NANOSYSTEMS: PHYSICS, CHEMISTRY, MATHEMATICS, 2014, 5 (1), P. 172–177

# SECONDARY NUCLEATION ON NANOSTRUCTURED CARBON FILMS IN THE PLASMA OF DIRECT CURRENT GLOW DISCHARGE

K. V. Mironovich[1], V. A. Krivchenko[1], P. V. Voronin[1], S. A. Evlashin[1]

[1] Skobeltsyn Institute of Nuclear Physics, Lomonosov Moscow State University,
Moscow, Russia

mironbasket@mail.ru

**PACS 68.55.A-**

The high specific surface area of carbon nanowalls (CNWs) makes them an attractive catalyst support material or electrode material for energy storage devices (e.g. supercapacitors, Li-ion batteries). Secondary nucleation processes (formation of secondary nanowalls on the surface of pre-grown primary structures) play an important role in CNWs growth. It can significantly increase CNW film surface area, but at the same time be a limiting step for the production of films with an open pore structure. Both of these factors may be important for the applications mentioned above. In this work, we discuss possible mechanisms of secondary nucleation during CNW growth in the plasma of a direct current glow discharge. We also demonstrate a novel multi-step synthesis process with controllable secondary nucleation rates at different stages, which is an effective way to modulate CNW film morphology and produce films with desirable surface area and porosity.

**Keywords:** Carbon nanowalls, PECVD, Synthesis, Secondary nucleation, Morphology, Surface area.

## 1. Introduction

Carbon nanowall (CNW) films consist of graphite sheets standing almost vertically on the substrate and forming self-supported network of wall structures. Their unique structural properties such as high specific surface area and high aspect ratio make them useful for a number of different applications such as electrochemical devices (e.g. supercapasitors, Li-ion batteries [1]), catalyst support [2], and field emitters [3]. The potential use of CNWs in applications demands the ability to produce films with adjusted morphological properties, and this requires an understanding of their growth mechanisms. The most popular method for CNWs synthesis is chemical vapor deposition (CVD) in hydrocarbon-containing plasma of MW, RF, or DC discharge [4].

In this work, we continue our investigation of CNWs growth in the plasma of a DC glow discharge on substrates placed at the anode. Previously, we demonstrated that the distinctive feature of this method is the possible catalyst-free nucleation of conic-shaped carbon nanotubes (CNTs) upon CNWs and additionally, we proposed phenomenological models for CNWs and CNTs nucleation and growth [5]. Here, we focus our attention on the secondary nucleation (SN) process that forms secondary nanowalls (SCNWs) on the surface of pre-grown primary structures. This plays an important role in CNWs growth and can significantly increase CNW film surface area but at the same time it can be a limiting step for producing films with open pore structure. Both these factors may be important for electrochemical and catalyst support applications. We discuss possible mechanisms of

SN during CNWs growth in the plasma of a DC glow discharge. We also demonstrate a novel multi-step synthesis process with controllable SN rates at different stages, which is an effective way to modulate CNW film morphology and produce films with desirable surface area and porosity.

## 2. Experimental

CNWs were synthesized via DC plasma enhanced CVD in a mixture of methane and hydrogen. Polished *p*-doped 400 $\mu$m thick Si (100) wafers with an area of 1 cm$^2$, were used as substrates and placed at the anode. Si wafers were previously ultrasonically treated in a diamond powder suspension for 5 min to assist the carbon film nucleation, then washed in distilled water and dried. Gas supply was realized with mass flow controllers, methane and hydrogen flow ratio defined their relative concentrations in gas mixture. Discharge current was controlled by a DC generator. Temperature was measured with a thermocouple connected to the bottom of Mo substrate holder. Typical experimental conditions were as follows: methane concentration 8–15%, hydrogen flow 10 l/h, pressure 150 Torr, discharge voltage and current 670 V and 0.6–0.9 A, respectively, and substrate holder temperature 680–800 °C (note that temperature of the substrate top surface was 150–200 °C higher). The duration of CNWs deposition was varied in from 20–35 min. After deposition, samples were studied by means of SEM (Carl Zeiss Supra 40 system) and Raman spectroscopy (Renishaw InVia).

## 3. Results and discussion

Fig. 1 (a) shows a typical CNW film, grown using the process described above at 700 °C. The Raman spectrum of such a film (Fig. 2 (a)) presents three well-distinguished peaks at 1350 cm$^{-1}$, 1575 cm$^{-1}$ and 2700 cm$^{-1}$ (D-, G- and 2D-mode, respectively) and is typical for graphite materials. The ratio of the D and G mode intensities is usually used to evaluate film crystallinity. A typical I(D)/I(G) value was 0.6, revealing a sufficient number of defects in the CNWs structure. The shape and FWHM of the 2D mode doesn't depend on the presence of defects and is related to the number of graphene layers and their stacking order in the graphite structure. Analyzing the data presented in previous literature [6], we conclude that our CNWs consist of 10–15 graphene layers stacked in a turbostratic (disordered) manner. Previously, we suggested phenomenological model for CNWs nucleation and growth which considered nucleation of CNWs as a result of overlapping of horizontal graphite layers formed on the substrate surface at the early stage of growth [5]. Once nucleated, CNWs grow due to direct attachment of neutral hydrocarbon radicals to active sites at the edge of the CNW via hydrogen abstraction reactions.

Synthesis at higher temperature (800 °C) is accompanied by catalyst-free growth of conical CNTs upon CNWs top edges (Fig. 1 (b)). Previously we showed that probable mechanism of their nucleation is folding of CNWs under high temperature in the presence of structural defects while their subsequent growth is mostly due to surface diffusion of hydrocarbon radicals from the bottom to the tip of the CNT [5]. Formation of such CNTs is a distinctive feature of DC PECVD synthesis probably due to absence of substrate bombardment by positive ions during growth. It should also be noted that higher temperature synthesis leads to the formation of less defective CNWs, as was confirmed by Raman spectroscopy analysis (I(D)/I(G) $\sim$ 0.25).

Synthesis under the experimental conditions in a certain range led to the formation of films described above (Fig. 1 a, b). Increasing the methane concentration or synthesis duration induced a SN process that forms secondary nanowalls (SCNWs) on the surface of

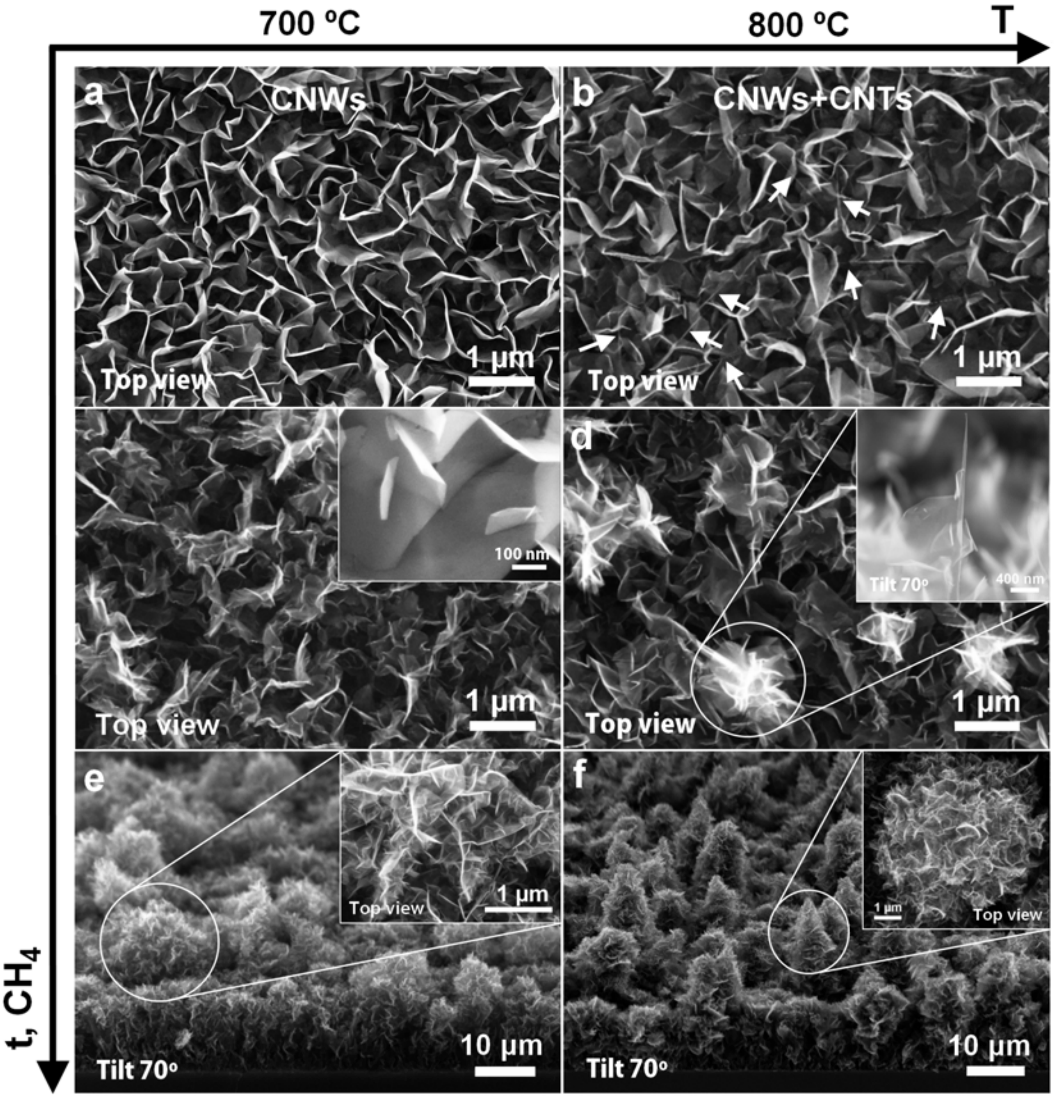

Fig. 1. CNW films obtained at different temperature, methane concentration and duration. White arrows mark CNTs

pre-grown primary structures. In the case of low temperature synthesis, SCNWs nucleated on the side surface of primary CNWs (Fig. 1 (c)) while at high temperatures, intense secondary nucleation took place at CNTs surface (Fig. 1 (d)). Further increasing of the duration or methane concentration led to the formation of globule-like clusters of SCNWs. At higher temperatures, these clusters grew in form of cones around primary CNTs (Fig. 1 (f)), while they had no definite shape in the absence of CNTs at lower temperatures (Fig. 1 (e)).

The probable mechanism of SN is as follows. As was mentioned above in our synthetic method, the role of building blocks is played by neutral hydrocarbon radicals. These radicals can be incorporated into the graphite lattice at a CNW edge, providing linear growth or be attached to defects on the CNW side surface. With increased radical density or duration, more radicals are attached to surface defects, forming additional graphene layers that broaden, overlap and give birth to SCNWs, just like nucleation of primary CNWs takes place on the substrate (Fig. 2 b, c). In addition, as was mentioned previously, CNWs obtained at lower temperatures have more defects, which increases the intensity of SN on their surface.

The SN process inevitably starts after some time, and there is no definite moment of its beginning, it gradually becomes more intense with CNWs growth. SN can significantly increase the CNW film surface area, but at the same time, it can be a limiting step for producing films with open pore structure. Both these factors may be important for electrochemical and catalyst support applications.

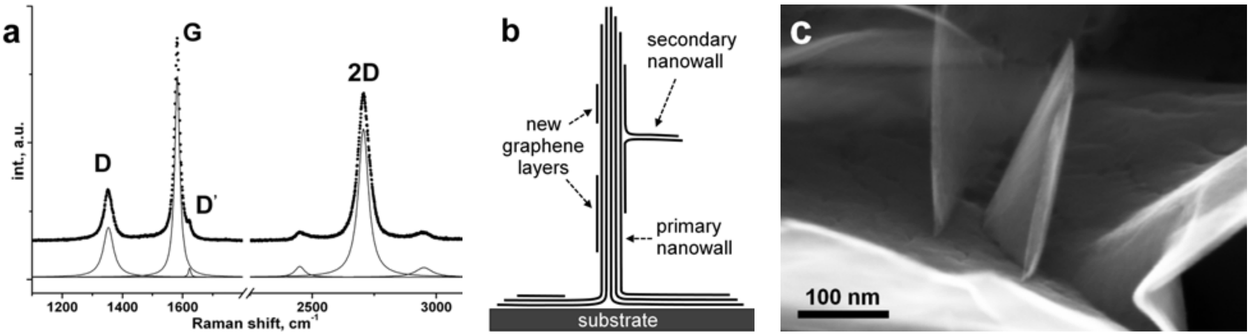

FIG. 2. (a) Typical Raman spectrum of obtained CNW films. (b) Schematic illustration of SN mechanism (c) SCNW on the surface of primary CNW

However, a controllable SN process gives one the opportunity to obtain films with a number of new morphologies. For this purpose, we suggest synthesizing CNWs in a multi-step process. In the first stage, deposition takes place under conditions that we call standard, leading to the formation of CNWs of certain size, before the beginning of SN process. At a certain time, the discharge conditions are abruptly changed (e.g. discharge current is increased), triggering an intense SN process. At this stage, prolonged growth of primary CNWs is accompanied by SCNWs nucleation and growth. It should be noted that the temperature at the first stage should be low enough to provide sufficient number of surface defects.

By varying the duration of each stage, it is possible to obtain films with an adjusted (in some range) size of primary and secondary CNWs and amount of the latter. The first column in Fig. 3 shows the CNWs obtained at 20, 25 and 30 minutes under standard conditions (150 Torr, relative methane concentration 10%, discharge current and voltage 0.6 A and 695 V, respectively at 680 °C). CNWs width and height increased proportionally with time (see inset). The other three columns demonstrate films obtained in different multi-step processes with SN initiated by an increase in the discharge current from 0.6 to 0.9 A (times of current change are depicted in the plots above the columns).

Fig. 3 (h) shows the film obtained after 20 minutes of standard growth followed by 5 minutes of high current regime. The primary vertical CNWs are covered with small SCNWs, while their width is almost the same as in the case of 25 minutes of standard synthesis without SN (Fig. 3 (b)). Similarly, the width of primary CNWs obtained in a process with a current increase after 25 minutes of standard growth (Fig. 3 (f)) corresponds to that of CNWs grown in standard process of the same total duration (Fig. 3 (c)). The amount of SCNWs and their size are higher than in the previously described film (Fig. 3 (h)), although the duration of the second stage was the same. This is due to the larger primary CNWs grown by the end of the first stage, in this case (see Fig. 3 (e)), in comparison to that of the film shown in Fig. 3 (h) (see Fig. 3 (g)), which implies more surface defects and thus, a more intense SN process.

Fig. 3 (i) shows the film obtained via the prolonged SN process, that led to an increase in the size and number of SCNWs, which in turn acted as a surface for nucleation

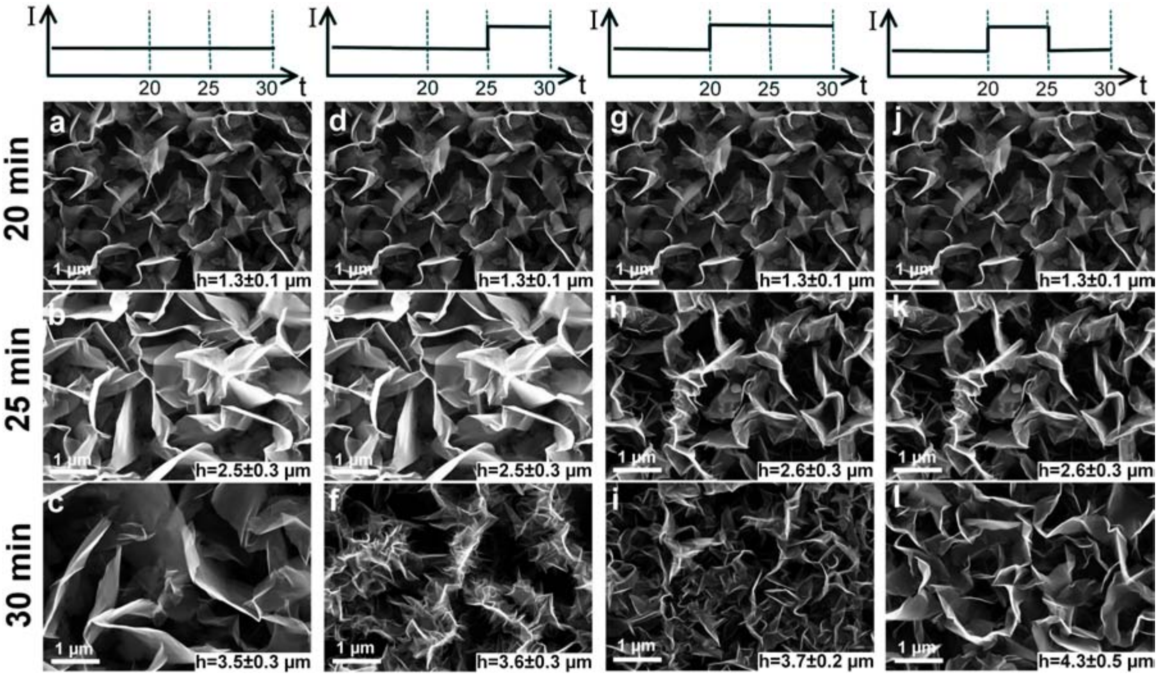

FIG. 3. CNW films obtained in different multi-step processes. Plots above denote times of current change. The right bottom corner of each image displays the height of the corresponding film

of tertiary CNWs and so on. This led to the formation of a densely branched network of CNWs, where the primary CNWs can't be identified. This film has considerably smaller pores in comparison to that of the film obtained in standard process of the same duration, while their heights are almost identical.

Fig. 3 (l) shows the film obtained in a three-step process. For the first 20 minutes, it grew under standard conditions (Fig. 3 (j)), then, the current was increased for 5 minutes, triggering a SN process (Fig. 3 (k)). For the last 5 minutes, current was decreased back to the initial value in order to suppress the SN process, thus only the primary and secondary CNWs present continued to grow without any change in number of the latter. This led to formation of CNW network with medium pore sizes in comparison to films c and i.

It should also be noted once more that the heights of all films presented in Fig. 3 depend only on the total process duration and were almost independent of the process type (within the error range). Thus, multi-step growth is a way to control film morphology without changing its height while these parameters are interrelated during conventional growth.

## Acknowledgements

This work was financially supported by grant MK-2773.2014.2.

## References

[1] V.A. Krivchenko, D.M. Itkis, S.A. Evlashin, D.A. Semenenko, E.A. Goodilin, A.T. Rakhimov, A.S. Stepanov, N.V. Suetin, A.A. Pilevsky, P.V. Voronin. Carbon nanowalls decorated with silicon for lithium-ion batteries. *Carbon*, **50**, P. 1438–1442 (2012).

[2] B.I. Podlovchenko, V.A. Krivchenko, Yu.M. Maksimov, T.D. Gladysheva, L.V. Yashina, S.A. Evlashin, A.A. Pilevsky. Specific features of the formation of Pt(Cu) catalysts by galvanic displacement with carbon nanowalls used as support. *Electrochimica Acta*, **76**, P. 137–144 (2012).

[3] V.A. Krivchenko, A.A. Pilevsky, A.T. Rakhimov, B.V. Seleznev, N. V. Suetin, M.A. Timofeyev, A.V. Bespalov, O.L. Golikova. Nanocrystalline graphite: promising material for high current field emission cathodes. *J. Appl. Phys.*, **107**, P. 014315 (2010).

[4] M. Hiramatsu, M. Hori. *Carbon Nanowalls, Synthesis and Emerging Applications.* Springer, Wien-NewYork, 161 p (2000).

[5] V.A. Krivchenko, V.V. Dvorkin, N.N. Dzbanovsky, M.A. Timofeyev, A.S. Stepanov, A.T. Rakhimov, N.V. Suetin, O.Yu. Vilkov, L.V. Yashina. Evolution of carbon film structure during its catalyst-free growth in the plasma of direct current glow discharge. *Carbon*, **50**, P. 1477–1487 (2012).

[6] D.S. Lee, C. Riedl, B. Krauss, K. Klitzing, U. Starke, J.H. Smet. Raman spectra of epitaxial grapheme on SiC and of epitaxial graphene transferred to $SiO_2$. *Nano Lett.*, **8**(12), P. 4320–4325 (2008).