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Growth of vertically aligned multi-wall carbon nanotubes on SiO_2/Si structures modified by ion irradiation

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Morphological parameters of layers of vertically aligned multi-walled carbon nanotubes at various stages of synthesis have been studied. It is shown that as a result of ion processing of the growth substrate, a more intensive and homogeneous growth of multi-walled carbon nanotubes occurs. Modification of the growth substrate increases the number of places where the catalyst particles are fixed on the surface, which leads to the formation of a more homogeneous layer of nanotubes on the substrate. The analysis of the data obtained by the method of energy dispersion analysis showed a correlation of the effect of increasing the density of carbon nanotubes with the dose of ion surface treatment. Pretreatment of the growth substrate surface by ion irradiation helps to reduce the inhomogeneity of the nanotubes layer.

Keywords: vertically aligned multi-walled carbon nanotubes, chemical vapor deposition, ion irradiation, scanning electron microscopy.

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1. Introduction

Researchers' interest in multi-walled carbon nanotubes (MCNTs) is due to their unique physicochemical properties. Mechanical strength, a wide range of conductivity, chemical inertness and autoemission properties make MCNTs a promising material for the production of sensors, sorbents, supercapacitor electrodes, elements of chemical current sources, etc. [1,2].

A rather common method for the synthesis of MCNTs is the chemical vapor deposition method (CVD). During the nanotubes synthesis using CVD method the pyrolysis of the hydrocarbon precursor occurs in the reactor area in the presence of a catalyst, resulting in the growth of vertically oriented MCNTs on SiO_2/Si substrate. A solution of acetonitrile and ferrocene is used as precursor and catalyst, which is supplied in the form of a spray to the reactor zone. This synthesis method has high productivity, is characterized by a relative simplicity of the technological process, and low cost. At the same time, the disadvantages of this synthesis method include a wide range of values of the outer diameter of the resulting nanotubes and heterogeneity in the thickness of the synthesized MCNT layer [3], which ultimately negatively affects the characteristics of devices built on their basis.

The outer diameter of carbon nanotubes synthesized by CVD method is most influenced by the synthesis temperature and the type of metal catalyst [4]. Optimization of the morphological characteristics of the resulting nanotube layers can be achieved by modifying the surface of the growth substrate by ion irradiation in order to more uniformly distribute catalyst particles over the surface during synthesis. In this paper, the parameters of MCNT layers obtained by CVD method at various stages of synthesis were studied when modifying the growth substrate.

2. Experiment

To study the influence of the surface state of the growth substrate on the morphology of the MCNT layer the rectangular plates of single-crystalline silicon with a layer of thermally oxidized silicon dioxide (SiO_2/Si) of size $2 \times 1\,\mathrm{cm}^2$ were prepared. Part of the substrate was shielded with a metal mask to protect the surface from ion exposure. The growth substrates prepared in this way were irradiated with Ar^+ ions with energy of 15 keV and current of 2 mA for 20, 40 and 60 min.

MCNT layers were grown by the CVD method by pyrolysis of acetonitrile on SiO_2/Si substrates; iron nanoparticles formed as a result of the thermal decomposition of ferrocene were used as growth catalysts. The temperature in the reaction zone was 800°C. The MCNT synthesis time varied from 5 to 30 min in order to determine the parameters of the nanotube layers at various stages of synthesis.

Determination of the parameters of MCNT layer at various stages of synthesis was carried out by scanning electron microscopy (SEM) on Jeol JSM 6610-LV microscope.

3. Results and discussions

Irradiation of the growth substrate with argon ions leads to the defects formation in the surface layer [5], due to the

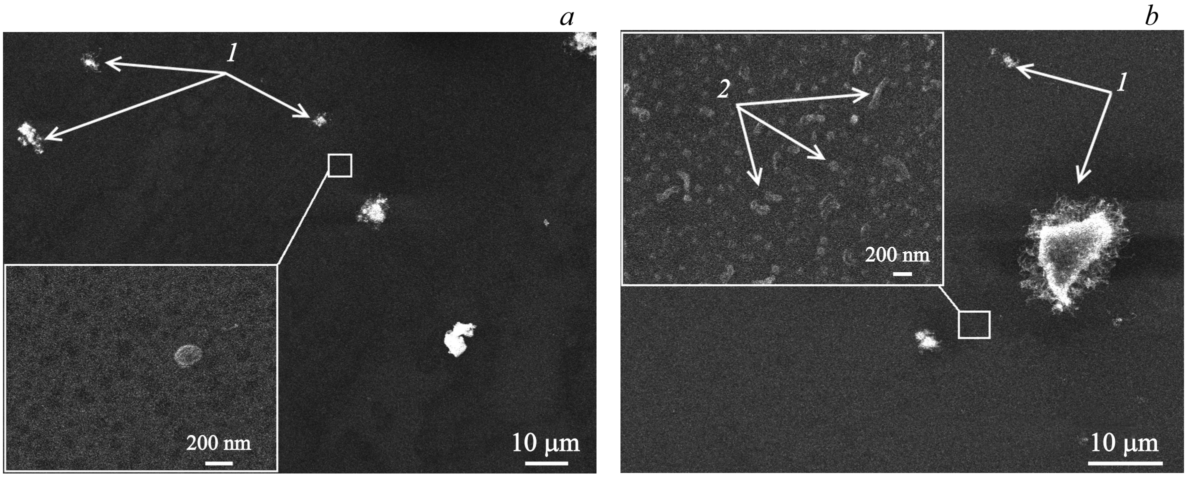

Figure 1. SEM-image of surface of growth substrate after 5 min CVD-synthesis of MCNT. *a* — Unmodified substrate; *b* — substrate after irradiation with ions Ar^+ with energy of 15 keV and current of 2 mA with duration 60 min. *1* — MCNTs clusters on surface of growth substrate, *2* — MCNT at initial stage of synthesis.

Data of EDA analysis and MCNT density on growth substrate

Mode of surface treatment	[C], at.%	[O], at.%	[Si], at.%	[Fe], at.%	Density of MCNT, μm^{-2}	Relative change of density
Unirradiated surface	6.07	11.88	82.05	–	2.5	1
Irradiation Ar^+ $E = 15$ keV, $I = 2$ mA, $t = 20$ min	8.86	16.74	74.24	0.16	3.96	1.6
Irradiation Ar^+ $E = 15$ keV, $I = 2$ mA, $t = 40$ min	17.19	9.13	73.55	0.13	7.9	3.16
Irradiation Ar^+ $E = 15$ keV, $I = 2$ mA, $t = 60$ min	24.73	7.22	67.8	0.25	10.7	4.28

formation of point defects in the structure of silicon oxide. The irradiation parameters used in the paper do not lead to significant sputtering of the surface of the growth substrate, while the surface modification is achieved at the submicron level [6].

The effect of preliminary irradiation of the growth substrate is clearly observed in the images of the initial stages of MCNT growth obtained by SEM. The study of the initial stages of growth of MCNT layers indicates a more uniform distribution of the catalyst over the surface and more intense growth of MCNTs on the modified substrate. This effect correlates with the pre-irradiation dose; the greatest increase in MCNT density in the initial growth phase was observed when the growth substrate was irradiated for 60 min (Figure 1).

The change in MCNT density was assessed using SEM images of the growth substrate surface. Data from EDA analysis of the growth substrate surface, as well as averaged MCNT density values per 1 μm^2 area for various pre-irradiation modes are given in the Table. Changes in element concentrations correlate with the calculated MCNT density values.

As can be seen from SEM images, at the initial growth stages the areas of MCNT clusters are formed on the substrate. Such areas are observed on both the irradiated and non-irradiated parts. The sizes of MCNT clusters are up to 10 μm. During the synthesis process a mixture of acetonitrile and ferrocene is continuously fed into the reaction zone in the form of an aerosol dispersion, and new growth centers of the MCNT film are formed. As a result, a continuous film of vertically oriented MCNTs is formed. Irradiation of the growth substrate creates defective areas where catalyst particles are fixed; as a result, increase in the density of MCNTs is observed in SEM images at the initial stages of synthesis.

A more uniform distribution of the catalyst over the growth substrate surface ultimately leads to a more uniform layer of vertically oriented MCNTs (Figure 2). SEM studies of MCNT layers after full synthesis cycle, on modified and unmodified substrate, showed differences in the morphological properties of the layers.

On the surface of the MCNT layer a boundary is clearly visible that separates the irradiated (Figure 2, left) and non-irradiated (Figure 2, right) regions of the substrate. On the part of the substrate that was not treated with ion beam, the surface of the nanotube layer has a more developed relief compared to the modified part of the substrate. On the surface of the layer grown on the non-irradiated part

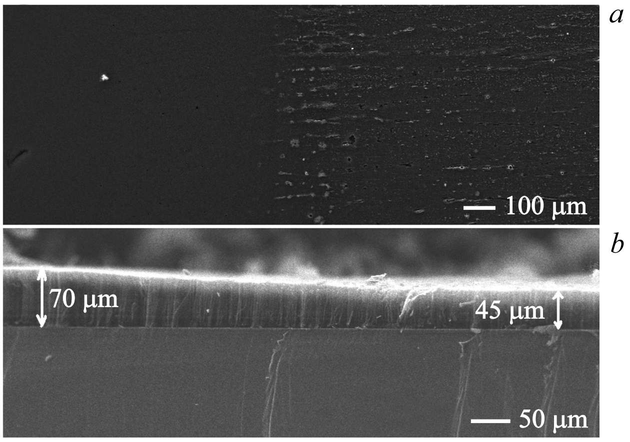

Figure 2. SEM image of MCNT layer. *a* — surface of layer of vertically oriented MCNTs; *b* — cross section of layer of vertically oriented MCNTs. On the right there is unmodified substrate, on the left there is substrate modified by irradiation with Ar^+ ions with energy of 15 keV and current of 2 mA for 60 min.

of the substrate, large pores and MCNT clusters protruding above the surface are observed. A study of the pretreatment effect on the diameter of carbon nanotubes did not reveal changes in the values of the outer diameter of the tubes in the areas with the modified and original substrate. A study of the cross-section of the MCNT layer showed that on the pre-irradiated part of the growth substrate the thickness of the nanotube layer is slightly greater than on the unmodified part.

Analysis of the obtained data allows us to highlight the features of the film growth of vertically oriented MCNTs on the substrate. The synthesis method described in this paper is based on the thermal decomposition of mixture of acetonitrile and ferrocene and subsequent deposition of the catalyst onto a substrate. At the initial stages of growth, the catalyst particles are fixed on the growth substrate with the formation of rather large clusters — MCNT islands (Figure 1). Next, the number and size of islands increase with the formation of a continuous layer of nanotubes. Modification of the growth substrate increases the number of sites for fixing catalyst particles on the surface, which leads to the formation of more uniform layer of nanotubes on the substrate. At the same time, the diameter of the nanotube is determined by the size of the catalyst particle and the synthesis temperature. The size of the catalyst particle is determined by the characteristics of the nozzle spraying the precursor mixture; as a result, modification of the growth substrate does not affect the MCNT diameter. Thus, modification of the growth substrate promotes the growth of more uniform layer of vertically oriented MCNTs.

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Conflict of interest

The authors declare that they have no conflict of interest.

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