to look into the growth aspect of CNT and its characteristics in order to have certain properties. For many years, researchers have tried to grow CNTs using various methods, including arc discharge, chemical vapor deposition (CVD), laser ablation, and others.

Initially, the arc discharge was considered as an ideal method for the growth process of bulk CNTs. In both methods, the condensation of hot gas and carbon atoms was performed by evaporation of solid carbon. But there are several drawbacks to these methods, such as: (1) only CNT bundles are produced in powder form, (2) systematic growth on substrates with a selective structure is impossible, and (3) the need for equipment and energy consumption is very high. These restrictions make these methods less favorable for the growth of CNTs compared to CVD. Also, the properties and structure of carbon nanotubes are influenced by the substrate material, the metallization layer material and its thickness, the catalyst layer and its thickness, as well as the flow rate and duration of the carbon precursor gas ($C_2H_2$) during chemical vapor deposition.

Copper and aluminum are used as a metal layer in the study. These samples are used to precipitate carbon nanotubes with an iron catalyst, as well as without it. As adjustable parameters for gas supply are the speed and amount of gas flow, as well as the time of its supply.

The purpose of this work is to obtain the necessary properties and parameters of carbon nanotubes for use in the manufacture of optical devices.

## 2. Experiment

In this work, we used silicon substrates previously purified with HF acid. Copper and aluminum layers were deposited with a thickness of 100 nm using magnetron sputtering. When coating by the magnetron sputtering method [3], the film grows due to the sublimation of target atoms, which are deposited on the substrate surface and on the fittings of the vacuum unit. To create the working pressure necessary for the stable operation of the magnetron, a working gas is needed, for which argon was used. Sputtering metal targets in a pure argon medium led to the formation of a metal film 100 nm thick. Before starting the process, the vacuum chamber was pumped out to a working pressure of about $2{,}5\times10^{-1}$ Pa. After that, a solution of iron nitrate was prepared. 5 mg of $Fe(NO_3)_3$ was added to 100 ml of water, this mixture was placed in an ultrasonic bath for 2 hours. After that, each of the samples was divided into two parts. One aluminum and one copper sample were placed in the solution for 40 minutes. The temperature of the system was maintained at 50 degrees. As a result, 2 aluminum and copper samples were obtained, one with iron deposited as a catalyst, the other without. After that, all samples were placed in a CVD chamber for heating to 400 degrees. As a result, oxide films formed on the surface. Further, using magnetron sputtering, aluminum and copper were deposited on the surfaces of the samples, but with a layer thickness of 10 nm. Next, carbon nanotubes were deposited on the samples by chemical vapor deposition. The substrates were placed in a tubular chamber CVD system. The diagram of CVD system is shown on Figure 1.

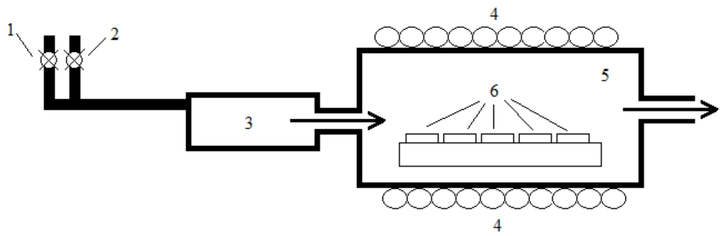


**Figure 1.** Schematic representation of the experimental chamber for the growth of nanotubes by chemical vapor deposition: 1 – Ar supply valve; 2 – $C_2H_2$ supply valve; 3 – manifold; 4 – heaters; 5 – chamber; 6 – samples.

The process of growing carbon nanotubes involves heating the substrates with a catalyst to a temperature of 800 degrees in a tube furnace, and then the gas supply of hydrocarbon gas $C_2H_2$ through the tube reactor is turned on for two minutes. Materials grown on the catalyst are collected while cooling the system to room temperature. The key parameters of nanotube growth by the CVD method are hydrocarbon (in our case it is $C_2H_2$), the catalyst (iron) and the temperature of growth (800 degrees). Active catalytic particles were formed on the carrier, in our case it is alumina and copper oxide. The general mechanism of nanotube growth in the CVD process involves the dissociation of hydrocarbon molecules catalyzed by the transition metal, their dissolution and the saturation of carbon atoms with metal nanoparticles. All samples with different materials and processes indicated in table number 1.

**Table 1.** Samples.

| № | Substrate | First metallic layer | Thick. (nm) | Catalyst | Second metallic layer | Thick. (nm) | Burn | Atmosphere of burning |
|---|---|---|---|---|---|---|---|---|
| 1 | Si | Al | 150 | Fe | Al | 10 | Fired | Ar |
| 2 | Si | Cu | 200 | Fe | Cu | 10 | Fired | Ar |
| 3 | Si | Al | 150 | Fe | Al | 10 | Unfired | - |
| 4 | Si | Cu | 200 | Fe | Cu | 10 | Unfired | - |
| 5 | Si | Cu | 200 | Fe | Cu | 10 | Fired | Oxygen (open chamber) + extra catalyst |
| 6 | Si | Al | 150 | Fe | Al | 10 | Fired | Oxygen (open chamber) + extra catalyst |

**3. Results and discussion**

Experiments were conducted using different materials as a metal layer, and samples were used with and without a catalyst layer. The obtained samples with deposited carbon nanotubes were analyzed on a scanning electron microscope and Roman spectroscopy. As a result, conditions were chosen under which results are obtained that are suitable for the manufacture of optical devices based on carbon nanotubes.

The figures show images of samples obtained from an electron beam microscope. Figure 2 and Figure 3 are images of the first sample with a resolution of 2 and 1 micrometer. A similar resolution is presented for the second sample in Figure 4 and Figure 5. In Figure 6, an image of the third sample with a resolution of 2 micrometers. The fourth sample is shown in Figure 7 with a resolution of 200 nanometers.

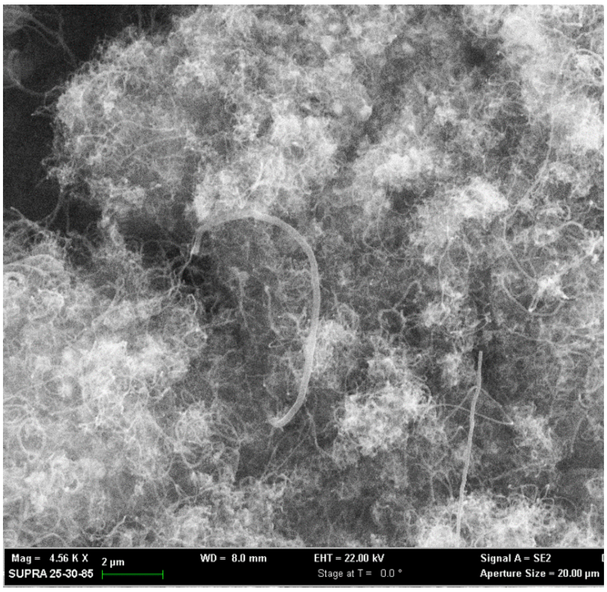


**Figure 2.** First sample with resolution 2 micrometres.

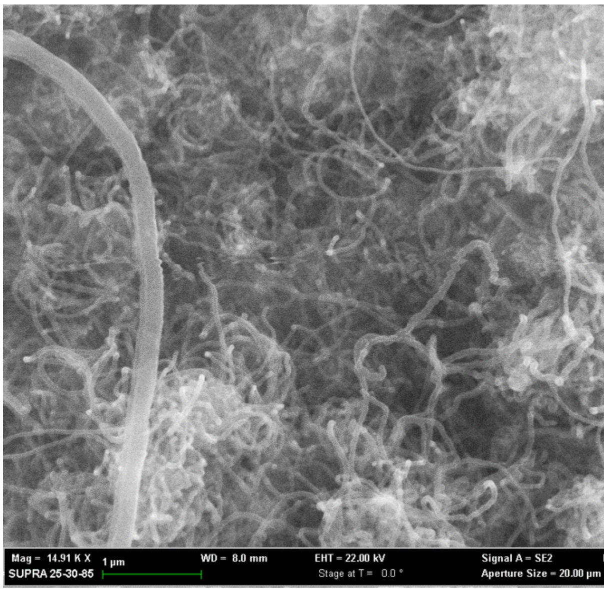


**Figure 3.** First sample with resolution 1 micrometres.

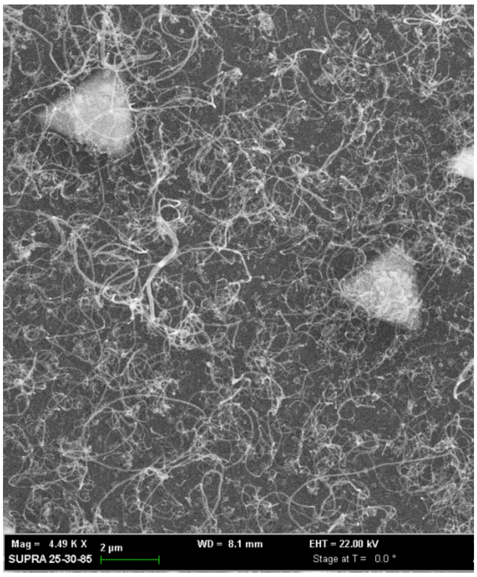


**Figure 4.** Second sample with resolution 2 micrometres.

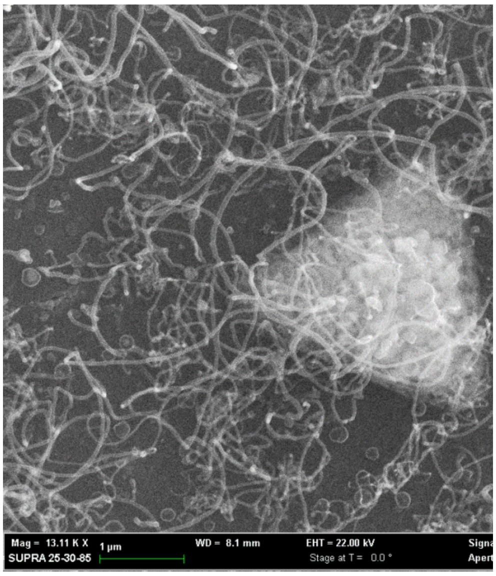


**Figure 5.** Second sample with resolution 1 micrometres.

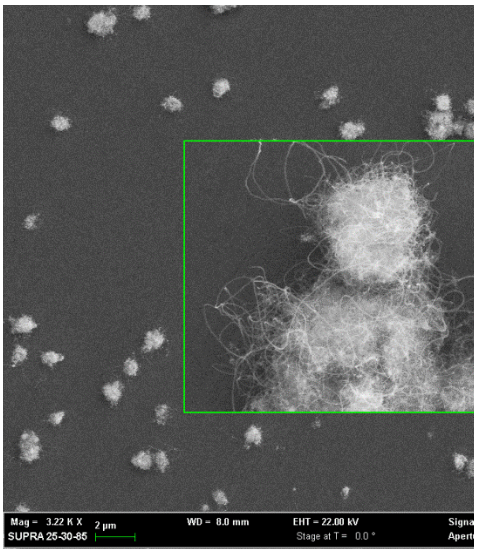


**Figure 6.** Third sample with resolution 2 micrometres.

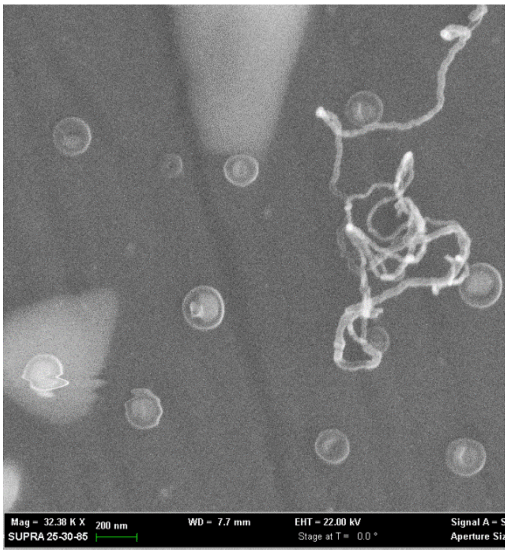


**Figure 7.** Fourth sample with resolution 200 nanometres.

Raman Spectroscopy is used to investigate the structural quality and defects of CNTs. In case of CNTs, there are three important peaks in Raman Spectra. RBM (100 - 300 $cm^{-1}$), D-Band (1323 $cm^{-1}$) and G - Band (1582 $cm^{-1}$). Presence of RBM is signature of SWNTs and intensity ratio of D-Band to G-Band gives structural quality of CNTs. The peak located at 500 $cm^{-1}$ represents silicon mode. For best quality of CNTs, ratio must be minimum. Figures 8-15 show the Raman spectra of the studied samples. For each sample there are two spectral images. On the first, the Raman shift range is from 0 $cm^{-1}$ to 2000 $cm^{-1}$, and on the second, from 1000 $cm^{-1}$ to 3000 $cm^{-1}$. All peaks which carry information about CNTs indicated on images.

The intensity values of all peaks, as well as the ratio of D-Band to G-Band are presented in table 2.

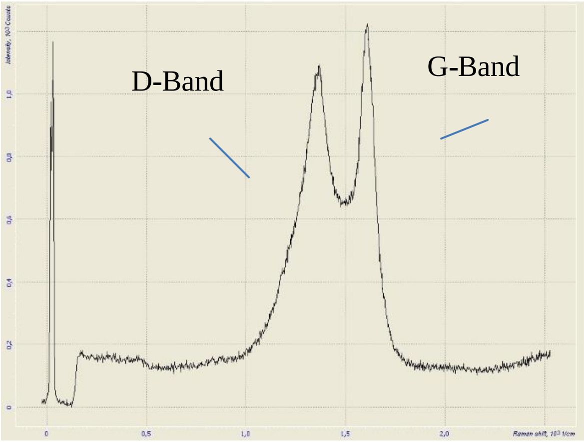


**Figure 8.** First sample with Roman shift from 0 to 2000 cm$^{-1}$.

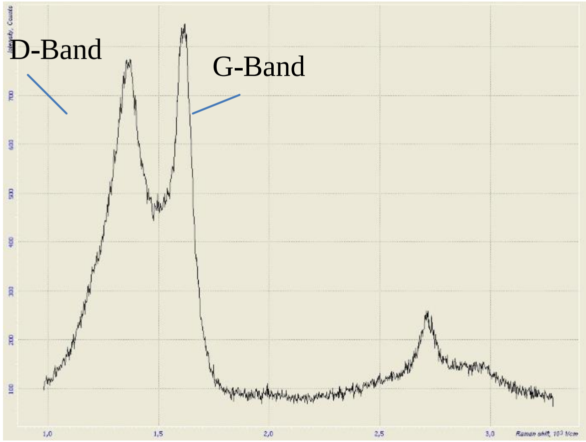


**Figure 9.** First sample with Roman shift from 1000 to 3000 cm$^{-1}$.

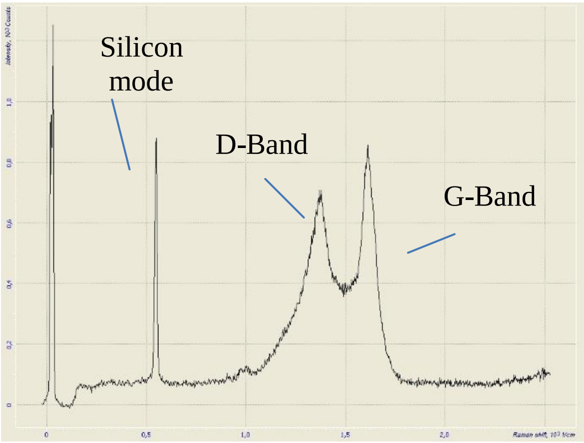


**Figure 10.** Second sample with Roman shift from 0 to 2000 cm$^{-1}$.

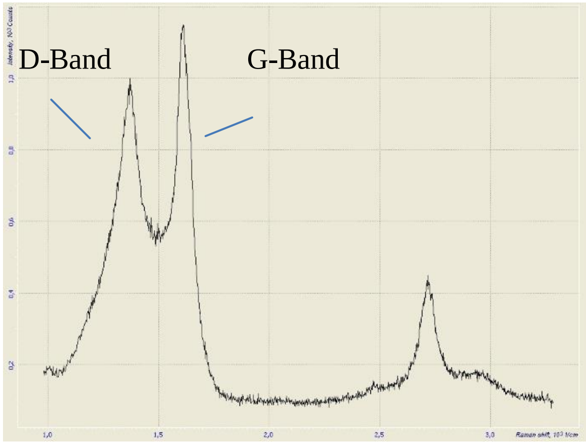


**Figure 11.** Second sample with Roman shift from 1000 to 3000 cm$^{-1}$.

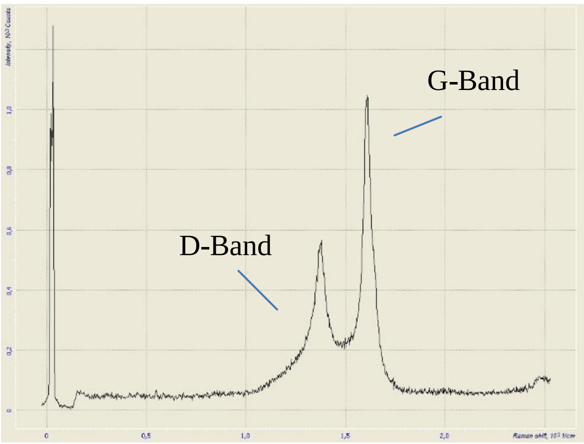


**Figure 12.** Third sample with Roman shift from 0 to 2000 cm$^{-1}$.

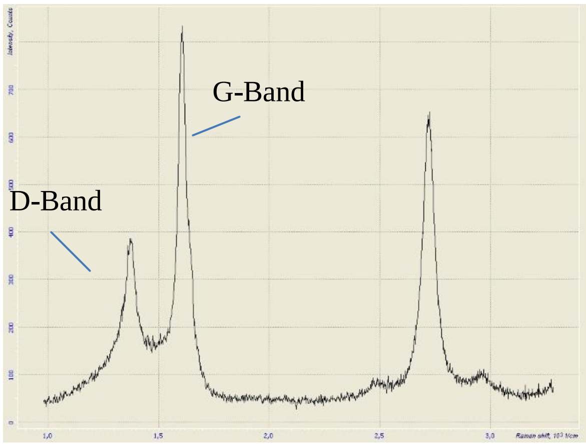


**Figure 13.** Third sample with Roman shift from 1000 to 3000 cm$^{-1}$.

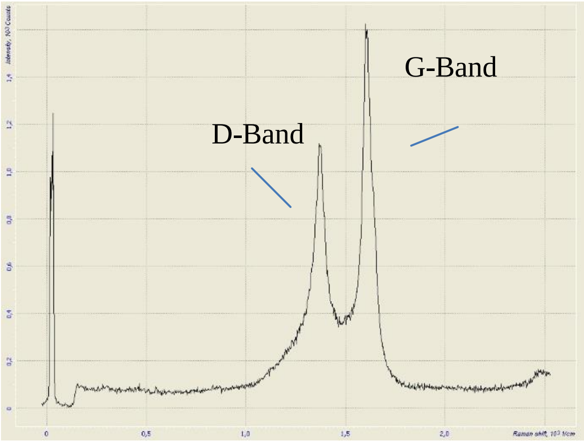


**Figure 14.** Fourth sample with Roman shift from 0 to 2000 cm$^{-1}$.

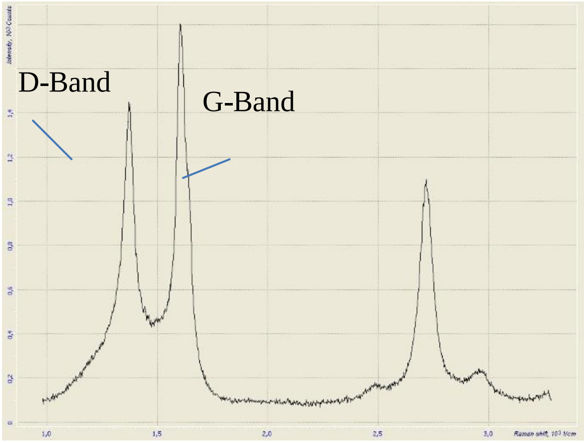


**Figure 15.** Fourth sample with Roman shift from 1000 to 3000 cm$^{-1}$.

**Table 2.** Intensity.

| № | Silicon mode | D-Band | G-Band | Ratio |
|---|---|---|---|---|
| 1 | 1139 | 596 | 628 | 0.94 |
| 2 | 1251 | 681 | 855 | 0.79 |
| 3 | 1278 | 565 | 1048 | 0.54 |
| 4 | 1248 | 1118 | 1600 | 0.69 |

The required ratio of D-Band to G-Band is in three samples: second has 0.79, third has 0.59 and the fourth has 0.69. But based on images obtained from a microscope, the necessary structure of carbon nanotubes is present only in the first and second samples. Accordingly, on the basis of these criteria, the most suitable sample is number two The technological process of this sample will be chosen for manufacturing.

## 4. Conclusion

The analysis and optimization of photonics devices manufacturing technologies based on carbon nanotubes applied for work in the terahertz range has been given. Various aspects of the synthesis and growth of the mechanism of CNT and their subsequent use as materials for prototypes of the waveguide and sensor of the terahertz range have been considered. Carbon nanotubes (CNTs) have been grown on a sandwich structure based on a silicon wafer using CVD technique, where a layer of aluminum and copper 100 nm thick was deposited, then an iron catalyst was applied about 5 nm thick, and then copper and aluminum was deposited again, but with a f of 10 nm layer is also using magnetron sputtering. Four samples, with and without a catalyst layer using different materials as a metal layer, have been studied.

Analysis of the Raman scattering spectrum of the grown CNTs has allowed to choosing sample 2 as suitable for the manufacture of photonics devices based on carbon nanotubes. The results of the work open the possibility of improvement photonics devices manufacturing technologies based on carbon nanotubes.

## 5. References

[1] Tripathi, N. Tunable growth of single-wall CNTs by monitoring temperature increasing rate / N. Tripathi, V. Pavelyev, S.S. Islam // International Nano Letters. – 2018. – Vol. 8(2). – P. 101-109.

[2] Kumar, S. A Review on chemiresistive gas sensors based on Carbon Nanotubes: Device and Technology transformation / S. Kumar, V. Pavelyev, P. Mishra, N. Tripathi // Sensors and Actuators A: Physical. – 2018. – Vol. 283. – P. 174-186.

[3] Bassett, G.A. Continuous observation of the growth of vacuum evaporated metal films / G.A. Bassett // Proceeding of the European Regional Conference on Electron Microscopy. – 1960. – Vol. 1. – P. 270-275.
[4] Kumar, S. Thin Film Chemiresistive gas sensor on Single- walled carbon nanotubes- doped with Polyethylenimine (PEI) for NO2 gas sensing / S. Kumar, V. Pavelyev, P. Mishra, N. Tripathi // Sensors & Actuators: A. Physical. (Submitted).
[5] Kumar, S. A review on recent advances in the development of carbon nanotubes based flexible sensors / S. Kumar, V. Pavelyev, P. Mishra, N. Tripathi, V. Platonov, P. Sharma // Materials Science and Engineering B. (Submitted).
[6] Kumar, S. Sensitive detection of nitrogen dioxide using gold nanoparticles decorated single walled carbon nanotubes / S. Kumar, V. Pavelyev, P. Mishra, N. Tripathi // CEUR Workshop Proceedings. – 2017. – Vol. 1900. – P. 74-77.
[7] Pavelyev, V.S. Sensitive element of CNT-based IR-sensor / V.S. Pavelyev, N. Tripathi, P. Mishra, A.V. Mezhenin, Yu.G. Kurenkova // IV International Conference on Information Technology and Nanotechnology (ITNT-2018). – Samara: Novaya Technika, 2018. – P. 352-356.
[8] Tripathi, N. Synthesis of carbon nanotubes using green plant extract as catalyst: unconventional concept and its realization / N. Tripathi, V. Pavelyev, S.S. Islam // Applied Nanoscience. – Vol. 7. – 2017. – P. 557-566.
[9] Tripathi, N. A new approach for orientation controlled growth of CNTs: an in-depth analysis on the role of oxygen plasma treatment to catalyst / N. Tripathi, S.S. Islam // Applied Nanoscience. – 2017. – Vol. 7. – P. 125-129.