Modification of CNT arrays morphology by nanosecond laser treatment

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Abstract. The effect of nanosecond pulses of laser radiation of different energy on the oriented CNT array synthesized by catalytic plasma-induced deposition from a gas phase on a silicon substrate was studied. It is shown that the following effects are possible: CNT ablation, the effect of CNT alignment (straightening), singling, and “splicing” of individual CNTs in a single structure, as well as changing the morphology of the array itself. Structuring of CNTs at a given area using impulse nanosecond radiation moving using a galvanometric scanner system is obtained. Nanotubes are less defective after laser modification. This is proved by Raman spectroscopy. This treatment can be used for electron emission devices, CNT-based detectors and topological elements.

1. Introduction

Carbon nanotubes are a promising material for the elements of nanoelectronics, microsystems and sensor technology. Due to its unique electrophysical properties, nanotubes are used as ultra-sensitive and low-power active elements in functional devices, reinforcing and electrically conductive fillers in composite materials. In addition, CNT are attractive objects for development of high efficiency field emission cathodes due to their high aspect ratio, relatively low work function and high activation energy for surface migration of the emitter atoms [1, 2].

To obtain effective field emission, it is advantageous to use CNT arrays grown on a substrate, which already have a given orientation. Individual nanotubes, although growing in the form of a forest perpendicular to the substrate, however, their length, direction of growth and general morphology can be different. Therefore, it is necessary to find methods for precise orientation of nanotubes in an array relative to the substrate. These methods can be useful in wide range of applications, which is not limited to the listed areas. Laser patterning is one of possible and promising ways.

So, using laser radiation with a wavelength near infrared range carbon nanotubes are patterned in nanoframe in polymer matrices [2, 3]. One of the first references about a cathode, whose emitter is made on the base of CNTs processed by a laser, is contained in [4]. A direct increase in the density of the emission current upon the laser radiation by excimer laser KrF (wavelength $\lambda = 248$ nm, pulse duration $\tau = 30$ ns, frequency $f = 10$ Hz) applied to an ordered CNT array was reached with decimation of an array [5]. Most effective alignment of CNT array was obtained with Nd-YAG laser ($\lambda = 355$ nm,
\[ \tau = 10 \text{ nm, energy density of pulse } E/S = 326 \text{ mJ/cm}^2 \] \[6, 7\]. It was shown building of \(22 \mu\text{m}\) conical microstructures with 5,73 \(\mu\text{m}\) period from CNT array on silicon wafer. This paper presents the results of laser patterning of an array of multi-walled carbon nanotubes synthesized on a silicon substrate. Patterning was carried out using pulsed laser radiation with a wavelength of 1064 nm, which was moved by means of galvanometric mirrors over the area of the CNT array 5x5 mm.

2. Materials and methods

2.1. Samples of the CNT array

The arrays of carbon nanotubes were synthesized directly on silicon substrates (figure 1). Catalyst pair Ti/Ni 10/2 nm was used as the catalyst. The plasma-enhanced chemical vapor deposition of nanotubes (PECVD) was carried out in a three-stage process using an Oxford Instruments Nanofab800Agile unit, which included: the oxidation stage of the catalyst in Ar-O\(_2\) plasma at 280°C for 5 minutes, the catalyst reduction stage in NH\(_3\)-Ar plasma at a temperature of 700°C for 5 min, the synthesis of CNTs by feeding C\(_2\)H\(_2\), NH\(_3\) and Ar at 700°C for 10 min. The flow rate of all gases was fixed at 100 cm\(^3\)/min, except for Ar – 300 cm\(^3\)/min. The pressure in the chamber was 3 Torr. Plasma power during oxidation and reduction was 100 W (RF), with synthesis - 20/30 W (RF/LF).

![Figure 1 (a, b). Initial CNT array with zoom x15000 (a) and x45000 (b).](image)

Thus, samples of silicon substrates with a size of at least 10x10 mm with a grown array of multi-walled CNTs were obtained for the experiment. MWNTs had an average height of 5 \(\mu\text{m}\). The diameters of the MWNTs were about 20 nm.

2.2. Laser units

In order to study the process of changing the structural properties of the CNT array, a pulsed laser based unit was used. In this case, the sample was mounted on the optical axis perpendicular to the focused laser radiation (figure 2). These studies revealed the influence of the energy characteristics of single pulses on the CNT array.

The main element of the optical system is a solid-state pulsed Nd: YAG laser (1). At a primary wavelength of 1064 nm, generation of the second harmonic of radiation with a wavelength of 532 nm is achieved by intracavity doubling of the laser generation frequency by means of a nonlinear crystal. The pulse duration was 16 ns. The pulse energy varied in the range 1.21-4.158 \(\mu\text{J}\). The energy density of the pulse was in the range 0.4-2.2 J/cm\(^2\). Leaving the laser, beam hits the Glan prism (5). The Glan prism is the simplest polarizer that converts radiation with arbitrary polarization into a linearly polarized, as well as regulating the energy of a beam incident on the sample. Rotation of the Glan prism allows us to adjust the energy of the beam with a given pitch. Then the beam hits the wedge quartz prism. The energy meter based on the Ophir PD-10 (7) sensor makes it possible to measure the
energy of the incident beam and is set so that the beam reflected from the wedge-like prism whose energy is \( \sim 10\% \) of the original beam hits it. At high energies of the incident beam, filters (6) are installed in front of the sensor. The lens (4) with a focal length \( L = 10 \text{ cm} \) is mounted directly in front of the sample. The sample (5) is placed on a mechanized stage to move the sample after laser exposure. Before the experiment, the spatial profile of the radiation pulse was measured using a Spiricon 620 CCD camera. Figure 4a shows the dependence of the energy density on the coordinate, which characterizes the spatial profile of the radiation. Using the optical unit shown in figure 2a, the action of single laser pulses was performed at different points of the CNT array.

![Figure 2](image_url)

**Figure 2.** Optical units for irradiating a CNT array based on an Nd:YAG laser operating in single-pulse mode (a) and on the basis of an ytterbium fiber laser connected to a galvanometric scanner system.

To study the process of changing the structural properties on a given area of the CNT array, an optical unit based on a pulsed laser connected to the scanner system was used. An ytterbium fiber laser emitting pulses of 100 ns duration at a wavelength of 1064 nm was used. The spatial profile of the beam was Gaussian. The scheme of the experiment is shown in figure 2b.

Laser radiation was generated using a pulsed ytterbium fiber laser (1) and was transmitted through the optical fiber to the mirrors of the galvanometric scanner (2) and (3) to position the beam along the X and Y coordinates. Further, the radiation through of the objective (3) was focused on the CNT array (4) on a silicon substrate (5). The objective was equipped with a distance sensor and had a focal length of 210 mm, while the waist length was \( \sim 1 \text{ mm} \).

The parameters and path of the laser beam were set using a computer program. In order to obtain a homogeneous region of the CNT array after irradiation, the following parameters were set: the pulse duration was 100 ns, the radiation frequency was 30 kHz, at which the overheating of CNTs was minimized. The diameter of the laser beam at the focus of the laser was 20 \( \mu \text{m} \). The moving rate of the laser beam of 500 mm/s was chosen in such a way that individual pulses formed a continuous line with a laser beam overlap to compensate the changing in laser spot power along the diameter. Thus, the processed square 5x5 mm was formed by parallel lines 5 mm long, consisting of individual pulses located at a distance of 17 \( \mu \text{m} \) from each other (6) in figure 4b.

2.3. **Electron microscopy**

The study of the CNT array before and after laser exposure was performed using a scanning electron microscope JSM-6010 PLUS / LA JEOL. In this microscope, a tungsten cathode and a system of magnetic lenses are used to form an electronic probe on the surface of the samples. The study was carried out in high vacuum mode at a pressure of not less than 1x10^{-4} Pa. The accelerating voltage of
the electronic column was set at around 20 kV. The inclination of the motorized stage with samples was 30°. The image was obtained with the help of the Everhart-Thornley scintillation detector by recording secondary electrons.

3. Results and discussion

3.1. Irradiation of a CNT array in the single-pulse mode

In the single-pulse mode, laser spots were formed on the surface of the CNT array (figure 3b). The areas of the laser spot bounded by the green contour corresponded to different values of the pulse energy with a Gaussian spatial profile (figure 3a).

The analysis of the regions in figure 3 allows us to conclude that the effect of CNT array aligning has been obtained. This effect was obtained at a pulse energy $E = 335 \mu J$ (energy density $E/S = 1.7 J/cm^2$ for a beam radius of 0.0112 cm). In region 1, on which the energy maximum of a Gaussian beam ($E/S_1 = 1.21 J/cm^2$), almost no CNTs were observed (figure 3c). Conversely, the CNTs in region 2 with a lower energy ($E/S_2 = 0.76 J/cm^2$) were oriented perpendicular to the substrate. However, their height was significantly lower due to laser burning than the height of the tubes in region 3 with an even lower energy ($E/S_3 = 0.21 J/cm^2$). The resulting effect of CNTs alignment can be compared with the region 4 to which the pulse of laser radiation is not reached. In region 4, the tubes were intertwined and entangled, and their tips were not directed perpendicularly.

Most likely, the effect of CNT structuring perpendicular to the substrate is associated with a change in the defects degree of the carbon structure of the tubes and «splicing» of several CNTs into one.
3.2. Scanning the area of a CNT array in the frequency mode

For practical application of this effect in the devices described in the introduction of this article, it is necessary to obtain the structuring of the CNT array on a given area. As a result of experiments in the single-pulse mode, the energy parameters of the CNTs structuring were obtained. The radiation power was 0.7 W, which corresponded to an energy density of 3.8 J/cm². These parameters formed the basis for the technology of processing of CNT array with the use of particular radiation, which moves along the area of the sample using a scanner system. Figure 4b shows the structuring of the CNT array with an area of 5x5 mm. This area consisted of strips left by a laser beam, which was moved by means of a scanner system (figure 4a).

3.3. Raman spectroscopy

A Raman spectroscopy study was carried out before and after the laser exposure of the samples. The laser action leads to a reduction in the defects degree of carbon nanotubes, as can be seen from the change in the ratio of G and D peaks (figure 5). At the same time, the intensity of the peaks increase, this indicates that the selected intensity of exposure does not lead to burning out the main mass of CNTs.
Figure 5. Raman spectra of CNT array before and after laser irradiation.

Thus, the efficiency of laser processing of CNT arrays has been demonstrated in terms of changing their morphology, structuring individual CNTs and reducing of defectiveness.

4. Conclusion
The technology of modification of the CNT array on a silicon substrate using laser radiation of nanosecond duration has been developed. The energy regime of irradiation of the array is determined with the aim of aligning the nanotubes perpendicular to the substrate. Structuring of CNTs at a given area using impulse nanosecond radiation moving using a galvanometric scanner system is obtained. The effect of CNT array structuring can be used to create new sensitive elements of photodetectors, solar cells, chemical sensors, temperature and pressure sensors, probes in microscopy and emitters.

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