A complex study of the structure “carbon nanotubes - silicon substrate” photoconductivity mechanism

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Abstract. The types of optical radiation photodetectors have been considered according to the principle of action. A theoretical and experimental study of the electron generation mechanism in the structure "carbon nanotubes – silicon substrate" under the influence of the far infrared range radiation has been carried out. It has been established that such structures are thermal radiation receivers of the bolometric type.

1. Introduction

Increasing of the electronic devices integration degree, response time improving and operating conditions toughening causes the constant search for new cheap and technological materials. Since the discovery of carbon nanotubes (CNTs), extensive research has been conducted and continues in the practical implementation field of their production methods [1], [2] for a fundamental understanding of their physical properties, as well as possible applications, since they are a candidate for existing materials replacement in almost every application. The main reasons for their widespread use are related with unusual size and size-dependent physical properties [3]–[5]. One of the promising applications of CNT is sensor technology, i.e. their use for registration of different physical and chemical effects, for example, as gas sensors [6], [7] and radiation sensors of various types [8]–[10].

A unique feature of nanotubes in terms of the optical [11] and terahertz radiation sensor technology [12], [13] is the ability to control their properties by changing the structure: the expansion of the absorption spectrum [14], selective adjustment to the desired wavelength [15], etc. For example, the transition metals doping leads to a sharp increase in the conductivity of both semiconductor CNTs (due to the appearance of metal electronic states in the forbidden zone) and metal CNTs (due to the states density increase near the Fermi level) [16].

Currently, there is a fairly broad classification of optical radiation receivers. According to Ref. [17], depending on the physical phenomena underlying the principle of operation, they are divided into three large groups: photovoltaic (photon-assisted), photoelectronic and thermal. Photovoltaic radiation receivers are based on the internal photoeffect. In photoelectronic devices, the physical operating principle is the external photoeffect. Thermal radiation receivers operate due to the resistance change of the sensing element with an increase in its temperature under the absorbed radiation action.

Thermal radiation receivers are non-selective devices, i.e. they have the same spectral response in a wide electromagnetic spectrum range. The operation of such receivers is based on the conversion of radiation energy first into thermal and then into electrical energy. Photovoltaic and photoelectronic
receivers are selective devices, i.e. they have sensitivity only in a certain range of the electromagnetic spectrum. The receivers based on internal photoeffect are built on three main physical phenomena caused by the radiation action on the semiconductor: the photoconductivity phenomenon, photovoltaic and photoelectric effects [18].

Photovoltaic radiation receivers are based on the use of internal photoeffect and semiconductor manufacturing technology. Photoresistor, photodiode, phototransistor and photothyristor structures made of semiconductor material sensitive to radiation in the working spectral region are used as a photosensitive element in photodetectors. In photoelectronic devices, the electron flow (beam) moves under the action of an electric field in a vacuum or gas-filled device.

Thermal detectors of optical radiation are divided into pyroelectric (pyrometers) and semiconductor (bolometers). Pyroelectric detectors based on the use of the pyroelectric effect caused by pyroactive crystal temperature change due to the radiation energy absorption. If the change in a conductor or semiconductor electrical resistance is caused by the temperature change then a receiver of such type is called a bolometric (bolometer) [17].

Existing detectors often require special operating conditions, such as liquid nitrogen temperature [17] or a sealed enclosure [19], not least because of the detector material properties. The sensors sensitivity increases continuously and, at the same time, their sensitivity spectrum expands [20]. The requirements for a detector sensitive element include: low self-noise level, small pixel size, low cost, area more than 5×5 mm² and high operation speed [11].

In Ref. [14], it has been shown the principal possibility of using a two-layer structure «CNT – silicon substrate» as a sensitive element for a detection of the visible range LEDs’ monochromatic radiation. Similar samples were used as a sensitive element for the far-infrared radiation registration in Ref. [21]. We have observed the change in the samples resistance under the influence of the illuminating beam. The dynamic range and transient characteristics of the sensor have been determined experimentally. The photoconductivity mechanism theoretical study for the structure «CNT – silicon substrate» was the purpose of the subsequent work [22].

The purpose of this work is a comprehensive study and the photoconductivity mechanism substantiation for composite structures of the type «CNT – silicon substrate».

2. Test samples

Broadly speaking, the technology of chemical vapour deposition (CVD) consists in blowing through the tubular cavity, where the temperature is maintained at 500–800 °C, of ethylene, acetylene, methane, natural gas, or other hydrocarbons. In this case, the catalyst, which is a fine powder of Fe, Co, Ni, or their mixture, deposited on a silicon (or other) inert substrate that plays the role of the catalyst carrier and future carbon structures, is preloaded into the reactor. Varying the operating modes of the reactor allows us to change the yields ratio of different manufactured products (in particular, CNTs) over a wide range [5]. To determine the possibility of the “CNT – silicon substrate” structures using as a sensitive element of the IR-sensor, two samples were made in the setup described in Ref. [21].

N-type silicon bars with orientation (100) having surface area ~30 mm² were used as the substrates. The substrates were cleaned by ultrasonic bath in acetone for 10 min. As a catalyst, a thin 2 nm Fe film was deposited on the substrates using RF-sputtering. Then the substrates were heated up to 800 °C during 90 min. and kept for 20 min. at 800 °C to create the nano-sized Fe particles of a catalyst film. After that, they were cooled to room temperature for 2 h.

Technological CVD-process was carried out at the following conditions. To prevent metal particles oxidation with temperature growth in the reaction chamber, a protective Ar atmosphere was created there. The inert gas flow rate was 35 ml/min. During the 90-min. heating stage, the temperature increased from room temperature up to 800 °C. In addition to argon, the stream of acetylene (C₂H₂) with the flow rate of 15 ml/min. was used as a precursor gas for 10 min. at the exposure stage. After this time, the C₂H₂ flow was turned over, and the chamber was turned off. A protective inert atmosphere was maintained in the reactor to prevent the CNTs burning when it was cooling to room temperature for 2 h. After the cooldown, the substrate together with the carbonic structures deposited on it was removed from the chamber for a subsequent analysis. Increasing the argon flow rate up to
40 ml/min. and reducing the acetylene flow rate up to 5 ml/min. at constant technological cycle time parameters made it possible to obtain a sample with a less dense structure deposited on the surface.

To determine the nanotubes parameters, the samples were studied on the scanning electron microscope (SUPRA 25). It was found that the CNTs are arranged on a silicon substrate horizontally in the form of an irregular network (Figure 1). Such a homogeneous network structure, uniformly distributed over the substrate surface, is characteristic of both samples. The difference is only in the network density. The characteristic diameter of the CNTs was from 10 to 20 nm.

![Figure 1. Snapshot of the CNT structure on a silicon substrate obtained on the SEM SUPRA 25 (30000 times magnification).](image)

The Raman spectrum obtained with a LabRAM HR800, JY microspectrometer indicates a small defects in the CNT structure. The ratio of lines representative of the carbon structure (G-band) and the defects in the nanotubes structure (D-band) is less than 0.9.

To conduct experiments devoted to the determination of photoconductivity properties, silver electrodes were deposited on the CNT network. For this, a silver paste was mixed with isopropyl alcohol in a 1:1 ratio. The resulting homogeneous mixture was laid on the samples with a brush. Further, they were placed in a reactor, where a protective argon atmosphere was created (flow rate 5 ml/min.), and heated up to 200 °C for one hour. Then, the samples were kept during 1 h at this temperature to dry the electrodes and cooled down to room temperature for 2 h.

3. Experimental part

The experiments were carried out on the setup that is shown in Figure 2. Radiation of the CO2-laser 1 at a wavelength of 10.6 μm was directed to the CNT sample 3 by a rotary mirror 2. The laser beam had a Gaussian intensity distribution and completely covered the distance between the electrodes equal to 5 mm in both cases. The copper electrodes of measuring device were tightly pressed to the sample electrodes by spring contacts. Resistance measurement was carried out by a multimeter 4 (MASTECH MY-62) having a measurement error in the range of 2 kΩ equal to ±0,8 %±1 account unit and in the range of 200 Ω equal to ±0,8 %±3 account unit.

![Figure 2. Measuring system: 1 – laser, 2 – rotary mirror, 3 – CNT sample, 4 – multimeter.](image)

The response in the form of a smooth monotonic resistance change was registered for both a sample with a dense (Figure 3) and with a sparse (Figure 4) network when exposed to far IR-radiation.
Figure 3. Dependence of the CNT sample resistance with a dense network on the laser beam power.

Figure 4. Dependence of the CNT sample resistance with a sparse network on the laser beam power.

The dependencies obtained for CNT samples with different network densities are close to linear. The straight-line equations obtained as an approximation result are:

\[ R = 1020 - 97P \]  
(1)

and

\[ R = 44 - 1,2P \]  
(2)

where \( R \) is the resistance, \( \Omega \); \( P \) is the power, W. Equations (1) and (2) were obtained for the samples with a dense and sparse network respectively.

The observed relative change in resistance in both cases is \( \sim 10 \% \). More rapid dependence takes place for samples with a dense CNT network. Sensitive elements demonstrate trouble-free operation in the power range of the illuminating beam up to 3 W. An irreversible drop-off in the CNT samples resistance to several Ohms is observed at increasing in power of more than 3 W. The similar form of equations (1) and (2) confirms the photoconductive properties similarity for the samples produced by the same method.

Besides the resistance drop magnitude registration at the prolonged exposure of laser radiation up to establishing a steady-state value, there were made the measurements of the response speed and the resistance recovery time. By sensor response speed (rate of response), we mean here the time over which the resistance drops to the minimum steady-state value at a fixed acting beam power. Also, an important sensor parameter is the recovery time defined as the time when a resistance is restored to its original value after exposure termination.

Figures 5 and 6 show the \( R = f(t) \) dependencies obtained at the measurements of the response speed and recovery time for a sensitive element based on the «CNT – silicon substrate» structure.

Figure 5. The changes in sample resistance with laser power for a dense type CNTs network over time.

Figure 6. The changes in sample resistance with laser power for a sparse type CNTs network over time.
The laser radiation impact led to a sharp drop in samples resistance at the initial stage and the subsequent slow final value establishment corresponding to a saturation. After this time, the laser was turned off and the sample resistance recovery was observing. The recovery process is also characterized by a nonlinear dependence on time, i.e. sharp increasing in resistance at the initial stage and a subsequent slow recovery to the original value. The approximation of the data shown in Figures 5 and 6 allows us to conclude that the transient processes are mathematically described by exponential dependencies. According to the measurement results, the response speed was 3 min. The characteristic recovery time was also 3 min.

Analysis of the results obtained by the measurements of response speed and resistance recovery time for the samples of «CNT – silicon substrate» structures leads to the observation of a hysteresis type characteristics (see Figures 14 and 15 in Ref. [21]). It shows that the resistance of such structures is determined by the exposure conditions at the current moment, and their state at the previous moment.

Taking into account the data presented in Ref. [14], where similar samples were studied experimentally, the obtained results indicate the possibility of creating a non-selective far-IR range CNT-based radiation sensor. This has certain prospects, since the “CNT – silicon substrate” structures manufacturing technology is proven and does not require a complex expensive equipment, as well as toxic and poison materials. In addition, it allows to ensure the reproducibility of the various samples photoconductive properties [14], [21]. The response is observed at a room temperature in contrast to, for example, the HgCdTe-based photodetectors operating at the wavelength of 10.6 μm at the temperature range of 77–80 K [18]. The disadvantages of the proposed CNT-based IR-sensors include their low response speed compared with cooling receivers. In fact, they record the value of power averaged during the registration.

4. “CNT – silicon substrate” structure working conditions simulation

The decrease in the resistance of the investigated «CNT – silicon substrate» structure when exposed to the far IR-range monochromatic radiation can be caused by either an increase in the charge carriers concentration inside the CNT layer volume or an increase in their mobility. However, the mobility of charge carriers within intrinsic semiconductors, as a rule, varies slightly or even decreases in the temperature range close to room temperature [23]. In this regard, the electron concentration increase will be considered as the main mechanism of change in conductivity. The latter can also be caused by a direct interband transition due to photons absorption and thermal carriers generation caused by the transfer of lattice vibrations energy to electrons [21], [22].

Generation of charge carriers within the frame of the first mechanism is possible provided that the illuminating beam quantum energy exceeds the nanotubes bandgap. According to Ref. [16], the energy-gap width $E_g$ decreases with increasing the CNT diameter $d_{CNT}$ (external in the case of multi-walled CNTs) in accordance with the dependence shown in Figure 7. The characteristic size of multi-walled nanotubes obtained in this work is in the range of 10–20 nm. So, their bandgap is in the range of 0.05–0.1 eV or $(0.8–1.6)\times10^{-20}$ J.

![Figure 7. The dependence of a band-gap on CNT diameter (the range corresponding to the nanotubes characteristic size for this article is marked with a red area).](image-url)
The growth condition of charge carriers due to the internal photoeffect can be written as

\[ h\nu \geq E_g, \]

where \( h\nu \) is the quantum energy of infrared radiation. Considering that the frequency \( \nu \) is related to the wavelength by the formula

\[ \nu = c/\lambda, \]

where \( c \) is the light speed in a vacuum, we find \( h\nu = 1.9 \times 10^{-20} \) J.

Based on such calculations, it can be concluded that the current carriers generation in CNTs is theoretically possible due to the internal photoeffect. However, the illuminating beam quantum energy exceeds the band-gap width slightly, and the states density in the conduction band may not be enough to significantly reduce the sample resistance. Therefore, it is worthwhile to check another mechanism.

Let us determine the contribution to carrier generation associated with an increase in the substrate temperature. When laser radiation affects the “CNT–silicon substrate” structure, a part of the energy is absorbed by the components crystal lattice. As a result, the temperature of this structure changes. The establishment of the temperature field dynamics in the sensitive element volume during heating and cooling cycles may allow us to classify the receiver based on the considered structure to the photon or bolometric type.

Modern means of physical modeling (ANSYS, COMSOL, etc.) make it possible to calculate heating and cooling processes quickly and efficiently. The thermal field formation is determined by the energy source parameters, material properties, exposure time and the conditions of heat exchange with the environment.

It has been assumed that the CNT network has a small thickness, which makes it possible to consider it as a coating on a silicon substrate. We also suppose that the nanotubes completely absorb the radiation incident on them, that is, they have the same optical characteristics as an absolutely black body. Nanotubes are in direct thermal contact with the substrate, which is a massive body in relation to them. We think that, when radiation affects, rapid heat exchange due to thermal conductivity occurs between the nanotubes and the substrate which leads to an instant equality establishment of their temperatures.

Heating-cooling cycles simulation for the sample constituting itself CNTs deposited on a silicon substrate was carried out according to the scheme shown in Figure 8, under the conditions similar to the experimental described above (see Section 3). Since the sample is a silicon substrate with a nanotubes network located on its surface several tens of microns thick, it is accepted that the object under study is characterized by the substrate dimensions \( L \times B \times H = 10 \times 10 \times 0.5 \) mm. The acting energy source is placed in the center of the upper face. A CNT network is, in fact, a coating on a silicon that tracks the change in massive body energy which is a substrate. Therefore, the properties of silicon are used as the thermophysical characteristics of the material in this problem.

To calculate the temperature fields, it is expedient to use the ANSYS software package [24]. It is a universal system of finite element analysis designed, in particular, to solve problems of heat transfer and heat exchange. In ANSYS, the finite element method is implemented to solve the problems
numerically. The decision itself is conducted within a specific project. The project is created by adding the corresponding modules to its structure, filling them and connecting with subsequent modules those produce further processing, until the result will be obtained. The task description is carried out in accordance with the selected project schematics in the following sequence: setting the material and its properties, connecting the object's geometry, building a computational grid, establishing initial and boundary conditions and energy source parameters.

In this case, the modeling process is divided into two subtasks. They are the heating simulation and cooling simulation. In the first, a beam with a diameter of 5 mm acts on the sample. The energy source is characterized by a circular Gaussian distribution of power density over the aperture. To reproduce the full-scale experiment conditions, the results of temperature field calculation at the heating stage are taken as the initial for cooling process modeling. In the second subtask, the acting energy source is absent. Cooling occurs due to natural convection. At the end of heating-cooling cycle, the thermal load magnitude changes in steps, and the new cycle is counted with the new power of energy source.

Figure 9 shows the result of the heating stage simulation at the power of incident radiation of 1 W. Analysis of the temperature field allows us to conclude that the entire substrate is heated uniformly, since the difference between the maximum temperature in its center and the minimum at the periphery is only 0.003 °C.

![Figure 9](image-url) Figure 9. The temperature field within the sample at the end of the heating stage (t=180 s). The power of exposure radiation is 1 W.

Cooling stage simulation makes it possible to establish the complete temperature field uniformity after 3 min. since the radiation effect termination. As an example, Figure 10 shows the temperature field calculating results.

![Figure 10](image-url) Figure 10. The temperature field within the sample at the cooling stage termination (t=360 s). The power of incident radiation at the heating stage is 1 W.

Figure 11 shows the calculation results of the maximal temperature change in the sample volume for six heating-cooling cycles corresponding to the thermal loads values at the heating stage. One can see the nonlinear increase of the temperature at the heating stage and its nonlinear decrease at the cooling stage. The maximum sample heating during the heating-cooling cycles does not exceed 4 °C even when the acting source power is $P=3$ W.
A behavior comparison for the curves demonstrating the samples temperature change over time at the different levels of acting beam power, shown in Figure 11, with the temporal resistance behavior of the structure under study at the same power levels (see Figures 5 and 6) allows us to conclude that the increase and decrease in the samples conductivity over time are due namely to a nonlinear change in their temperature. So, the thermal receiver implemented on the basis of the “CNT – silicon substrate” structure can be attributed to the bolometric type.

In addition to the above, we can calculate the temperature coefficient of resistance for the structure under study, defined as \((\Delta R/R)/\Delta T\) [25]. For our samples, it is in the order of 0.2 °C\(^{−1}\) (a slightly larger value takes place for the structure with a lower network density).

5. Conclusion

Based on the analysis of existing literature sources, it is shown that the properties of CNTs allow us to consider them as a promising material for sensors in various applications. The classification of optical radiation receivers according to the operating principle is given, the current trends in the research of photodetectors are considered, and the requirements for optical radiation detectors are revealed.

An experimental study of the photoconductive properties for the “CNT – silicon substrate” structure obtained by the CVD technique under the influence of far IR monochromatic radiation was carried out. There were studied the samples with a different density of a homogeneous disordered network of horizontally located carbon nanotubes with a diameter of 10–20 nm. The response in the form of a change in the samples electrical resistance was observed in the power range of the acting laser radiation from 0 to 3 W. The detector response speed and the resistance recovery time after radiation exposure were 3 min. The dependence of the “CNT – silicon substrate” structure conductivity on the power of the acting source is close to linear over the entire dynamic range. The relative change in resistance for samples with different network density is ~10 %. A steeper dependence exists for samples with a dense CNT network. Transient processes are described by exponential time dependencies which give a hysteresis type characteristics when superimposed.

Analysis of photoconductivity change possible mechanisms for the sensor based on the “CNT – silicon substrate” structure permitted to establish that it is caused by the thermal charge carriers generation. The temperature field dynamics numerical simulation shows that the increase and decrease in resistance track the change in samples temperature. This fact makes it possible to attribute the sensor based on the “CNT – silicon substrate” structure to the bolometric type. The calculated temperature coefficient of resistance for the structures is ~0.2 °C\(^{−1}\).

The results of this work indicate that it is possible to create a non-selective radiation sensor based on the “CNT – silicon substrate” structures. Such structures permit to detect the power value averaged during the time of registration. They are easy to manufacture and non-toxic. Their fabrication technology is well-proven, does not require expensive equipment and ensures the photoconductive properties reproducibility. Sensors based on such structures do not require sealing and operate at room temperature.
6. References

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