

06 Effect of nickel catalyst carburization on carbon nanotube growth on silicon substrates

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Received November 13, 2025

Revised March 6, 2026

Accepted March 17, 2026

This work proposes atomic layer deposition of a thin NiO layer as the catalyst source for carbon nanotube growth. Samples with NiO thickness from 1.5 to 3.5 nm were considered. Silicon substrates with their native oxide layer were used. Carbon nanotube arrays were deposited using plasma-enhanced chemical vapor deposition. The resulting arrays exhibited either short nanotube length or low nanotube density. The addition a nickel film carburization step during the treatment phase significantly improved these array characteristics. This process can be easily implemented in any chemical vapor deposition system.

Keywords: Carbon nanotubes, catalyst, carburization, carbon layer.

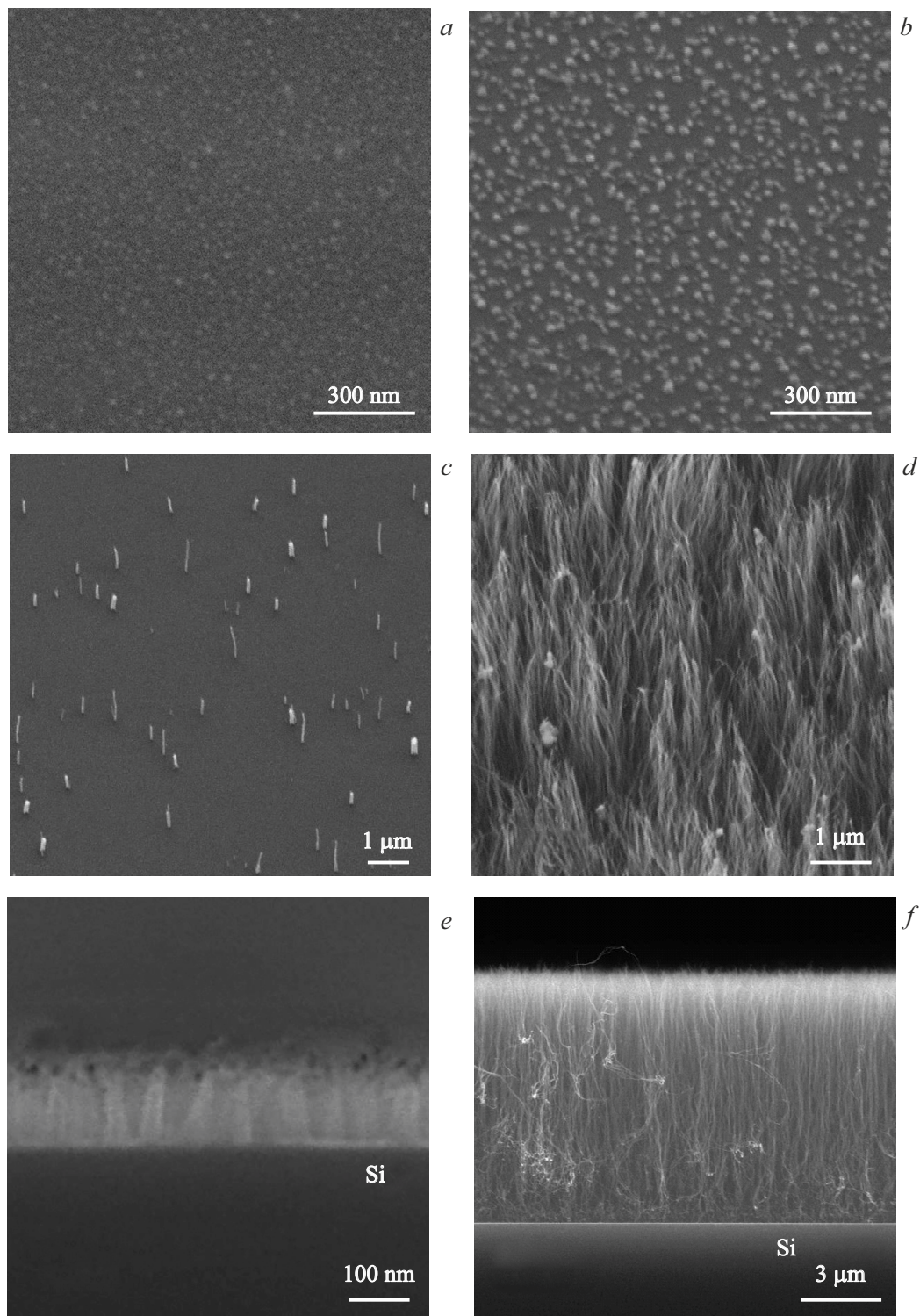
DOI: 10.61011/TPL.2026.06.63801.20571

Carbon nanotube (CNT) coatings have broad prospects for the use as a cathode material in electronic emission devices, sensor elements on the basis of various concepts, highly-porous conducting platform for various conversion and energy storage devices, etc. Such coatings are generally formed via chemical vapor deposition (CVD) onto flat silicon wafers with a metal catalyst film having a special island or grain structure. Growth is described by a VLS (vapour–liquid–solid) mechanism where the composition and sizes of metal catalyst particles to a great extent define the possibility to form tubes and their properties [1]. However, the metal nanoparticles interact with the wafer material, thus, reducing their utilization as catalyst. Therefore, modern CNT techniques imply introduction of additional processes to activate or stabilize the catalyst particles. For this, diffusion barrier layers are used between silicon and catalyst, catalyst composition gets more complex or the produced catalytic structure undergoes additional treatment before CNT deposition [1].

This study proposes and investigates a new catalyst preparation technique, including a catalyst carburization stage, to control the morphology of the grown CNT. Island nickel film formed on a silicon wafer with a native oxide layer is used as catalyst. Carburizing modifies many nickel properties, for example, thermodynamic phase properties, diffusion permeability, catalyst poisoning rate, surface energy, etc. Such modifications shall affect the interaction between the catalyst and wafer, catalyst morphology and activity. Nickel island films were formed from thin nickel oxide film through metal reduction followed by continuous film dewetting at high temperature. Initial NiO was obtained using an atomic layer deposition method that has prospects in the CNT

growing technique due to its benefits [2], CNT were formed using a plasma-chemical deposition method.

Atomic layer deposition of NiO was performed onto KDB-10 (100) silicon wafers with native oxide using the Picosun R-150 (Picosun, Finland) system. Bis(cyclopentadienyl)nickel/ozone reagent system and nitrogen as plunger gas were used, deposition temperature was 250 °C, and nickelocene evaporator temperature was 90 °C. Deposition cycle mode included the following stages: nickelocene pulse/purge/ ozone pulse/purge with times 4/20/6/20 s, respectively. Growth per cycle of film was 0.20 ± 0.02 Å. The number of cycles varied to obtain films with the desired thickness, a NiO thickness range of 1.3–3.7 nm was used for the study. Ni reduction was performed in a plasma-chemical deposition system by heating the samples in reducing atmosphere: $\text{NH}_3/\text{Ar} = 1/5$, total flow rate = 60 sccm, pressure = 300 Pa. After reaching a deposition temperature of 680 °C, they were held for 10 min and then CNT synthesis was performed during 2 min. Total pressure of 300 Pa in the $\text{NH}_3/\text{C}_2\text{H}_2 = 3$ mixture flow with a total flow rate of 180 sccm were maintained during the process. The process was activated using a DC discharge with an electrode voltage of 460 V and current of 5 mA, substrates were placed on a graphite cathode 40 mm in diameter. When the carburization stage was enabled in the above-mentioned („base“) process, the sample temperature in the heating phase was fixed at 450 °C for 10 min, during which acetylene was additionally fed into the chamber with a flow rate of 20 sccm. For correct comparison of results of two different processes, the same heat treatment step mode was also reproduced in the base mode (but without acetylene introduction). Surface morphology analysis of the obtained samples was performed via scanning electron



SEM patterns of the samples. *a* — surface of a sample with 3.5 nm NiO layer after Ni reduction (at 450 °C); *b* — the same sample after carburization; *c* and *d* — surface of samples with 1.8 nm NiO layer after CNT deposition without and with carburization, respectively; *e* and *f* — cross-section of samples with 2.4 nm NiO after CNT deposition without and with carburization, respectively. Electron beam orientation with respect to the sample: *a* — normal to the surface; *b–d* — at 45°; *e, f* — normal to the sample cross-section.

microscopy (SEM) using the SUPRA-55VP microscope (Carl Zeiss).

Starting from 300 °C in the sample heating phase in reducing atmosphere, Ni in a thin NiO film is rapidly reduced to the metal [3]. Then the film on the wafer surface is dispersed into individual nanoparticles under the action of surface forces [1]. After heating and holding at 450 °C for 10 min, the dispersed Ni film represents an array of nanoparticles (see Figure *a*) having a diameter up to 20 nm and a height of about 8 nm on average. In the same process, but with introduction of acetylene at the isothermal stage, the height of particles on the sample surface increases severalfold (see Figure *b*). Moreover, they acquire comparable diameter and height (25 nm and 30 nm on average, respectively). A reference silicon wafer sample without NiO remained clean after carburization. Consequently, morphology variation can be caused only by carbon precipitation on the wafer in Ni-containing areas. Surface coking is observed in various reactions of nickel-assisted hydrocarbons [4], indicating that concurrent carbon dissolution occurs in metal followed by carbon precipitation as a separate phase [5]. The process proceeds in concentration gradient conditions with local carbon supersaturation in the solid solution phase. Thus, from carbon precipitations on Ni particles, it can be also expected that Ni itself is saturated with carbon.

After completion of the base CNT deposition mode, various carbon nanostructures occur on the wafer surface. Samples with an initial NiO layer thickness lower than 2 nm feature a growth of array consisting of, widely-spaced nanotubes. At large thicknesses of initial oxide, the grown CNT arrays were denser, indicating fuller utilization of the catalyst. For example, Figure *c* shows a sample with a 1.8 nm initial layer, where the tube length is $0.8 \pm 0.4 \mu\text{m}$, and a diameter was from 10 nm to 50 nm; in Figure *e* for a 2.4 nm initial layer, the tube length is $130 \pm 10 \text{ nm}$ and a diameter is $22 \pm 5 \text{ nm}$. A series of deposition time experiments (from 0.5 min to 10 min for a 2.4 nm NiO layer) showed that a near-limiting height is reached by nanotubes during less than 30 s, which is associated with quick catalyst deactivation. Note that poisoning is inherent in any employed catalysts and CNT growth conditions, and causes of poisoning have not been reliably identified yet [1]. In this case, not all Ni particles become involved and CNT growth gets stopped quickly. The observed low activity of the main proportion of catalyst particles cannot be associated with formation of NiSi_2 on the wafer, though it is a typical cause of loss of catalyst on silicon without barrier layers as early as at insignificant temperatures [1]. However, silicon and metal are not in direct contact in this work. When native silicon oxide is maintained on the wafer — in the $\text{Ni/SiO}_x/\text{Si}$ structure — silicide is not formed during heat treatment up to 700 °C, inclusive [6]. Nevertheless, chemical composition in the metal layer can vary. This was observed in [7] when using a similar CNT deposition procedure and 30 nm thin Ni film. Si-doping of Ni particles through Si input from the native silicon oxide layer was

detected. According to the findings of [7], tube growth was retarded, but did not stop at all specified time step up to 10 min. Dissolved silicon can facilitate catalyst particle poisoning. This results either in retarded growth of CNT as in [7] or to poisoning of many catalyst particles, and to quick stop of the growth of nucleated CNT, which is observed in this work. However, the contribution of such non-controlled doping of nickel to the CNT formation mechanism hasn't been studied yet.

However, the role of catalyst carburization in the following CNT growth was discussed at the next stage. Preliminary carbonization of samples with identical catalyst considerably modifies the morphology of CNT arrays: the length of grown nanotubes increases or the nanotube length and packing density in arrays increase simultaneously. For example, a sample with an initial NiO thickness of 1.8 nm demonstrated a much larger number of used catalyst particles and a threefold increase in the nanotube length (up to $3 \mu\text{m}$; compare fragments *c* and *d* in the figure), while the array already had a much smaller spread of nanotube diameters ($14 \pm 3 \text{ nm}$). For a sample with 2.4 nm oxide, the CNT layer thickness increased 70-fold (to $10 \mu\text{m}$, compare fragments *e* and *f* in the figure), but the tube diameter remained unchanged and was equal to $20 \pm 3 \text{ nm}$, i.e. introduction of an additional stage proves effective. For CNT deposition, activity of catalyst particles produced from NiO was considerably increased.

Study of the observed effect mechanism requires a separate detailed examination using sophisticated procedures. However, the experimental data obtained in the present study and known patterns of formation and breakdown of Ni:C solid solutions in nanosystems allow for a number of conclusions. The pattern of carbon phase distribution on the sample surface (see Figure *b*) indicates catalytic dehydrogenation of acetylene on Ni nanoparticles and coking of Ni nanoparticles — a well known phenomenon in hydrocarbon catalysis [4]. The process is accompanied by carbon atom dissolution in metal followed by breakdown of supersaturated solid solution to form the secondary carbon phase. This phase is prone to precipitate in the form of graphene packages, whose networks of atoms (001) repeat the shape of Ni surface [8], i.e. a mechanism inherent in formation of graphene on nickel during CVD is implemented [9]. When the solid solution is supersaturated, graphene layers in these systems precipitate both on the outside of the Ni thin film and at the wafer interface, Ni/SiO_2 , though to a lesser extent [10]. Studies of catalytic hydrocarbon conversion [11], where the fact of Ni particle „carry-over“ by carbon deposits from the silica support surface was detected, can speak in favor of appearance of such layer between Ni and SiO. If the intermediate layer is also formed during experiments described in this work, then it can reduce the interaction between Ni and wafer (interphase reactions, diffusion loss, non-controlled doping), and this in turn explains higher catalytic activity of catalyst nanoparticles by the time of CNT growth. For example, the Ni/a-C/SiO_2 structure with amorphous carbon interlayer

doesn't show any changes at high temperatures [12], and graphene is considered to be one of reliable barriers for diffusion between Si and metals [13]. It could be noted additionally that to preserve the structure of carburized samples, there shall be no significant phase changes with further heating up to the CNT deposition time (i.e. from 450 to 680 °C). It is known that carbon solubility limit in nickel increases with temperature. However, carbon concentration in solution can easily increase due to make-up from the carbon shell [14]. For stability of Ni nanoparticles, it is important for the barrier part of the carbon layer to dissolve partially. For example, findings of [15] can suggest that the interlayer between Ni and wafer is maintained. At temperatures above 600 °C under a continuous carbon supply from the outer shell of the nickel nanoparticles, the underlying graphene buffer layer is not only maintained, but also expands laterally across the particle-free substrate surface [15]. A sufficiently thick external carbon layer left on Ni after carburization (see Figure b) in synthesis conditions is not able to prevent CNT nucleation for a long time. When plasma with excess ammonia is generated in ammonia-acetylene mixture, plasma-chemical removal of various carbon phases, except for growing CNT, takes place on the wafer surface. Thus, stability of Ni nanoparticles before the start of CNT growth most probably provides a multilayer graphene layer between the wafer and nanoparticles during carburization.

The work proposes and studies an optimized technique for deposition of dense CNT arrays onto Si wafers with Ni catalyst that doesn't use previously formed barrier layers. For stabilization of Ni nanoparticles used as CNT growth catalyst and as an additional control parameter for a CNT array microstructure, a carburization stage is introduced into the CNT array preparation process. The study experimentally investigates physicochemical effects of such operation, and proposes the most probable mechanism of the effects. The described process technique can be implemented on the basis of typical equipment for CVD of carbon nanotubes.

Funding

The study was supported by SPbSU (project code 125021702335-5.)

Conflict of interest

The authors declare that no conflict of interest.

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Translated by E.Ilyinskaya