Fabrication of carbon nanowalls by radio frequency magnetron sputtering of graphite target in argon plasma

S A Grudinkin and A Ya Vinogradov
Ioffe Institute, 26 Polytekhnicheskaya, St Petersburg, 194021, Russia

E-mail: grudink.gvg@mail.ioffe.ru

Abstract. Vertical carbon nanowalls have been fabricated by RF magnetron sputtering of a graphite target in an argon plasma without hydrogen presence. The effect of deposition parameters such as substrate temperature, argon pressure, deposition time and RF power on the morphology and the structure of carbon nanowalls was investigated by using Raman spectroscopy and atomic force microscopy. The argon ion bombardment of the substrate is crucial for the nucleation and growth of carbon nanowalls. A specific range of RF power and argon pressure values was established at which nanowalls formation is possible. The height of nanowalls produced at minimal RF power increases non-monotonically with the deposition time. It turned out that the nanowalls growth rate has an extremum, after reaching which the growth rate of the thickness of nanowalls increases.

1. Introduction
Carbon nanowall (CNW) is a two-dimensional carbon structure composed of stacks of planar graphene sheets standing almost vertically on the substrate [1, 2]. CNW film on a substrate forms a three-dimensional structure with a high surface-to-volume ratio, high aspect ratio vertically oriented graphene sheets, a high density of atomic-scale graphene edges [2]. Due to their inherent properties, CNWs are among promising material for applications in field emission sources, templates for fabricating a variety of nanostructures, supercapacitors with improved performance, electrochemical biosensors, solar cells [1-4]. The CNWs are synthesized by chemical vapor deposition method [2, 5]. In the most works, a mixture of the gaseous hydrocarbons and hydrogen is used to produce CNWs. The role of atomic hydrogen is to etch amorphous carbon and to prevent formation of additional graphene layers by etching weakly bounded carbon atoms [2, 6].

In a number of works, during the deposition of CNWs, Ar was added to the gas mixture to enhance formation of critical species for nanowalls growth, to improve the plasma stability and allow to reduce the deposition temperature [5, 7]. CNWs are most frequently synthesized using a mixture of CH\textsubscript{4} with H\textsubscript{2} and Ar [5]. The formation of H atoms in the gas phase also occurs due to the dissociation of hydrocarbons.

The possibility of obtaining CNWs by methods in which H\textsubscript{2} is completely absent in the gas phase, for example by RF magnetron sputtering of graphite target in Ar plasma, was demonstrated in [3, 8]. The addition of CH\textsubscript{4} is unnecessary for the growth of CNWs by RF sputtering [8]. There are few studies on the CNWs growth without the presence of H\textsubscript{2}. The investigation of the features of magnetron deposition of CNWs in argon is of considerable interest, both from a practical point of view and for understanding the mechanism of formation of CNWs.
In the present paper CNW films were fabricated by RF magnetron sputtering of a graphite target in Ar plasma without H$_2$ presence. We studied the influence of the deposition parameters on morphology and structure of CNW films.

2. Experimental
The films were deposited by RF (13.56 MHz) magnetron sputtering using target of graphite 6516pT (Mersen, France) in Ar plasma. The substrate was grounded. Tungsten filaments were used to heat substrate holder. The substrate temperature was controlled by chromel-alumel thermocouple mounted inside the substrate holder. Preliminary the substrate surface temperature calibration was performed using additional thermocouple in direct contact with the substrate surface. Polished crystalline silicon (100) wafers were used as substrate. A catalyst was not applied to stimulate the nucleation. Substrate temperature ($T_s$), argon pressure ($P$), RF power ($W$) and deposition time ($t$) were variable parameters in this research. The deposition parameters are listed in table 1.

| Sample # | $T_s$ (°C) | $P$ (mTorr) | $W$ (W) | $t$ (min) |
|----------|------------|-------------|---------|-----------|
| 1        | 400        | 20          | 30      | 50        |
| 2        | 500        | 20          | 30      | 50        |
| 3        | 600        | 20          | 30      | 50        |
| 4        | 600        | 20          | 30      | 36        |
| 5        | 600        | 20          | 30      | 60        |
| 6        | 600        | 20          | 30      | 85        |
| 7        | 600        | 50          | 30      | 50        |
| 8        | 600        | 20          | 65      | 14        |
| 9        | 600        | 20          | 100     | 10        |
| 10       | 600        | 20          | 160     | 10        |
| 11       | 600        | 5           | 100     | 40        |
| 12       | 600        | 5           | 190     | 40        |
| 13       | 600        | 5           | 190     | 120       |
| 14       | 600        | 5           | 190     | 13        |

Matching of the impedances of the generator and the magnetron block influences on energy and flux of ion bombarding of the electrodes (both target and substrate). The values of the RF power given in the article were determined as the difference between the incident and reflected powers, i.e. power absorbed by plasma particles. Reflected power values were maintained ≤1 % of incident power in order to provide reproducibility of the deposition processes.

Raman spectroscopy was used to determine the structure of films with a Horiba Jobin Yvon LabRam HR800 spectrometer.

The film morphology and thickness were examined by atomic force microscope (AFM) Smena NT-MDT in the tapping mode. The film thickness was determined by measuring the profile of the step between the surface of the film and scratch to the surface of the substrate [9]. We accept that the CNWs height is equivalent to the film thickness.

3. Results and discussion
$T_s$, $P$, $W$ and $t$ were found to be key deposition parameters influenced on the films morphology.
Figure 1. Raman spectra of the films prepared at different substrate temperatures and the results of deconvolution of the spectra into components.

Table 2. Results of Raman spectra deconvolution.

| T<sub>s</sub> (°C) | Position of G band (cm<sup>-1</sup>) | Width of G band (cm<sup>-1</sup>) | Position of D band (cm<sup>-1</sup>) | I<sub>D</sub>/I<sub>G</sub> |
|------------------|-----------------------------------|---------------------------------|---------------------------------|------------------|
| 400              | 1608                              | 44                              | 1342                            | 1.91             |
| 500              | 1593                              | 47                              | 1354                            | 2.9              |
| 600              | 1590                              | 39                              | 1353                            | 2.25             |

Figure 1 demonstrates the Raman spectra of the films #1-3 obtained at T<sub>s</sub>=400 °C, 500 °C and 600 °C. The Raman spectra show the G band (1580-1610 cm<sup>-1</sup>), the D band (1340-1350 cm<sup>-1</sup>), the D'' band (~1250 cm<sup>-1</sup>), the D' band (~1620 cm<sup>-1</sup>) and the band at ~1500 cm<sup>-1</sup> assigned to the presence of amorphous carbon. The G band is a doubly-degenerate in-plane sp<sup>2</sup>C–C stretching mode (E<sub>2g</sub> symmetry) at the Brillouin zone centre [10]. The most intensive D band originate from a second-order process, involving an iTO phonon around the K-point and one defect [10]. The D' band, which can be observed as shoulder on the G band, corresponds to a graphitic lattice mode with E<sub>2g</sub> symmetry. The D' band requires the presence of a defect of sp<sup>2</sup>-hybridized crystal structure for the momentum conservation [11]. The D'' band in the region of 1250 cm<sup>-1</sup> is attributed to scattering with the participation of a crystal-lattice defect. Raman spectra were deconvoluted in the range of 1000–1800 cm<sup>-1</sup> into five Lorentzian bands by curve fitting. As the substrate temperature decreases, G and D bands exhibit a shift to higher frequencies because of increasing disorder in graphene nanosheets [12]. The presence of the D and the D' bands in Raman spectra suggests nanocrystalline graphite structure for the films obtained at T<sub>s</sub>=500 °C and T<sub>s</sub>=600 °C [12]. The maximum of the G band at ~1608 cm<sup>-1</sup> and the D band at ~1342 cm<sup>-1</sup> indicate amorphous structure of the film obtained at T<sub>s</sub>=400 °C [12].

For crystalline graphite structures the ratio I<sub>D</sub>/I<sub>G</sub> is inversely proportional to in plane sp<sup>2</sup> crystallite size [12]. This dependence is valid only for films produced at T<sub>s</sub>=500 °C and T<sub>s</sub>=600 °C. For these films the ratio I<sub>D</sub>/I<sub>G</sub> decreases with increasing disorder. The film obtained at T<sub>s</sub>=600 °C has the larger value of in plane sp<sup>2</sup> crystallite size (see table 2). The higher T<sub>s</sub> was favourable for improving the crystallinity of graphene structures. To study the effect of W, P and t on the morphology of the films the deposition processes were carried out at a fixed T<sub>s</sub>=600 °C.

As it will be shown below the films morphology substantially depends on P, W and t. Raman spectra of the CNW films deposited at T<sub>s</sub>=600 °C and different P, W and t did not have noticeable difference. It can be assumed that these films had similar structure and phase composition.
Figure 2. AFM images of the films deposited at P=20 mTorr, W=30 W and different substrate temperature: (a) - sample #1 – 400 °C, (b) - #2 – 500 °C, (c) - #3 – 600 °C. The films thickness is about 140 nm.

Figure 3. AFM images of the films deposited at T_s=600 °C, P=20 mTorr, W=30 W and different deposition time: (a) - sample #4 (36 min), (b) - #3 (50 min), (c) - #5 (60 min), (d) - #6 (85 min).

Figure 4. Dependencies of the films thickness on deposition time at T_s=600 °C, P=20 mTorr. The sample numbers are marked on the curves.

It was found that CNWs were obtained at T_s≥500 °C (figure 2(b, c)) and were not formed at T_s≤400 °C.

The change in the morphology of the films during deposition at T_s=600 °C, P=20 mTorr, W=30 W (samples # 3 - 6) can be traced according to figure 3. At the first stage from the beginning to about 40 min nanoislands with size in the range of 10 – 50 nm are formed. The nanoislands act as nucleation sites for CNWs. With the formation of the nucleation sites CNWs start to grow (figure 3(a)). In the
time interval 45-55 min the height of the CNW increases and the average spacing between adjacent CNWs practically doesn’t change. The height of ~150 nm and the thickness of ~20 nm of the CNWs were estimated from figure 3(b). CNWs with minimal thickness ~20 nm and maximal height ~300 nm were produced in 55 min. The radius of the AFM tip is ~20 nm, that can be the reason of surface feature broadening. In the time interval 55-75 min the thickness of CNWs increases (figure 3(c)) until the CNWs completely merge into a continuous film (figure 3(d)). The height and the thickness of the CNWs are ~350 nm and ~200 nm, respectively (figure 3(c)).

It can be seen in figure 4 that the film deposition at W=30 W (samples # 3 – 6) is characterized by a nonlinear dependence of the film thickness on the deposition time in contrast to the regimes with higher W (samples #8 and #11). In addition, the stages of the film deposition considered above occur at different growth rates – minimal rate during islands formation, maximal rate during CNWs growth and intermediate rate of growth when CNWs merge into a continuous film.

It was found in [13] that ion energy and flux depend on RF power. Also an increase of Ar pressure increases the scattering of ions and as a result reduces their energy and flow. The values of P and W affect the growth rate and the morphology of the films. The films #7 and #8 are composed of CNWs but their thicknesses are larger compared to the CNWs thickness of film #3. At lower P (5 mTorr) and higher W (190 W) (films #12-14) the islands formed at the initial stage coalescence into a continuous film without formation of CNWs (figure 5).

The Ar ion bombardment of the substrate is crucial for the growth of CNWs. In the initial stages of growth, the Ar ion irradiation stimulate the formation of nucleation sites for CNWs growth [14]. However, the bombardment by high-energy Ar ions at high power and low pressure (samples # 11-14) leads to etching that results in CNWs growth inhibition [14]. Also at high power when the Ar ion flux is too large, the deposition rate of carbons becomes higher, and then amorphous carbon films would be formed [14]. Note that we were unable to synthesize the CNWs by DC magnetron sputtering of a graphite target in Ar plasma but only graphite-like films [9]. Apparently, it is due to lack of Ar ions bombardment of the substrate in DC magnetron sputtering process.

The increase in the height of the CNWs occurs due to the processes of adsorption of carbon atoms on its surface, moving carbon atoms along the graphene sheets and bonding of carbon atoms to the edge of graphene sheets before being re-evaporated. With an increase in the deposition time, the height of the CNWs increases. As a result, the diffusion length of carbon atoms along the CNW becomes comparable with its size [15]. Then the adsorbed carbon atoms moving along the surface of CNW without reaching its edge form secondary nucleation centres that facilitate the growth of new graphene sheets. As a result, an experimentally observed decrease in the growth rate of the CNWs and an increase in their thickness occur.

The reasons for the evolution of the morphology of films can also be considered in the framework of the theory of crystal growth. The observed increase in the thickness of the CNWs is realized by the the mechanism of layer-by-layer growth. The condition for the beginning of layer-by-layer growth is
the formation of a two-dimensional nucleus with a size of more than four times smaller than the linear size of graphene sheet [16]. Otherwise, the given mechanism cannot take place. In our case, this condition is satisfied when the size of the CNWs height is in the range of 300-400 nm.

4. Conclusions
Carbon nanowall films were obtained by the RF magnetron sputtering of a graphite target in argon plasma. A feature of the deposition process was the absence of hydrogen in gas phase. The formation of the CNWs occurs at substrate temperatures of more than 500 °C. The Ar ion bombardment of the substrate is a key factor of the formation and growth of the CNWs. The range of Ar pressures and RF powers was determined at which carbon nanowalls are formed. CNWs of a minimum thickness of ~20 nm and a maximum height of ~300 nm are obtained at a substrate temperature of 600 °C, low argon pressure and RF power (20 mTorr and 30 W in this research). It was found that the growth rate of films obtained at RF power of 30 W varies with deposition time. The film growth rate is maximal at the time interval at which the fastest height nanowalls rate occurs. A decrease in the growth rate is accompanied by a noticeable increase in the thickness of the CNWs, up to their merging. The increase in carbon nanowalls thickness is due to the process of secondary nucleation, the possible mechanisms of which was discussed in the work. Dependence of the film morphology on substrate temperature, Ar pressure, RF power and deposition time should be taken into account to develop a process map of vertical carbon nanowalls fabrication.

Acknowledgments
The work was financed in the framework of the state budget agreement (0040-2019-0012)

References
[1] Santhosh N M, Filipič G, Tatarova E, Baranov O, Kondo H, Sekine M, Hori M, Ostrikov K K and Cvelbar U 2018 Micromachines 9 565A
[2] Hiramatsu M and Hori M 2010 Carbon nanowalls: synthesis and emerging applications (Springer Science & Business Media)
[3] Guzmán-Olivos F, Espinoza-González R, Fuenzalida V and Morell G 2019 Appl. Phys. A 125 354
[4] Srivastava S K, Kumar V and Vankar V D 2018 Nanomaterials and Their Applications (Springer) pp 27–71
[5] Vesel A et al. 2019 Materials (Basel). 12 2968
[6] Suzuki S, Chatterjee A, Cheng C-L and Yoshimura M 2011 Jpn. J. Appl. Phys. 50 01AF08
[7] Bo Z, Yang Y, Chen J, Yu K, Yan J and Cen K 2013 Nanoscale 5 5180–204
[8] Shih W-C, Jeng J-M, Huang C-T and Lo J-T 2010 Vacuum 84 1452–6
[9] Vinogradov A Y, Grudinikin S A, Besedina N A, Koniaikhin S V, Rabchinskii M K, Eidelman E D and Golubev V G 2018 Semiconductors 52 914–20
[10] Malard L M, Pimenta M A A, Dresselhaus G and Dresselhaus M S 2009 Phys. Rep. 473 51–87
[11] Ferrari A C and Basko D M 2013 Nat. Nanotechnol. 8 235
[12] Ferrari A C and Robertson J 2000 Phys. Rev. B 61 14095
[13] Vinogradov A Y, Abramov A S, Orlov K E and Smirnov A S 2004 Vacuum 73 131–5
[14] Hori M, Kondo H and Hiramatsu M 2011 J. Phys. D. Appl. Phys. 44 174027
[15] Zhang Y, Du J, Tang S, Liu P, Deng S, Chen J and Xu N 2011 Nanotechnology 23 15202
[16] Kukushkin S A and Sakalo T V 1993 Acta Metall. Mater. 41 1237–41