

TRANSFER PROCESSES UNDER PLASMA AND LASER ACTION ON GASEOUS AND CONDENSED MEDIA

LOW-TEMPERATURE PLASMA-CHEMICAL SYNTHESIS OF CARBON NANOTUBES ON NICKEL PATTERNS OBTAINED BY THE PHOTOCATALYTIC-LITHOGRAPHY METHOD

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Ordered carbon nanosize structures have been obtained on a catalytic substrate at a low temperature (200°C). The carbon-containing blend was activated by the plasma of a pulsed barrier discharge at atmospheric pressure.

Introduction. The interest in carbon nanotubes as individual formations and ordered arrays stems from the complex of their electronic, sorption, mechanical, and electrochemical properties [1], which opens up prospects for various practical applications, including the creation of carbon-nanotube-based field emitters [2], active elements of energy-storage devices [3], chemical sensors [4], probes of atomic-force microscopes [5], nanoelectronic elements [6, 7], and others. Further use of carbon nanotubes assumes a radical reduction in the synthesis temperature, which will enable one to substantially extend the range of the substrates used; also, it assumes solution of the problem of spatial selective growth of nanotube arrays. Pyrolytic synthesis of a carbon nanophase can be activated at low temperatures by the action of a nonequilibrium plasma [8, 9] (in particular, of that generated under barrier-discharge conditions [10]), whereas the selective formation of catalytic substrates ensuring the growth of carbon nanotubes was demonstrated with the use of structured metal-containing anode oxides [10, 11], different versions of microprinting [12, 13], and traditional photolithography [14].

In the present paper, we give results of investigations aimed at developing methods of growth of carbon nanotubes and nanofibers of different morphology on the catalytic surface of a nickel pattern under the activating action of a barrier-discharge plasma; this action enables one to reduce the synthesis temperature to 200°C.

Experimental Procedure. Plasma-chemical synthesis of carbon nanotubes under pulsed barrier discharge was carried out with the use of a setup whose schematic diagram is given in Fig. 1. The carbon source was carbon monoxide which, together with a carrier gas (He), entered the planar slit barrier-discharge reactor with an interelectrode gap of 1 mm and a 40 × 15 mm deposition site. The catalytic substrate was placed on the lower (grounded) electrode, whereas the upper (high-voltage) one was equipped with a 1.5-mm-thick surface ceramic barrier layer. Pulsed voltage of amplitude 5 kV with a pulse rise time of ~150 nsec and a pulse repetition frequency of 25 kHz was applied between the electrodes. The necessary temperature in the reactor was maintained by the heater integrated with the lower electrode. All the experiments were performed at atmospheric pressure. The He and CO flow rate was 5 liters/min and 50 cm³/min respectively. The deposition of the carbon nanophase lasted for 30 min. The catalytic substrate for growing carbon nanotubes was a nickel pattern in the form of a net with a line width of 12 μm (see the inset in Fig. 2a); the nickel pattern had been obtained on the substrate from monocrystalline silicon by the photocatalytic-lithography

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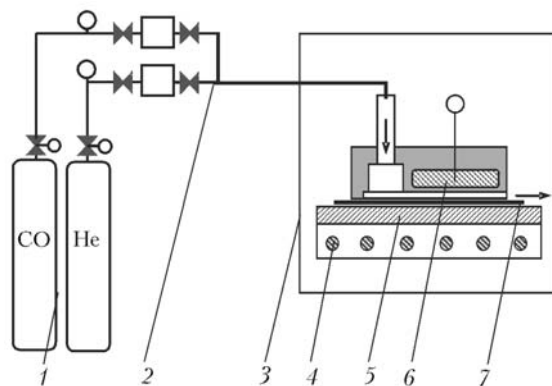


Fig. 1. Diagram of the setup for growth of carbon nanotubes under pulsed barrier discharge: 1) gas station; 2) system for batching gases; 3) hermetic box; 4) reactor's heater; 5) working table (lower electrode); 6) high-voltage electrode; 7) catalytic substrate.

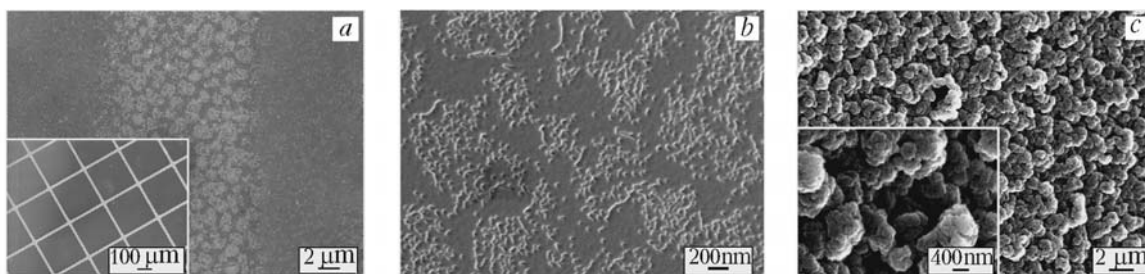


Fig. 2. Electron-microscopic pictures: a) surface of the nickel track after carbon deposition at 200°C under pulsed barrier discharge (the inset gives the initial track); b) track with deposited carbon nanotubes; c) nickel surface after carbon deposition at 350°C under pulsed barrier discharge (the inset gives a magnified picture of the surface portion).

method with the use of films of amorphous palladium-ion-doped titanium dioxide as the photosensitive layer [15]. The $\text{TiO}_2:\text{Pd}^{2+}$ films were obtained by pouring, over the rotating substrate, an isopropanol solution of polybutyl titanate (0.5%) additionally containing H_2PdCl_4 (0.05%) and oxalic acid (0.5%) acting as a chemical sensitizer. The procedure of obtaining metallic patterns included the: (a) exposure through a contact quartz photomask using a DRT-1000 mercury lamp; (b) flushing in an aqueous solution of isopropanol (10 vol.%), which enabled us to get rid of the Pd^{2+} ions not used in the photocatalytic process; (c) the palladium-catalyzed chemical deposition of nickel on the exposed portions. The electron-microscopic investigation of the resulting carbon nanotubes was performed with the use of an LEO-1455VP scanning electron microscope.

Results and Discussion. The photocatalytic-lithography method used in the work is based on the reduction of palladium ions involving photoelectrons generated in the film of amorphous titanium dioxide on UV irradiation. The primary photoreduction product is Pd(I) [14] converted to the palladium phase as a result of the disproportionation in contact with the aqueous solution in the flushing stage. Such a mechanism of collection of the photoinduced charge ensures the formation of small palladium particles (with an average size of 3.3 nm under the specified exposure conditions) characterized by a high monodispersity level and a high catalytic activity in relation to the process of reduction of nickel from the hypophosphite solution of chemical deposition [16]. Gradual growth in the nickel particles on palladium centers and their subsequent intergrowth give rise to a 0.2- μm -thick nickel film in the form of a pattern negative to the photomask used. The resulting nickel deposit is x-ray amorphous due to the amorphizing action of the phosphorus impurity, whose source is hypophosphite. The above circumstance ensures the formation of numerous catalytic sites with dimensions smaller than the diffusion length of atomic carbon on the nickel-pattern surface, which of-

fers favorable conditions for growth of coaxially cylindrical carbon nanoformations by the "carbide-cycle" mechanism [17]. The large number of growth sites of the nickel phase (~ 900 particles per μm^2) and the high selectivity of chemical deposition enable one to obtain nickel patterns with a high resolution (3–5 μm).

In Fig. 2a, it is seen that the disproportionation of carbon monoxide, which occurs at 200°C as a result of the activating action of the barrier-discharge plasma, gives rise to bunch-like arrays of loosely packed carbon nanotubes on the nickel-pattern surface; these arrays have the same diameter (~ 60 nm), as is seen in Fig. 2b. The tube length is relatively small, which is attributable to the reduction in the growth rate at moderate temperatures [18]. Individual tubes may attain a length of 300 nm. A considerable amount of amorphous carbon uniformly deposited on the sample surface is simultaneously formed. The electron-microscopic picture (given in Fig. 2b) of the track edge demonstrates the high selectivity of the process of nanotube synthesis. The increase in the substrate temperature to 350°C produces an increase in the rate of growth in the carbon phase and a radical change in its morphology: as is seen in Fig. 2c, spiral fibers of diameter ~ 1 μm consisting of individual carbon concretions are formed instead of straight nanotubes.

CONCLUSIONS

The process of chemical carbon deposition carried out in the nonequilibrium plasma of a pulsed barrier discharge enables one to reduce the synthesis temperature of carbon nanotubes to 200°C and to grow nanotube arrays on the catalyst in the form of a nickel pattern.

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