CNT-based IR-sensor

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Abstract. A literature review of the works presenting the far infrared sensors characteristics has been provided. In principle, the possibility of using CNT samples with different network density as a sensitive element for far IR radiation range detecting has been shown. The dynamic range and transient characteristics of the sensor have been determined.

1. Introduction
Lots of events in nature are followed by the emission of electromagnetic radiation in certain wavelengths regions. The necessity to observe, measure and analyze such events have driven the development of suitable radiation detectors [1]. Electromagnetic radiation of the visible range [2], ultraviolet, as well as infrared [3]–[5] and terahertz [6], [7] radiation are of great interest, since they occur in various observed phenomena, from solar radiation to fluorescence of molecules.

The use of short-wave range of electromagnetic radiation spectrum is one of the general trends in the electronic equipment development. The extremely high information capacity of the light field and the optical signals propagation speed, the fundamental ease of carrying out mathematical operations with two-dimensional light fields predetermined a wide interest in the use of optical methods for receiving information in various types of radio electronic and optoelectronic equipment.

An indispensable element of the overwhelming majority of apparatus types using optical radiation for information processing is an optical radiation receiver. Thence, the constant growth in the nomenclature of the optical radiation receivers based on various physical operating principles is natural [8].

According to the operating principle, IR receivers are conditionally divided into three main groups: thermal, photochemical and photonic. The work of thermal receivers is based on the absorbed energy transformation first into thermal, and then into electrical energy. These include: thermoelements, thermistors, bolometers, pyroelectric receivers, and so on. The photochemical ones include receivers changing their chemical properties under the radiation influence. These are photographic plates, photographic films, photo paper, and so on. In photonic receivers, the radiation quanta interact with the electrons of the sensitive element material. They are divided into receivers with an external photoeffect (photocells, photomultipliers, electron-optical converters, etc.) and receivers with an internal photoeffect (photoresistors, photodiodes, phototransistors, etc.) [9], [10].

Thermal radiation receivers are non-selective devices, i.e. they have identical spectral characteristic over a wide range of electromagnetic spectrum (up to hundreds micrometers). Photochemical converters belong to the selective type of receivers, which have sensitivity only in a certain spectrum
region. The photonic receiver sensitivity is proportional to the absorbed photons number. Such receiver is selective, it reacts only to radiation quanta of a certain frequency.

In modern infrared systems, the radiation receivers with an internal photoeffect are the most widespread. These receivers are called photodetectors or photoelectric semiconductor detectors (PSD). In the receivers with an internal photoeffect, three basic physical phenomena, caused by the action of radiation on a semiconductor, are used: photoconductivity phenomenon, photovoltaic and photoelectric effects [9].

The IR radiation receivers, produced by various companies, based on such components as Ge, Hg, Cd and Te have, as a rule, high speed (of the order of several microseconds). Their disadvantages include the high cost of components, as well as specific requirements for working conditions: cooling to the liquid nitrogen temperature, package closure, etc. [8].

Today in the research of photodetectors, the trend to increasing their sensitivity is observed [3], [4]. Moreover, the photodetector sensitivity spectrum is extended beyond the visible region limits, to the optical range boundaries [1], [3]–[5]. Requirements for the IR detector sensitive element for today are low level of intrinsic noise, especially thermal noise, which makes it difficult to use it at above-room temperature [3], [4]; presence of fine pixels [1]; low cost, broad area (sizes larger than 5 × 5 mm²) and high speed [2].

Recent progress in the field of IR-radiation detection has become possible owing to the development of nanotechnologies. Nanoimprinting technique, for example, is already being used for creating compact new generation spectrometers and photosensors [1].

One of the promising materials for detectors sensing element is carbon nanotubes (CNTs). Since the CNT discovery, extensive research work has continued for a basic understanding of their physical properties, as well as possible applications, since they are a potential candidate to replace existing materials in virtually every field. For example, they can be elements of chemical current sources, nanosensors for recording various physical and chemical effects; probes for scanning microscopy, atomic manipulators, nanomechanical storage devices; nanoconductors, nanoresistors, nanotransistors, nano-optical elements for new generation nano-optoelectronics. The unique nanotubes properties lie at the base of radiation sensors of various types. The fundamental reasons for this are their unusual size and size-dependent outstanding physical properties [1], [11].

The aim of this work is an experimental study of a photodetector sensitive element based on carbon nanotubes for far infrared range laser radiation detecting through changing the photoconductivity.

2. Test samples
Initially, nanotubes were obtained by the method of electric arc or laser graphite evaporation and its subsequent condensation in an inert gas atmosphere. The various heating modes, variation of inert gas (helium, argon) pressure in the chamber and the temperature of the substrate where carbon atoms and clusters were deposited, addition of various catalysts made it possible to obtain those or other nanostructures with yield up to 25 % of the total deposit weight [11].

A much higher productivity and yield of nanotubes can be achieved by catalytic pyrolysis of gaseous hydrocarbons [12]. In general, the technology of chemical vapor deposition (CVD) consists in blowing ethylene, acetylene, methane, natural gas or other hydrocarbon raw material through a tubular cavity with a temperature of 500–800° C. Preliminarily, a fine powder of Fe, Co, Ni, or their mixture, playing the role of a catalyst in pyrolysis, inflicted on a silicon (or other) inert substrate, that serves a carrier of the catalyst and future carbon structures, is put into the furnace. Variation of the operation parameters of such device makes it possible to change the yields ratio of different obtained products (in particular, CNTs) within a wide range.

Three samples have been made to determine the possibility of using CNTs as a sensitive element of the IR detector. The CNT growth has been carried out using the CVD-system (figure 1), which is the horizontal reactor – the quartz tube with an inside diameter of 50 mm and 650 mm in length. The reactor was placed in an electric furnace. In a 230 mm heating zone, temperature was regulated from 20 up to 1000 °C. All technological processes were carried out at atmospheric pressure.
The CNTs were grown on n-type silicon (100) substrates with a square of ~30 mm$^2$. The substrates were cleaned in acetone using ultrasonics for 10 min. As a catalyst for the CNT growth, a thin Fe film with the thickness of 2 nm was deposited on the substrates by HF sputtering. Subsequently, the substrates were heated up to 800 °C for 90 min and exposed at this temperature for about 20 min for the nanosize Fe particles formation from the catalyst film.

The CVD process was carried out at the following conditions. A protective atmosphere of Ar was created in the chamber to prevent the metal particles oxidation with rising temperature inside the furnace. Inert gas flow rate was 40 ml/min. Temperature rise from the room temperature to 800 °C on the heating stage was carried out within 90 min. In addition to argon, acetylene (C$_2$H$_2$) was used as a precursor gas at a flow rate of 5 ml/min within 10 min. After this time the C$_2$H$_2$ flow was shut off, and the furnace was turned off. During the furnace cooling to room temperature (about 2 h), a protective inert atmosphere was maintained in it to prevent CNT burning at high temperature. After cooling, the substrate with the sparse CNT network was extracted from chamber for further analysis.

Decrease of argon consumption to 35 ml/min while the flow rate of acetylene was increased to 15 ml/min at constant time parameters of the heating-cooling cycle made it possible to obtain a denser CNT structure. This technology was used for producing two more samples.

Identification and attestation of the products obtained as a result of synthesis are traditionally carried out by a complex of physical methods: high-resolution transmission electron microscopy, diffraction and spectral methods (especially Raman scattering), scanning probe microscopy, etc. [12].

To determine the CNT parameters, the samples were studied with a high resolution scanning electron microscope (SEM SUPRA 25) and a Raman microspectrometer with an Ar$^+$-laser emitting at a wavelength of 488 nm (LabRAM HR800, JY). Figure 2 shows a network image of CNTs disposed horizontally on a silicon substrate. A similar homogeneous net structure of nanotubes uniformly distributed over the substrate surface is characteristic for all samples. The only difference is the network density.

![Figure 1. Schematic diagram of the CVD-system.](image1)

**Figure 1.** Schematic diagram of the CVD-system.

**Figure 2.** Images of the CNT structure on a silicon substrate, obtained by means of SEM SUPRA 25 (magnification 340 times).
The scanning electron microscopy also permits to determine nanoobjects dimensions. The characteristic diameter of the obtained CNTs was in the range of 10–20 nm (figure 3).

![Figure 3](image1.png)

**Figure 3.** Images of the CNT structure on a silicon substrate, obtained by means of SEM SUPRA 25 (magnification 30000 times).

Figure 4 represents the Raman spectrum of the obtained CNT samples. The ratio of lines characterizing the graphite structure (G-line) and defects in the CNT structure (D-line) is less than 0.9, which indicates the low quantity of defects in the individual CNTs bond structure.

![Figure 4](image2.png)

**Figure 4.** Raman spectrum of CNTs grown by CVD-technique.

The dependence of the bandgap width on the CNT diameter (external, in the case of multiwalled nanotubes), given in [13], allows us to suggest that the obtained nanostructures have properties characteristic of semiconductors. The bandgap width is estimated to be 0.07 eV. Therefore, there is a fundamental possibility of creating a sensor based on CNT for detecting far infrared laser radiation (wavelength is 10.6 μm) through changing the conductivity. Carrier generation in CNT samples under these conditions can be realized due to the electrons transition from the valence band to the conduction band upon IR quanta absorption [14].

To carry out experiments on determining the CNTs photoconducting properties, the nanotube network was coated with silver electrodes in order to improve the contact of the measuring instrument clamps with the samples. For this purpose, the silver paste was mixed with isopropyl alcohol in a ratio of 1:1. The resulting homogeneous mixture was applied by brush to the sample. Then the sample was placed in a furnace chamber with a protective argon atmosphere at a flow rate of 5 ml/min and heated during an hour to 200 °C. Then the sample was aged for 1 h at this temperature to dry the solution forming the electrodes and cooled for 2 h to room temperature. In the first experiments, the electrodes were not applied to the samples, since the principal response presence was examined.

### 3. Experimental study of IR-radiation sensor

The experiments have been carried out on the setup which is shown in figure 5. Radiation of the CO$_2$-laser $J$ (LCD-1A, wavelength is 10.6 μm) was directed to the CNT sample $J$ by means of rotating
mirror 2. The laser beam with a Gaussian intensity distribution was guided between the electrodes, the distance between them was 5 mm. The electrodes were pressed tightly against the CNT sample by spring contacts. The resistance measurement has been carried out with the multimeter 4 (MASTECH MY-62) having a measurement error in the 2 kΩ and 20 kΩ ranges of ±0.8% ±1 count unit.

Figure 5. Setup for determining the dependence of the resistance on the laser beam power: 1 – laser, 2 – mirror, 3 – CNT sample, 4 – multimeter.

The purpose of the first experiment was to establish the presence of a response as a change in the CNT sample resistance under the influence of IR radiation. For this, one of the samples with a dense nanotube network was taken. In this experiment, the radiation power was stepwise increased in steps of 0.4 W. Figure 6 shows the obtained dependence of the resistance on the incident beam power. Figure 7 shows how the relative resistance of sample changes in this case.

The obtained dependence is characterized by a smooth monotonic decrease in the resistance. The observed dependence is close to linear. The equation of the right line obtained as a result of approximation has the form

$$R = 13.71 - 0.51P,$$

where $R$ is sample resistance, kΩ; $P$ is illuminating beam power, W.

The results of the first experiment showed that far infrared laser radiation exposure leads to a decrease in the CNT sample resistance by 1.53 kΩ at a maximum incident beam power (about 3 W). The observed relative change in resistance is significant and is equal to ~10 %.

It should be noted that when the laser power was increased more than 3 W, in order to determine the dynamic range of the sensor operation, an irreversible fall in the CNT sample resistance to several ohms was observed. So, further experiments were carried out with new samples in the illuminating beam power range from 0 to 3 W.

Subsequent experiments were conducted to determine the response magnitude for samples with a different net density. Figures 8 and 9 show graphs of the resistance versus the illuminating beam power, obtained for the samples with a sparse and dense network. A new sample with a dense network was manufactured using the same technology as the previous one, in order to show the reproducibility of the results.
Figure 8. Dependence of the CNT sample resistance with a dense network on the laser beam power.

Both dependences are close to linear. The equations of lines obtained as a result of approximation have the form:

\[
R = 13.71 - 0.51P
\]  
(2)

and

\[
R = 503.35 - 16.43P
\]  
(3)

respectively for samples with a dense and sparse network, where \(R\) is the resistance, k\(\Omega\) (2) or \(\Omega\) (3), \(P\) is the power, W.

Despite the significant difference in resistance at \(P=0\) (13.71 k\(\Omega\) for a sample with a dense network and 503.35 \(\Omega\) for a sample with a sparse network), a relative reduction in resistance equal about 10% of the initial value is observed for both samples at a maximum illuminating beam power. Both received dependences are characterized by a smooth monotonic decrease in resistance. The identity of equations (1) and (2) confirms the reproducibility of photoconducting properties for the samples manufactured using the same technology.

Onwards, to improve the electrical connection with the clamping spring contacts of the device entering the measuring circuit, according to the technology described in paragraph 2, silver electrodes were deposited on the CNT samples. This led to a decrease in the resistance of the samples by approximately an order of magnitude. In further experiments, a laser beam 4 mm in diameter, obtained by divergence, was directed to the samples in the region between the silver electrodes, completely covering the distance between them in both cases.

In addition to establishing the response magnitude, the experiments were conducted to determine its operation speed and the resistance recovery time. At the speed-of-response (response rate) of the sensing element, we mean here the time while the resistance decreases to a minimum value at the set illuminating beam power. An important sensor characteristic is also the recovery time, while the resistance is restored to the initial value after the exposure cessation.

Figures 10 and 11 show the experimental dependences \(R = f(t, P)\) obtained by measuring the response rate of a sensitive element based on CNTs. The laser radiation impact on the samples led to a sharp drop in resistance at the initial stage and a subsequent slow establishment of a final value corresponding to saturation. Based on the results of measurements, the response rate was 3 min. After this time, the laser was turned off, and the sample resistance recovery was observed.

The results of the resistance recovery time measuring for the samples are given in figures 12 and 13 as a dependence \(R = f(t, P)\).

It can be seen that the recovery process is also characterized by a nonlinear time dependence – a sharp increase in resistance at the initial stage and a subsequent slow initial value establishment. The characteristic recovery time was also 3 min.
The approximation of the data given in figures 10–13 allows us to conclude that transient processes are mathematically described by exponential dependencies.

Combining the obtained measurement results of response time and resistance recovery time for the samples, e.g., at an output laser power \( P = 2 \) W, leads to the observation of a hysteresis-type characteristic (figures 14 and 15).

The obtained results attest to the possibility of creating a selective CNT-based far-infrared sensor. This has certain perspectives, since the process of obtaining nanotubes is carried out on the basis of...
proven technology and does not require complicated high-cost equipment, as well as toxic and poisonous materials. In addition, the technology of making samples permits to ensure their photoconductive properties reproducibility. The response is observed at room temperature, in contrast, for example, to HgCdTe-based photodetectors operating at a wavelength of 10.6 μm at temperatures of 77–80 K [9]. The disadvantages of the proposed CNT-based IR-sensors can consist in their low speed-of-response compared to the receivers those require cooling.

4. Conclusion
A literature review of the works representing the characteristics of infrared radiation sensors is given. The physical operation principles of the existing IR receivers and their main characteristics are considered. The analysis of modern trends in the photodetectors studies and requirements for IR sensors is carried out.

We propose the creation of a far infrared radiation photodetector based on samples of multi-walled nanotubes grown on a silicon substrate by CVD-technology. Samples with different density of a disordered homogeneous network of carbon nanotubes 10–20 nm in diameter are studied. Raman spectra data of the samples attest to the high structural perfection of individual CNTs.

An experimental study of the far infrared sensor allows us to observe a response as electrical resistance change in the laser output power range from zero to 3 W. The dependence of CNTs conductivity on impact radiation power is linear throughout the dynamic range. The response rate and the resistance recovery time of the detector after irradiation are 3 min. Transient processes are described by exponential time dependence with a strongly marked hysteresis-type characteristic.

The research results open the possibility of creating CNT-based far infrared sensors, which are easy to manufacture and non-toxic. At present, work is underway to increase the photodetector sensitivity and to improve its dynamic characteristics. Such detectors can subsequently be applied to control the intensity distribution formed by diffractive optical elements calculated, for example, in [15].

5. References
[1] Ambrosio A and Aramo C 2011 Carbon Nanotubes-Based Radiation Detectors Carbon Nanotubes Applications on Electron Devices 19 455-470
[2] Mishra P, Harsh and Islam S S 2014 Development of MWCNTs-based wideband photodetector in the visible range: wavelength and power-dependent response studies Appl. Phys. A 117 1119-1123
[3] Chen H, Xi N, Lai K W C, Fung C K M and Yang R 2010 Development of Infrared Detectors Using Single Carbon-Nanotube-Based Field-Effect Transistors IEEE Transactions on Nanotechnology 9 582-589
[4] Zhang J Xi N, Lai K W C, Chen H and Luo Y 2007 Single Carbon Nanotube based Photodiodes for Infrared Detection Proc. of the 7th IEEE Int. Conf. on Nanotechnology (Hong Kong) 1156-1160
[5] Lai K W Ch, Xi N, Zhang J, Li G and Chen H 2007 Packaging Carbon Nanotube Based Infrared Detector Proc. of the 7th IEEE Int. Conf. on Nanotechnology (Hong Kong) 778-781
[6] Hartmann R R, Kono J and Portnoi M E 2013 Terahertz Science and Technology of Carbon Nanomaterials Nanotechnology 1-27
[7] He X 2014 Carbon Nanotube Terahertz Detector Nano Lett. 14 1-20
[8] Aksenenko M D and Baranochnikov M L 1987 Optical Radiation Receivers (Moscow: Radio and Connection Publ.)
[9] Baranochnikov M L 1985 Infrared Radiation Receivers (Moscow: Radio and Connection Publ.)
[10] Miroshnokov M M 1977 Theoretical Basics of Opto-Electronic Devices (SPb: Mashinostroenie Publ.)
[11] Vikarchuk A A 2006 Promising Materials. Structure and Research Methods (Togliatti, Moscow: TSU, MISA)
[12] Tripathi N, Mishra P, Hash H and Islam S S 2015 Fine-tuning control on CNT diameter
distribution, length and density using thermal CVD growth at atmospheric pressure: an in-depth analysis on the role of flow rate and flow duration of acetylene (C2H2) Appl. Nanosci. 5 19-28

[13] D’yachkov P N 2000 Materials for 21st Century Computers Priroda 11 23-30

[14] Paveleyev V S, Mishra P, Triphati N, Mezhenin A V and Kurenkova Yu G 2018 Sensitive element of CNT-based IR-sensor Proceedings of the 4th International Conference “ITNT-2018”(Samara) 352-356

[15] Kharitonov S I, Doskolovich L L and Kazanskiy N L 2016 Solving the inverse problem of focusing laser radiation in a plane region using geometrical optics Computer Optics 40(4) 439-450 DOI: 10.18287/2412-6179-2016-40-4-439-450

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