Sensitive element of CNT-based IR-sensor

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Abstract. A literature review of the works presenting the results of CNT studies as optical range radiation sensors has been provided. In principle, the possibility of using a CNT sample as a sensitive element for detecting IR radiation has been shown. The dependence of the CNT sample resistance on the CO₂-laser radiation intensity has been determined.

Keywords: carbon nanotube, infrared radiation, sensitive element, optical sensor, electrical resistance.

1. Introduction

Since 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.

Today, the trend in the research of photodetectors is ambivalent. On the one hand, their sensitivity is constantly increasing during development [3], [4]. On the other hand, photodetector sensitivity spectrum is extended beyond the limits of the visible region, to the optical range boundaries [1], [3]–[5]. Requirements for the IR detector sensitive elementfor today are low intrinsic noise level, especially thermal noise, which makes it difficult to use it when living above room temperature [3], [4]; presence of fine pixels [1]; low cost, large area (sizes larger than $5 \times 5 \text{ mm}^2$) and high speed [2].

Recent progress in the field of IR-radiation review became possible with the development of nanotechnology. Nanoimprinting technique, for example, is already being used to create compact new generation spectrometers and photosensors [1].

One of the promising materials for sensing elements of sensors is carbon nanotubes (CNTs). Since the CNT discovery, extensive research work was 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 properties of nanotubes lie at the base of various radiation sensors. The fundamental reasons for this are their unusual size and size-dependent outstanding physical properties [1], [8].

Initially, nanotubes were obtained by the method of electric arc or laser evaporation of graphite and subsequent condensation in an inert gas blanket. The various modes of heating, carbon vapor removal by an inert gas jet (helium, argon), its pressure in the chamber, substrate temperature variation where carbon atoms and clusters were deposited, the presence and efficiency of introduced catalysts made it possible to obtain certain nanostructures with the yield up to 25% of total deposit weight[8].

A much higher productivity and yield of nanotubes can be achieved by catalytic pyrolysis (chemical vapor deposition – CVD) of gaseous hydrocarbons [9]. In general, this technology 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, is loaded into the furnace on a silicon (or other) inert support that serves as a catalyst and future carbon structures carrier. Variationof operatingconditions of such device makes it possible to change the ratio of the yields of differentissued products (in particular, CNTs) within a wide range.

Identification and certification of the products obtained as a synthesis result are carried out by a complex of physical methods: high-resolution transmission electron microscopy, diffractive and spectral methods (especially, Raman scattering), scanning probe microscopy, etc. [8].

The aim of this work is to study the response of nanotube samples obtained on a silicon substrate by CVDexperimentally as electrical resistance change depending on the far-infrared range laser radiationintensity.

2. Studying samples

To determine the possibility of using CNTs as IR-detectorsensitive element, two samples were fabricated. The CNT-growth wascarried out using the CVD-system (figure 1) which is a horizontal reactor, a quartz tube with adiameter of 65 mm and 650 mm in length. The reactor was placed in an electric furnace with a controlled temperature changing up to 1000 $^{\circ}$ C in a 230 mm heating zone. All reactions were carried out at atmospheric pressure.



Figure 1. Schematic diagram of the CVD system.

The CNTs were grown on n-type silicon(100) substrates with a square of ~30 mm². The substrates were cleaned in acetone using ultrasonics for 10 minutes. A thin Fe film with thethickness of 2 nm,served as a catalyst for CNT-growth, was deposited on the substrate by HF sputtering. Subsequently, the substrate was heated to 800 °C for 90 minutes and aged at this temperature for about 20 minutes for the formation of nanosize Fe particles of the catalyst film. The CVD-process wascarried out at an Ar flow rate in the chamber of 40 ml/min. A protective atmosphere was created to prevent the oxidation of metal particles when the furnace temperature had risen from room temperature to 800 °C. In addition to argon,acetylene (C₂H₂) wasused as a precursor gasat a flow rate of 5 ml/min within 10 minutes. After it the C₂H₂ flowwasshut off, and the furnace was turned off while maintaining the Arflow until the furnace had cooled to room temperature (about 2 h). A protective inert gas blank etwasmaintained to prevent the CNT-burning at high temperature. After cooling, the substrate with the CNT networkwasready for extraction from the chamber for subsequent analysis (figure 2).

Increase of the acetylene consumption up to 15 ml/min while the argon flow rate was reduced to 35 ml/min at constant time parameters of the heating-cooling cycle has made it possible to obtain a denser network of CNTs horizontally located on a silicon substrate (figure 3).



Figure 2. The sampleof CNTs grown by CVD on the substrate (sparsenetwork).



Figure 3. The sample of CNTs grown by CVD on the substrate (dencenetwork).

To determine the CNT networkparameters, the samples were studied with a high resolution scanning electron microscope (SUPRA 25) and a Raman microspectrometer with an Ar^+ -laser emitting at a wavelength of 488 nm (LabRAM HR800, JY). Figure 4 shows an image of a homogeneous CNT networklocated horizontally on a silicon substrate. A similar network structure was characteristic for both samples. The characteristic diameter of the obtained CNTs was about 10–20 nm.



Figure 4. AFM image of the CNT-structure formed on a silicon substrate obtained with the SUPRA 25 (magnification 30000).

Figure 5 represents the obtained CNT Raman spectrum. The ratio of lines characterizing the carbon structure (G-line) and defects in the CNT-structure (D-line) is less than 1 which indicates the low quantity of defects in the bondstructure of individual CNTs.



Figure 5. Raman spectrumof grown CNTs.

The nanostructures obtained in this work should have the properties of semiconductors. Possible mechanisms for changing the CNT-sampleconductivity under the optical range radiation influence are

listed in [1]. In the opinion of the authors of this article, the most probable of them, under the conditions of this experimental work, may be the generation of electron-hole pairs due to the transition of electrons from the valence band to the conduction band upon absorption of light quanta and the overcoming of the energy barrier in the form of a forbidden band due to sample heating. Below, as in [1], [4], considerations that confirm the operation of the first mechanism will be given.

3. Experiments to determine the response to IR-radiation

The experiments were carried out on a stand which photo is shown in figure 6. The CO₂-laser radiation at a wavelength of 10.6 μ m with Gaussian intensity distribution was applied to the CNT samples described in p. 2. The laser beam wasdirected between the electrodes, the distance between them was 4 mm. The electrodes were pressed tightly against the CNT-sample by spring contacts. The resistance measurement wascarried out with the MASTECH MY-62 multimeter having a measurement error of \pm 0.8% \pm 1 count unit in the 2 k Ω and 20 k Ω ranges.



Figure 6. The experimental setup for determination the dependence of CNT-sample resistance on the laser beam power: 1 - laser, 2 - mirror, 3 - multimeter, 4 - CNT-sample on a substrate.

In the experiments, the laser LCD-1A was used. The radiation power wasincreased stepwise in steps of 0.4 W. Figures 7 and 8 show the dependences of the resistance of CNT samples, described earlier, on the incident beam power.



Figure 7. The dependence of CNT-sample resistance on laser beam power (sparsenetwork).



Figure 8. The dependence of CNT-sample resistance on laser beam power (dencenetwork).

Despite the significant difference in the initial resistance values (500 Ω and 13.7 k Ω for samples with sparse and dense CNT network, respectively) in the absence of active radiation, the observed resistance change at the maximum incident beam power (about 3 W) was ~10 % in both cases. The obtained dependences are characterized by a smooth monotonic resistance decrease.

The response speed or the speed of detector sensing element operation corresponding to the time while the maximum resistance drop occurs with the maximum impact beampower was 3 min. The characteristic time for restoring the resistance to the initial value was also 3 min.

We also note one interesting, in our opinion, result of the experiments. When the CNT-sample with a sparsenetworkwas initially exposed tolaser beam, its resistance irreversibly increased from 370 to 500 Ω . As we see, this indicates that it is impossible to generate carriers due to thermal effects.

4. Conclusion

A literature review of the workswhere presented the research results of CNT as optical range radiation sensors has been given. Modern requirements to IR-radiation detectorsensitive element as well as charge carrier generation physical mechanisms for CNT-based structures under the laser radiation impact been considered.

The samples of multi-walled CNTs with a diameter of 10–20 nm grown using CVD technique on a silicon substrate and located horizontally on it in the form of a homogeneous disordered network are proposed as a photosensitive element of the detector. Two samples, with a sparse and dense nanotube network, have been studied. The Raman scattering spectrum of the grown CNTs has attested to the high structural perfection of individual CNTs.

The experiments for determination the response CNT samples depending on the intensity of impactinfrared laser radiation have made it possible to observe the significant (about 10%) decrease in electrical resistance at the beam power of \sim 3 W. Response timeon exposure and recovery time after irradiation have been about 3 minutes. The sensitivity mechanism has been explained by the interband transition of free carriers at the absorption of photons because the samples exhibited the properties characteristic of semiconductors.

Thus, the results of investigations open the possibility of using CNT-based structures as a sensitive element of the IR-detector.

5. Acknowledgments

This work was supported by the Federal Agency of Scientific Organizations (agreement No 007-G3/Ch3363/26) and has been carried out within the framework of the strategic academic unit 'Nanophotonics, emerging technologies of remote sensing and intellectual geoinformation systems' of the Samara National Research University's competitiveness improving program. The sensor investigation was partly supported by the Ministry of Education and Science project No. 16.7894.2017.6.7.

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