Arrays of vertically aligned multi-walled carbon nanotubes
grown on silicon and copper substrates by thermal
decomposition of ferrocene-toluene aerosol

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Abstract. Arrays of multi-walled carbon nanotubes (MWCNTs) were grown vertically on the
surfaces of SiO₂/Si substrates using aerosol-assisted catalytic chemical vapour deposition
(CCVD) method. Aerosol was produced by injecting a solution of ferrocene (catalyst source)
in toluene (carbon source) into a hot zone of a horizontal CVD reactor. Dependences of the
height and density of the MWCNT array on the synthesis temperature and ferrocene
concentration were determined. The found optimal parameters were used for the MWCNT
growth on copper substrates. For this purpose, a copper foil was covered by alumina layer and
we showed that the thickness of this layer should be not less than 17 nm to provide the
MWCNT growth over the entire foil surface. The vertically aligned MWCNT array tightly
bonded with copper substrate can be used as a heat-exchange surface in various micro and
nano heat-transfer devices.

1. Introduction
Recently, the great attention of researchers is directed to the study of the influence of nanostructured,
including porous surfaces on heat transfer and development of crisis phenomena at liquid boiling [1].
The heat transfer and critical heat fluxes can be improved by creating on heat exchange surface an
array of ordered, co-directed carbon nanotubes (CNTs) [2]. One of the scalable and inexpensive
methods for the synthesis of CNT arrays vertically oriented relative to the substrate surface is the
aerosol version of catalytic chemical vapor deposition (CCVD) method [3]. The principle of the
synthesis consists in injection of an organic solution of a metal-containing compound into reaction
zone, where the molecules decompose on the substrate with the formation of catalyst particles and
atomic carbon, which is the source of the CNT nucleation and growth [4]. The structure of the CNT
array is determined by the synthesis parameters, particularly, the catalyst concentration, the
temperature and duration of the synthesis, the carrier gas flow rate, which are optimized for the
selected precursor compounds and depend on the design of the CVD reactor [5].

The most popular substrate for vertical growth of the CNTs is silicon covered by thin oxide layer.
This kind of substrates, however, has disadvantages for the thermal interface materials because of
fragility, low conductivity, and comparatively high thickness and weight. Copper could be a perfect component for the CNTs as a heat collector and the problem to use it in the CCVD process is a diffusion of catalyst iron into the bulk of Cu substrate at high temperatures [6]. This limits the growth of the CNTs on Cu surfaces [7]. Deposition of buffer layer on Cu substrate can prevent the catalyst diffusion, while the structure and composition of this layer may influence the alignment of CNTs in the array [6, 7].

In the present work we find dependencies of the height and density of the arrays of multi-walled CNTs (MWCNTs), produced by thermal decomposition of aerosol, consisting of a mixture of ferrocene and toluene, on the synthesis temperature and the ferrocene fraction. The found optimal parameters are used for the CCVD growth of MWCNTs on pure copper foil and the foil coated by alumina buffer layer. We determine the thickness of this layer necessary for vertical alignment of the MWCNTs.

2. Experimental section
Scheme of horizontal tubular setup used for aerosol-assisted CCVD synthesis is shown on figure 1. The setup is made of stainless steel 800 mm in length and 36 mm in diameter. A removable quartz reactor is inserted into the inner cavity of this tube. The reactor is connected with an input block consisting of an injection device and channels for different gases. With the help of a manipulator, substrates are placed in the central part of the reactor. After that the reactor is hermetically sealed, pumped out, filled with argon to atmospheric pressure, and heated to the synthesis temperature by an electric furnace. A solution of ferrocene in toluene is injected into the reactor at a rate of 0.25 mL/min. The vapors of the reaction mixture are carried to the substrates by argon flow at a rate of 600 mL/min. This rate allows maintain the thickness of the array within ~5% on a substrate with an area of 1 cm². The substrates were cut from n-doped silicon wafer with a crystal orientation [100] or electrolytic copper foil 35 µm thick.

3. Result and Discussion
3.1. Growth of MWCNT arrays on silicon substrates
At first, we optimized the parameters of CCVD growth of MWCNT arrays on silicon substrates having a naturally formed thin oxide surface layer. One of the important parameters is temperature, which influences decomposition of toluene molecules on the catalyst surface, solubility and diffusion of carbon species in iron nanoparticle. The experiments were carried out decomposing the toluene containing 2 wt. % of ferrocene at a temperature varied from 700 to 900°C with a step of 50°C. The volume of injected reaction mixture was 10 mL. An average thickness of an array was determined from scanning electron microscopy (SEM) images obtained on a Hitachi S–3400 N microscope.

![Figure 1. Scheme of setup for aerosol-assisted CCVD growth of CNTs on substrates.](image-url)
Figure 2a shows that the array thickness has a nonlinear dependence on the synthesis temperature. At a given concentration of ferrocene in the reaction mixture, the thicker array is produced at 800°C.

Side-view SEM image of an array grown at 800°C is presented in figure 2b. This array has a thickness of about 680 µm and the nanotubes are vertically oriented relative to the surface of silicon substrate.

In the aerosol version of the CCVD synthesis, the formation of catalyst occurs in situ as a result of the decomposition of ferrocene. Hence, the density of catalytic nanoparticles on the substrate surface can be controlled by changing the concentration of ferrocene in toluene. To study the effect of this parameter on the structure of the MW CNT array, a set of experiments was done. The array thickness was examined depending on the ferrocene concentration varied from 0.25 to 2 wt. %. The density was determined for arrays produced with a ferrocene content in toluene growing from 1 to 5 wt. %. All syntheses were carried out at 800°C, the volume of the reaction mixture was 5 mL.

Figure 3a shows the dependence of average array thickness on the ferrocene concentration in feedstock. At a concentration less than 0.75 wt. %, a sharp decrease in the thickness of the MW CNT array occurs. In addition, the lack of iron species for the formation of catalyst nanoparticles with the size necessary the CNT nucleation leads to appearance of a layer of amorphous carbon on the surface of the array.

Figure 2. Dependence of the thickness of MWCNT array on the synthesis temperature (a). SEM side-view image of MWCNTs vertically grown on silicon substrate (b).

Figure 3. Dependence of the thickness (a) and the density (b) of MWCNT array on the concentration of ferrocene in toluene. Array density is calculated with and without accounting the iron content in samples.
The density of the MWCNT in an array was calculated by dividing the weight of the array to its volume. The former value was obtained from the difference in substrate weights before and after the synthesis, the latter value was estimated, knowing the area of the substrate coated with the MWCNTs and the thickness of the array. The calculated density of the MWCNT array has a linear dependence on the ferrocene concentration (figure 3b). This could be associated with an increase of number of the catalytic centers on the substrate. However, the iron remaining in the array after the synthesis contributes to the weight of the sample. The amount of iron was determined by atomic absorption spectroscopy (AAS) on a Hitachi Z–800 spectrometer. The data obtained (table 1) show that the iron content in the sample always exceeds the content of ferrocene in the reaction mixture. Taking into account the iron content in the sample results in slightly smaller values of the density of the MWCNT array (figure 3b).

### Table 1. Iron content in MWCNT samples synthesized at different ferrocene concentrations in toluene, determined by AAS method.

| Ferrocene, wt.% | 1  | 2  | 3  | 4  | 5  |
|-----------------|----|----|----|----|----|
| Iron, wt. %     | 2.3| 2.9| 3.3| 6.9| 7.5|

The density of the MWCNT in an array was calculated by dividing the weight of the array to its volume. The former value was obtained from the difference in substrate weights before and after the synthesis, the latter value was estimated, knowing the area of the substrate coated with the MWCNTs and the thickness of the array. The calculated density of the MWCNT array has a linear dependence on the ferrocene concentration (figure 3b). This could be associated with an increase of number of the catalytic centers on the substrate. However, the iron remaining in the array after the synthesis contributes to the weight of the sample. The amount of iron was determined by atomic absorption spectroscopy (AAS) on a Hitachi Z–800 spectrometer. The data obtained (table 1) show that the iron content in the sample always exceeds the content of ferrocene in the reaction mixture. Taking into account the iron content in the sample results in slightly smaller values of the density of the MWCNT array (figure 3b).

#### 3.2. Growth of MWCNT arrays on copper substrates

The optimal parameters for the CCVD growth of MWCNT array, particularly, the temperature of 800°C and the ferrocene concentration in toluene of 2 wt. % were used for the syntheses using copper substrates. The experiments showed that the pure Cu is not suitable for the CNT growth. SEM images detected formation of rare deposits from the tangled MWCNTs (figure 4a). A dissolution of iron in copper at high temperatures hinders formation of catalyst centers needed for nanotube nucleation and growth. To prevent this process, the copper foils were covered by thin alumina layers, 12 and 17 nm thick, using atomic layer deposition (ALD) technique.

Figures 4b and 4c show SEM images of the substrate surface after the CCVD procedure. On the substrate with a 12-nm-alumina coating, the bundles of MWCNTs with a characteristic size of about 30 µm have grew (figure 4b). These bundles are separated from each other by rather large nanotube-free areas. The MWCNTs constituting perimeter of a bundle lose the alignment with the central MWCNTs because of the absence of neighbors at the periphery. The fact that the MWCNTs did not grow on the entire substrate indicates diffusion of part of the catalytic iron through the 12-nm-thick alumina. This process is strongly limited when the alumina coating has a thickness of 17 nm. Such coating provides uniform growth of MWCNT array on the copper substrate (figure 4c). SEM image of the MWCNTs at an array crack (insert in figure 4c) demonstrates their vertical alignment relative to the substrate surface.

![Figure 4. SEM images of MWCNTs grown on pure copper foil (a) and copper foil covered by 12-nm alumina layer (b) and 17-nm alumina layer (c). The insert shows that arrays consist of well-aligned MWCNTs.](image-url)
4. Conclusion
The aerosol-assisted CCVD method allows growing arrays of MWCNTs vertically aligned to the substrate surface. Silicon with thin, naturally formed oxide surface layer is a perfect substrate for the array formation. The height of array can vary from few tens to hundreds of microns by change of the synthesis temperature, amount of a reaction mixture injected into reactor, and fraction of catalyst source in the mixture. For the reaction mixture consisting of toluene and ferrocene, the greatest height of the array is reached at the synthesis temperature of 800°C. The density of the MWCNTs in array varies between about 0.105 and 0.135 g/cm$^3$ when the ferrocene concentration in toluene increases from 1 to 5 wt. %. Experiments on the MWCNT growth on copper foil reveal the necessity of surface buffer layer for preventing the diffusion of iron catalyst into copper bulk. We showed that in our synthesis conditions, 17-nm alumina layer is sufficient for the growth of well-aligned and density-packed MWCNTs vertically to the copper surface.

Acknowledgments
We are grateful to Dr. M A Kanygin for the SEM images. The work was financially supported by the Complex Program of Basic Research SB RAS “Interdisciplinary Joint Investigations” (project No. 23, theme AAAA-A18-118022090033-1). A G Kurenya thanks the Russian Foundation of Basic Research (grant No. 18-33-01088).

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