Creation of 3D Networks of Single-walled Carbon Nanotubes for Use in Bioelectronics

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***Abstract*—This paper presents a method for creating three-dimensional networks of carbon nanotubes by welding nanotubes under laser radiation. To carry out nanowelding, single-walled carbon nanotubes were deposited on a SiO_2 substrate, after which they were irradiated with an ytterbium laser. Structural parameters and hardness characteristics of the samples were studied. Such 3D networks can act as electrically conductive nanoframes in biomaterials.**

Keywords—carbon nanotubes; nanoweldind; 3d networks; laser irradiation

I. Introduction

It is known that carbon nanotubes have unique physical characteristics: high strength, good electrical conductivity, high thermal conductivity [1]. Materials based on carbon nanotubes make it possible to use their unique properties when creating bioelectronic devices, micro- and nanoelectronic components. Combining nanotubes in network by nanowelding method will improve strength, electrical and thermal characteristics. Various methods are used for implementation of welding nanoparticles, such as: mechanical manipulation with the atomic force microscope [2], electron beam irradiation [3], ion irradiation [4], heat welding [5-8] and welding by laser irradiation [9,10].

3D networks of welded nanotubes can be used as nanoframes of bionanoconstructions [11]. To increase the absorption of biomaterials, both organic and inorganic dyes are used [12]. It is known that dispersions based on carbon nanotubes have nonlinear properties of laser energy absorption. Therefore, carbon nanotubes can be used to increase the absorption coefficient of materials.

As a part of presented work, pulsed laser radiation with a power from 1.2 to 3 W is used to carry out nanowelding of single-walled carbon nanotubes (SWCNTs). Nanotubes were deposited on a SiO2 substrate and dried to obtain a uniform film, after which they were irradiated with a laser. Experimental studies have confirmed that composition of the dispersion with nanotubes and method of their deposition on the substrate have the greatest influence on the efficiency of nanowelding.

Scanning electron microscope (SEM) studies have confirmed that the effect of nanowelding with formation of 3D networks of nanotubes was achieved. A mechanism that describes the principle of connecting nanotubes into a single network is proposed. The studied hardness characteristics confirmed the improvement of the mechanical properties of the sample.

II. Materials And Methods

A. Creation of SWCNT film

A thin film of SWCNTs was prepared from a homogeneous dispersion of nanotubes by spin-coating (centrifugation) method. SWCNTs (c-SWCNT-90A, Carbon ChG) were synthesized by the electric arc method, carboxylated, and were delivered in the form of a paste with a nanotubes content of ~ 2.5 wt%. The length of nanotubes was in the range 0.3–0.8 µm, and the average diameter was 1.4–1.6 nm.

A dispersion of SWCNTs in an amide solvent N-methyl pyrrolidone (NMP) was prepared. For this, the required number of nanotubes was calculated and a solvent was added. Then, ultrasound was used to disperse and separate the SWCNTs bundles in the dispersion. Processing in an ultrasonic bath was carried out at a temperature of 30–37°C for 20 minutes. After that, to form a homogeneous dispersion, the treatment in immersion ultrasonic homogenizer was carried out for 15 minutes. The concentration of nanotubes in resulting dispersion was 0.7 wt.% SWCNTs. The resulting dispersion was applied to pre-treated silicon oxide (SiO2) substrate. Substrate was treated with acetone, ethanol, and distilled water in an ultrasonic bath for 10 minutes each to improve the adhesion of nanotubes. After processing, substrate was dried in a thermostat.

B. Laser treatment of SWCNT film

The processing of samples with nanotubes was carried out using system, based on an ytterbium fiber laser emitting at wavelength of 1064 nm. To create materials for micro- and nanoelectronics, it is necessary to form structures with a given area. Since the laser had a pulsed type of radiation, a uniform pattern of samples surface irradiation was created in accordance with the radiation parameters: the duration of one pulse was 100 ns, and the pulse frequency was 30 kHz. Figure 1 shows a laser system scheme where the laser energy irradiation pattern (4) of a SWCNT film, deposited on a silicon substrate (5), is a 1.25x1.25 mm square, consisting of individual laser pulses with a spot diameter of 35 µm and a distance between the centers of the spots 17 microns. Laser beam was positioned on the surface of a sample with nanotubes using a system of two rotating mirrors – galvanometric scanner

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(2). The speed of the beam was 500 mm/s. To focus the beam, a condenser lens (3) was used.

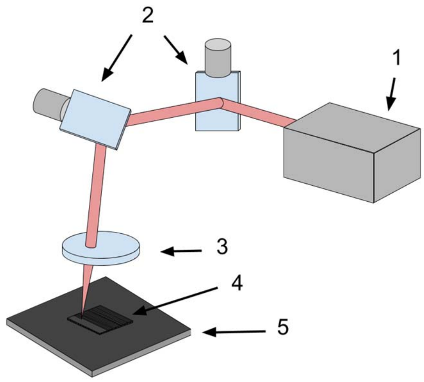


Fig. 1. Scheme of laser system, used for nanowelding of SWCNT: 1 – pulsed laser, 2 – scanner mirrors, 3 – condensing lens, 4 – laser irradiation pattern, 5 substrate with nanotubes.

To achieve the effect of nanowelding and to study the effect of laser radiation power on the mechanical properties of nanotubes, SWCNT film was processed with power values 1.2 W, 2.1 W and 3 W. Figure 2 shows image of a square area processed by a laser. The image was obtained using an optical microscope.

The sample structure was studied using a FEI Helios NanoLab 650 scanning electron microscope. Accelerating voltage of the electron column was 2 kV, and the current of the electron probe was 21 pA.

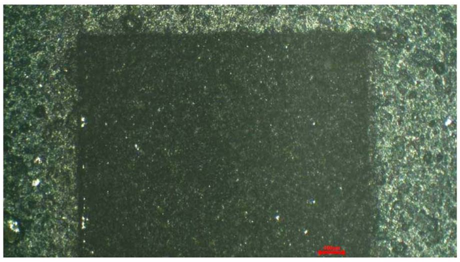


Fig. 2. Optical microscope image of square area of nanotubes, processed by laser.

C. Hardness measurement

To study the effect of laser radiation power on the mechanical properties of the sample, experimental hardness tests were carried out.

Hardness is the property of material to resist a change in its constant shape under the action of applied compressive force. This parameter is related to such mechanical characteristics as strength, fatigue resistance, viscosity. For this reason, hardness measurement can be considered as quick, simple and relatively cheap way to evaluate the quality of the material. The most commonly determined parameter is indentation hardness. To determine this hardness, the nanoindentation method is used. Such a method consists in continuously pressing a tip of known shape into the surface of the sample under the action of gradually increasing load with its subsequent removal, and continuous, thorough registration of indenter location of the load dependence.

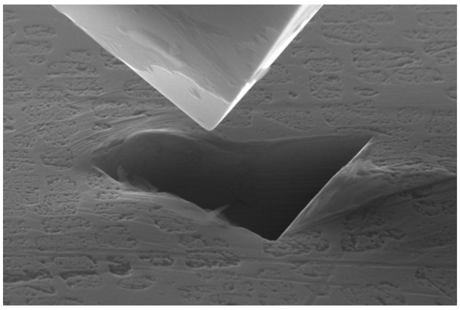


Fig. 3. The appearance of indenter tip and the imprint it leaves in material.

For carrying out measurements, a NanoScan-4D Compact nanohardness meter with an indenting tip of Berkovich form was used. Typical indenter and fingerprint shapes are shown in Figure 3.

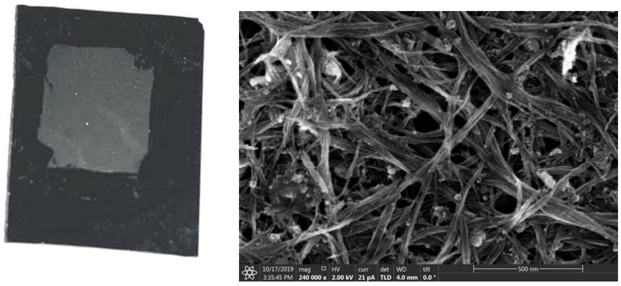
To obtain more accurate hardness estimate, minimum of 5 measurements were performed on the surface of each film section. The applied load was 60 mN.

III. RESULTS AND DISCUSSION

A. SWCNT film

SWCNT film image is presented in Fig. 4a. Also structure of the SWCNT film was studied the by SEM (Figure 4b).

In image with x240000 magnification, SWCNT bundles are clearly visible. The diameter of bundles reaches 40 nm. This indicates that the action of the solvent is not sufficient for complete mixing and separation of nanotubes.

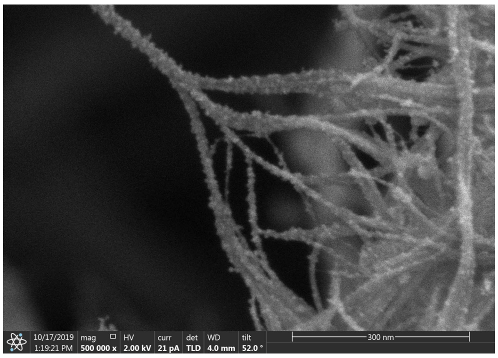


a b

Fig. 4. Sample of SWCNT film on the SiO2 substrate (a), SEM image of SWCNT film (b).

B. Nanowelding of SWCNT

As a result of high intensity laser treatment, the effect of nanowelding of SWCNTs was achieved. SEM images demonstrate the formation of SWCNTs network after processing of film with power of 1.2 W (Figure 5a). Such network consists of welded individual nanotubes and SWCNT bundles. In places of cross and perpendicular SWCNT joints, "T" shaped joints (Figure 5b), "X" and "Y" shaped joints (Figure 5c) were formed.



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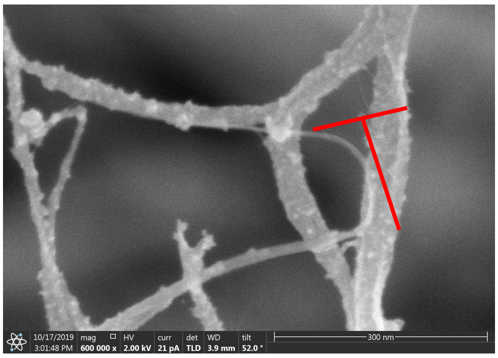

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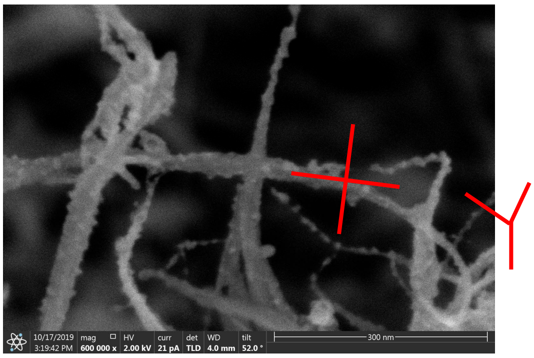

c

Fig. 5. SEM images of welded SWCNTs: SWCNTs network, made by laser irradiation (a), SWCNTs nanowelded joints of “T” (b), “X” and “Y” (c) shape.

It is known that high temperatures contribute to destruction of SWCNTs and C–C bonds with subsequent formation of new bonds [13–16]. High-intensity laser radiation heats nanotubes to high temperatures around 1800°C. This contributes to formation of welded SWCNTs networks. In addition to the effect of nanowelding, new chemical bonds are formed on the contact surfaces of heated nanotubes. This is evidenced by presence of small particles on the surface of the nanotubes in Figure 5.

Formation of “T” shaped joint occurs upon the formation of atomic bonds at the end of single walled carbon nanotube with atoms in the places of defects in nanotube wall (Figure 6a). “X” -shaped connection of two SWCNTs is formed when nanotubes are crossed at the moment of laser irradiation (Figure 6b). “Y” connection is formed by connecting of three ends of SWCNT.

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a b c

Fig. 6. Schematic representation of “T” shaped (a), “X” shaped (b), “Y” shaped (c) SWCNTs joints, formed by laser radiation.

C. *Hardness of SWCNT film*

Hardness measurements were performed on four areas of SWCNT film: initial area and three areas treated with different power values. The hardness measurements results depending on the power of laser radiation are shown in Table 1.

TABLE I. HARDNESS MEASUREMENT RESULTS

Laser power, W	Hardness, GPa
Initial area	0.07
1.2	0.16
2.1	0.06
3	0.05

Based on the obtained data, it can be seen that sample area, irradiated with power 1.2 W has the highest hardness. This can be explained by the fact that in this area effect of nanowelding between nanotubes was achieved, which led to an increase in hardness. However, with a further increase in power, a decrease in hardness was observed, which can be justified by the fact that a high laser power leads to burning of nanotubes. Therefore, the area irradiated with power 3 W has the lowest hardness.

IV. CONCLUSION

A method for creating 3D networks of single-walled carbon nanotubes for use in bioelectronics is presented. The effect of nanowelding of SWCNTs was achieved under the influence of pulsed ytterbium laser radiation with wavelength of 1064 nm. Sample was a SiO_2 substrate on which a dispersion of SWCNTs and N-methyl pyrrolidone was applied by spin-coating method. A galvanometric system of mirrors was used to create square structures of welded nanotubes on the film from dried SWCNTs dispersion surface. Three areas of the film with different laser power values were processed by laser: 1.2 W, 2.1 W, 3 W. SEM images confirmed formation of 3D network of nanotubes after irradiation with laser power of 1.2 W. The mechanism of nanotube joints formation with “T”, “X” and “Y” shapes is described. Hardness studies were carried out to study mechanical properties of treated areas of the film. It was determined that irradiation of a film with laser power of 1.2 W contributes to increase in hardness by more than 2 times compared to the original. A subsequent increase in power leads to sharp drop in the hardness value. Such an effect can be explained by burning and sublimation of nanotubes at high laser power and formation of network with unstable structure.

Thus, a new technique for creating 3D networks of single-walled carbon nanotubes was developed.

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