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Investigation and evaluation of the morphology properties of carbon nanowalls based on fractal analysis and Minkowski functionals

Ye. Yerlanuly[1,2], R. R. Nemkayeva[1], R. Ye. Zhumadilov[1] and M. T. Gabdullin[1*]

[1]Kazakh-British Technical University, Almaty, Kazakhstan
[2]Institute of Applied Science and Information Technologies, Almaty, Kazakhstan
*e-mail: *gabdullin@physics.kz
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It is well-known that at the nano-scale, morphology can play a crucial role in the properties of nanomaterials and there is still a challenging task to control it during the synthesis. In this work, the morphology of carbon nanowalls (CNWs) is studied and evaluated on the basis of fractal analysis and Minkowski functionals. Synthesis of CNWs was carried out using ICP-PECVD method at different growth times. The obtained samples were examined using atomic force microscopy (AFM) with subsequent processing of the obtained data using the Gwyddion 2.55 program, which provides a fractal analysis including the height-height correlation function and the power spectral density function. The Minkowski functionals were plotted for evaluation of the morphology of the CNWs. The process of the formation of CNWs was considered depending on the synthesis duration. A possible time-dependent growth mechanism with certain stages of nanostructures formation is proposed. The correlation between the calculated parameters of morphology and the electrical properties of CNWs was revealed.

Keywords: carbon nanowalls, Minkowski functionals, fractal analysis, atomic force microscopy, Gwyddion 2.55 program.
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1 Introduction

Today, nanomaterials and nanotechnology play an increasingly important role in many key sectors of human activity in the new millennium [1]. An analysis of the state and trends in the current developing nanotechnology allows us to assert that nanostructured carbon materials are very promising objects for practical application in various industries [2–5]. One of the promising carbon nanomaterials is carbon nanowalls, which are a type of carbon nanostructure consisting of graphene sheets arranged vertically on a substrate in the form of walls with a wall thickness of several to tens of nanometers [6, 7]. To date, materials based on CNWs have already been applied in various electronic devices, such as solar cells [8, 9], LEDs [10, 11], gas sensors [12,13], etc.

Currently, work on the synthesis of carbon nanowalls with a predefined morphology is being actively carried out [6, 14, 15]. Recently the effect of morphology on various physical properties (optical, electrical, etc.) of CNWs has been revealed [16]. In this regard, one of the important issues of nanotechnology is the characterization of morphological properties of nanomaterials. It is well known that today the study of morphology is carried out using scanning electron microscopy and scanning probe microscopy [17], etc. However, the results obtained require additional interpretation; therefore, Minkowski functionals and fractal analysis currently used for these purposes provide information on the geometrical parameters of the structure and morphology of the nanomaterial system [18–20]. This work emphasizes on the study and the evaluation of the morphological characteristics of CNWs synthesized on a quartz substrate [16] based on the Minkowski functionals and fractal analysis. In addition, the correlation of the electrical properties of CNWs with the obtained morphological parameters is analyzed.

2 Methods and analysis

CNW films on quartz substrates were synthesized by the ICP-PECVD method. The synthesis process and characteristics of the resulting material are presented in more detail in our previous work [16]. Since this article is aimed at the evaluation of the morphological characteristics of CNWs depending on the synthesis time and assessing the relationship between morphology and electrical properties, the results of the morphology analysis were processed using the Gwyddion 2.55 program [21, 22], where the height-height correlation function, the power spectral density function and Minkowski functionals were calculated. More details about the analysis methods and the Gwyddion 2.55 program are described in [20].

3 Results and discussion

The electrical properties of the synthesized CNWs as a function of growth time were previously reported in [16] and are given in Table 1. As can be seen, there is a trend towards an increase in height and a decrease in surface resistance as a function of synthesis time. The specific conductivity of the samples is approximately the same depending on the synthesis time, with the exception of the sample grown for 50 min, which demonstrates a small minimum. In [16], this effect was explained by a change of the morphological and structural properties (ratio of Raman peaks and degree of graphitization) of CNWs depending on the synthesis time. However, a complete morphological analysis based on the calculated height-height correlation function, power spectral density function, and Minkowski functionals was not carried out.

Figure 1 shows 3D models of the CNWs at different synthesis durations. As can be seen, the morphology of the obtained CNWs differs significantly, both in height and in the topology. As in previously reported papers [20,23,24], the fractal analysis was carried out by means of the height-height correlation H(r) and power spectral density (PSD) functions. Figure 2a shows log plots of H(r) for four surfaces. H(r) is a function for determining fractal dimension using the power of difference between the points on different surface structural units (roughness). The resultanting plots are characterized by two modes; the first is a linear region at small *r* values and the second is a nonlinear region at large *r* values. Nonlinear regions have oscillatory characteristics. Such observations are typical for self-affine surfaces [20,23,24]. The graph shows an increase in the value of H (r) depending on the time of CNWs synthesis. It is noteworthy that the curve of the sample obtained at 50 min differs from the others. The value of α for the samples synthesized at 30,40,60 min is very similar and has a value of the order of ~1.2, while for the case of 50 min it equals to ~1.3. An increase in the value of α indicates a higher surface roughness [25].

Table 1 – Thickness and electrical properties of CNWs as a function of growth time [16]

Synthesis duration	Height, nm	Sheet resistance, Ω/cm	Electrical conductivity, $\Omega^{-1}cm^{-1}$
30 min	60	~2000	~80
40 min	85	~1600	~70
50 min	160	~900	~60
60 min	190	~600	~70

Next, fractal analysis was performed using Power Spectral Density Functions (PSDF), corresponding results are presented in logarithmic scales in Figure 2b. The plots are characterized by approximately constant PSDF values, which is smooth region at very low spatial frequencies, an area of constant slope, and a plateau at very high spatial frequencies. These characteristics are typical for surfaces with dominant random properties (self-affine) and less periodic behavior [26]. In addition, an increase in the PSDF value depending on the time of synthesis of CNWs is observed. The slope of the PSDF curve (γ) corresponds to various evolutionary processes occurring on the surface [27]. The γ value was estimated from the slope of the linear approximation of the high-frequency region of the PSDF curve (see Fig. 2b). The value of γ is ~2.4 for CNW films synthesized at 30–40 min. While in the case of synthesis at 50–60 min, an increase in the γ value up to ~2.5 of is observed. Thus, the obtained values of γ, which are rather close ~2.4–2.5, indicate diffusion processes associated with the morphological evolution of CNW films [25, 28].

Two-dimensional Minkowski functionals, volume (V), boundary length (S), and connectivity/Euler characteristic (χ), depicted in Figure 3, are used to describe morphological features that cannot be determined using classical image analysis methods. Minkowski functionals imply the division of the received images into two parts (upper and lower) based on a threshold value. The upper and lower regions correspond to plateaus and valleys, respectively.

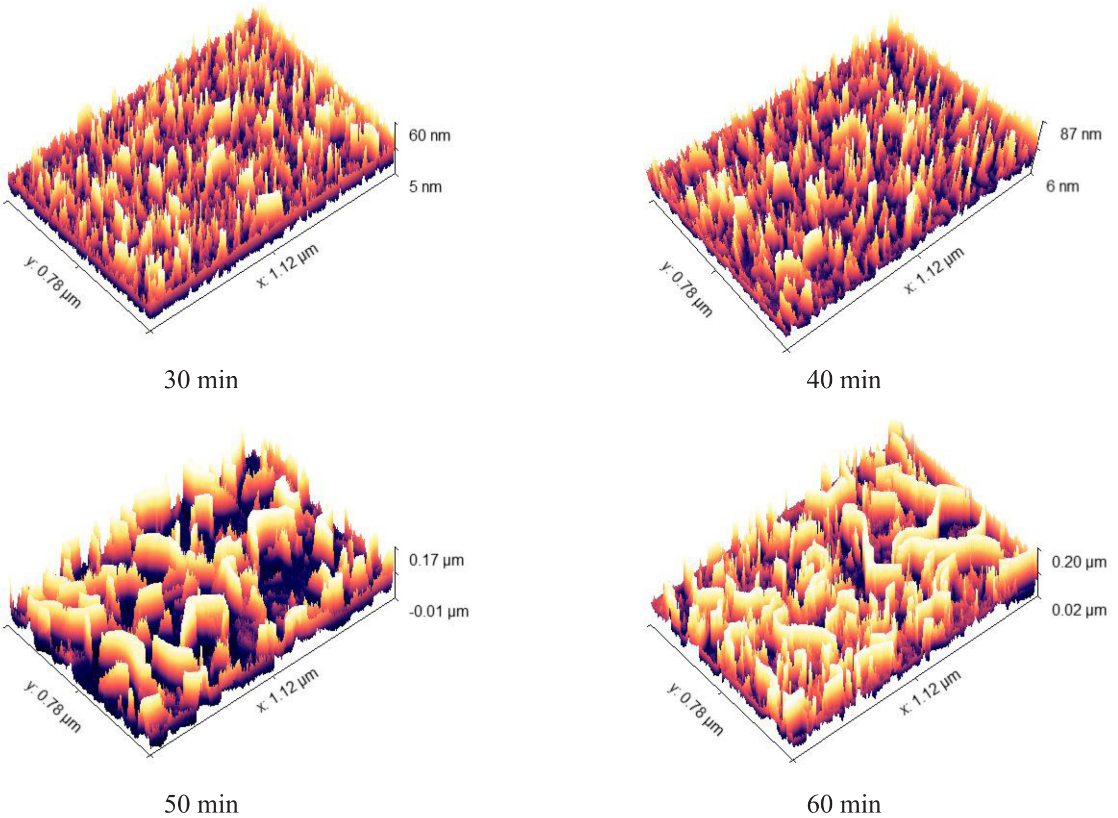

Figure 1 – 3D models of CNWs synthesized at different growth times

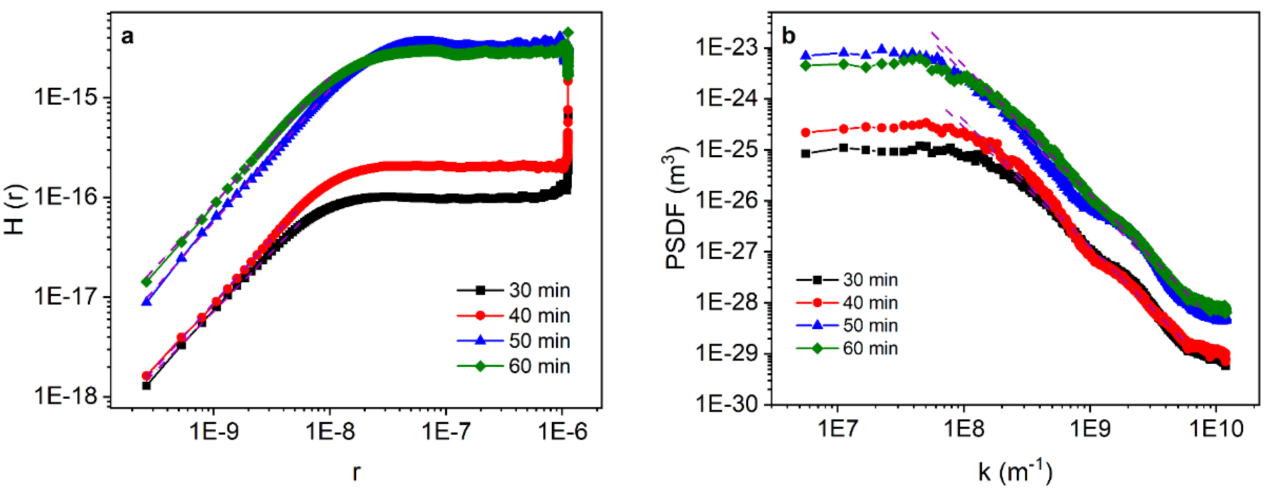

Figure 2 – (a) Double log plots of height–height correlation (H) as a function of shift (r) for CNWs, (b) double log plots of power spectral density (PSDF) as a function of the spatial frequency for CNWs

The Minkowski volume functional V, which basically shows surface coverage, varies across the samples. Figure 3a shows that the distributions in the samples obtained at 30, 40 and 60 minutes are very similar and the functionals are symmetrical. While the functional of the sample synthesized at 50 min is very different and asymmetric. Large V values indicate the dominance of high regions (plateaus), while small values are due to the dominance of trenches and tiny holes (valleys) on the surface.

The Minkowski boundary length (S) characterizes the global perimeter of any region (low or high region) and has the dimension of length. This parameter describes the character of the morphology of the film surface. Figure 3b shows curves similar for samples obtained at 30-, 40- and 60-minutes growth times, however, with increasing duration of synthesis of the CNWs leads to decrease in the value of S, which also indicates a decrease in the specific surface area and in roughness. The analysis results for the samples at 50 min are quite different. A shift of the peak is observed and the intensity is much greater compared to that for the samples at 40 and 60 min. This is apparently due to an increase in the roughness of the sample and a decrease in the density of the walls.

The Minkowski connectivity (χ) characterizes the difference in the number of high- and low-level regions and describes the topological pattern (fractal nature) of a microphotograph. χ is a characteristic of properties that depend on the relationship of nanostructures in the network, such as the percolation threshold, conductivity, and others associated with the transfer of gas, heat, electrons, etc. between nanostructures [29].

Positive values of χ mean the predominance of high-domain features on the surfaces. Negative values indicate the prevalence of valleys, a minimum indicates the highest density of valleys, and a maximum value corresponds to the densest peaks. As it is seen from Figure 3c, the χ value decreases depending on the synthesis time at 30, 40, and 60 min, which also indicates a decrease in the degree of roughness. There is a considerable difference at the synthesis time of 50 min, which is not consistent with other curves of connectivity. In particular, there is a noticeable shift in the peak position, which most likely describes the distinctive morphology of this sample.

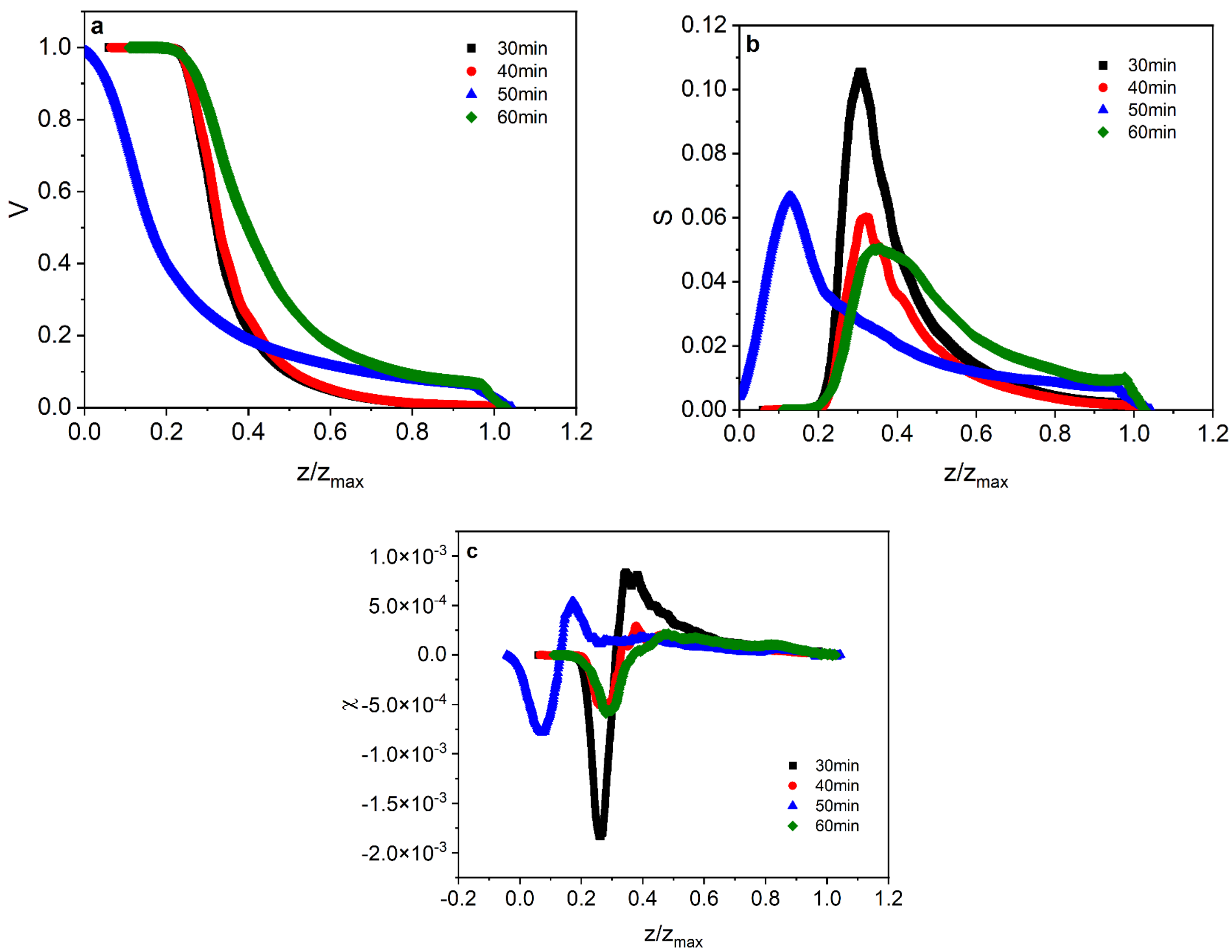

Figure 3 – Two-dimensional Minkowski functionals of carbon nanowalls (a) volume, (b) boundary length, (c) connectivity

The significant difference in the morphology of the samples obtained at 50 min from the rest is probably can be explained by the fact that depending on time a kind of cyclic growth process occurs during the synthesis of CNWs [30–32]. After the formation of initial CNWs, an increase in time leads to vertical growth of certain walls, the density of which comparatively low. A further increase in time leads to a growth of the CNWs in the horizontal direction, i.e., the wall density increases. Thus, an increase in synthesis time leads to the synthesis of CNWs with different morphology and structure, which in turn leads to a change in the electrical properties. Analysis of the results based on fractal analysis and Minkowski functionals (see Figure 2-3) indicate a distinctive morphology for the sample synthesized at 50 min, the density of CNWs in these samples is much lower compared to others, which leads to a minimum value of conductivity (see table one).

4 Conclusions

In this work, we studied and evaluated the morphological characteristics of CNWs synthesized on quartz substrates by the ICP-PECVD method. Morphology was evaluated usifn fractal analysis and Minkowski functionals. The dependence of the morphology of the obtained CNWs on the synthesis time was determined, which is also significantly noticeable when evaluating the fractality, roughness, and Minkowski functionals. The analysis results of the height-height correlation, power spectral density functions and two-dimensional Minkowski functionals, boundary length (S), volume (V), and connectivity / Euler characteristic (χ) indicate a significant difference in the morphology of the samples obtained at 50 min, which further explains the minimum value of specific electrical conductivity for this sample. The process of CNWs formation was considered depending on the synthesis time, and the effect of morphology on the electrical properties of CNWs was revealed.

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References

1. E. Inshakova, A. Inshakova. Nanomaterials and nanotechnology: prospects for technological re-equipment in the power engineering industry // IOP Conf. Ser. Mater. Sci. Eng. – 2020. -Vol. 709. -P. 033020. https://doi.org/10.1088/1757-899X/709/3/033020.

2. A. Roshani, M. Mousavizadegan, M. Hosseini. Carbon nanomaterials-based sensors for biomedical applications, in: Carbon Nanomater. Sensors, Elsevier, 2022: pp. 59–75. https://doi.org/10.1016/B978-0-323-91174-0.00003-2.

3. S. Doddamani, V.H. Mariswamy, V.K. Boraiah, S. Ningaiah. Trends in carbon nanomaterial-based sensors in the food industry, in: Carbon Nanomater. Sensors, Elsevier, 2022: pp. 95–103. https://doi.org/10.1016/B978-0-323-91174-0.00002-0.

4. M.I.S. J, S. S, P. Senthil Kumar, V.G. K, New analytical strategies amplified with carbon-based nanomaterial for sensing food pollutants // Chemosphere. -2022. -Vol. -P. 133847. https://doi.org/10.1016/j.chemosphere.2022.133847

5. U. Chadha, S.K. Selvaraj, S. Vishak Thanu, V. Cholapadath, A.M. Abraham, M. Zaiyan, M. Manikandan, V. Paramasivam. A review of the function of using carbon nanomaterials in membrane filtration for contaminant removal from wastewater // Mater. Res. Express. – 2022 – Vol.9 – P.012003 https://doi.org/10.1088/2053-1591/ac48b8

6. Y. Yerlanuly, D. Christy, N. Van Nong, H. Kondo, B. Alpysbayeva, R. Nemkayeva, M. Kadyr, T. Ramazanov, M. Gabdullin, D. Batryshev, M. Hori. Synthesis of carbon nanowalls on the surface of nanoporous alumina membranes by RI-PECVD method // Appl. Surf. Sci. – 2020. – Vol.523. – P.146533. https://doi.org/10.1016/j.apsusc.2020.146533

7. M. Hiramatsu, M. Hori. Carbon Nanowalls, Springer Vienna, Vienna, 2010. https://doi.org/10.1007/978-3-211-99718-5.

8. C. Yang, H. Bi, D. Wan, F. Huang, X. Xie, M. Jiang. Direct PECVD growth of vertically erected graphene walls on dielectric substrates as excellent multifunctional electrodes // J. Mater. Chem. A. – 2013. – Vol.1. – P.770–775. https://doi.org/10.1039/C2TA00234E

9. J. Liu, W. Sun, D. Wei, X. Song, T. Jiao, S. He, W. Zhang, C. Du. Direct growth of graphene nanowalls on the crystalline silicon for solar cells // Appl. Phys. Lett. – 2015 – Vol.106. – P.043904. https://doi.org/10.1063/1.4907284.

10. T.-H. Han, Y. Lee, M.-R. Choi, S.-H. Woo, S.-H. Bae, B.H. Hong, J.-H. Ahn, T.-W. Lee. Extremely efficient flexible organic light-emitting diodes with modified graphene anode // Nat. Photonics. – 2012. – Vol. 6. – P.105–110. https://doi.org/10.1038/nphoton.2011.318

11. H. Ci, H. Chang, R. Wang, T. Wei, Y. Wang, Z. Chen, Y. Sun, Z. Dou, Z. Liu, J. Li, P. Gao, Z. Liu. Enhancement of Heat Dissipation in Ultraviolet Light□Emitting Diodes by a Vertically Oriented Graphene Nanowall Buffer Layer// Adv. Mater. – 2019. – Vol.31. – P.1901624. https://doi.org/10.1002/adma.201901624

12. S. Kwon, H. Choi, S. Lee, G. Lee, Y. Kim, W. Choi, H. Kang. Room Temperature Gas Sensor Application of Carbon Nanowalls using Electrical Resistance Change by Surface Adsorption of Toxic Gases//Mater. Res. Bull. – 2021. – Vol.141. – P.111377. https://doi.org/10.1016/j.materresbull.2021.111377

13. P. Slobodian, U. Cvelbar, P. Riha, R. Olejnik, J. Matyas, G. Filipič, H. Watanabe, S. Tajima, H. Kondo, M. Sekine, M. Hori. High sensitivity of a carbon nanowall-based sensor for detection of organic vapours//RSC Adv. – 2015. – Vol.5. – P.90515–90520. https://doi.org/10.1039/C5RA12000D

14. T. Ichikawa, N. Shimizu, K. Ishikawa, M. Hiramatsu, M. Hori. Synthesis of isolated carbon nanowalls via high-voltage nanosecond pulses in conjunction with CH4/H2 plasma enhanced chemical vapor deposition // Carbon N. Y. – 2020. – Vol.161. – P.403–412. https://doi.org/10.1016/j.carbon.2020.01.064

15. M. Wang, Y. Kim, L. Zhang, W.K. Seong, M. Kim, S. Chatterjee, M. Wang, Y. Li, P. V. Bakharev, G. Lee, S.H. Lee, R.S. Ruoff. Controllable electrodeposition of ordered carbon nanowalls on Cu(111) substrates//Mater. Today. – 2022. – Vol.57. – P.75-83 https://doi.org/10.1016/j.mattod.2022.05.018

16. Y. Yerlanuly, R. Zhumadilov, R. Nemkayeva, B. Uzakbaiuly, A.R. Beisenbayev, Z. Bakenov, T. Ramazanov, M. Gabdullin, A. Ng, V. V. Brus, A.N. Jumabekov. Physical properties of carbon nanowalls synthesized by the ICP-PECVD method vs. the growth time // Sci. Rep. – 2021. – Vol.11. – P.19287. https://doi.org/10.1038/s41598-021-97997-8

17. E. Ortiz Ortega, H. Hosseinian, M.J. Rosales López, A. Rodríguez Vera, S. Hosseini. Characterization Techniques for Morphology Analysis, in: 2022: pp. 1–45. https://doi.org/10.1007/978-981-16-9569-8_1

18. I. Levchenko, J. Fang, K. (Ken) Ostrikov, L. Lorello, M. Keidar. Morphological Characterization of Graphene Flake Networks Using Minkowski Functionals//Graphene. – 2016. – Vol.05. – P.25–34. https://doi.org/10.4236/graphene.2016.51003

19. A. Grayeli Korpi, Ş. Ţălu, M. Bramowicz, A. Arman, S. Kulesza, B. Pszczolkowski, S. Jurečka, M. Mardani, C. Luna, P. Balashabadi, S. Rezaee, S. Gopikishan. Minkowski functional characterization and fractal analysis of surfaces of titanium nitride films//Mater. Res. Express. – 2019. – Vol. 6. – P.086463. https://doi.org/10.1088/2053-1591/ab26be

20. Y. Yerlanuly, R. Nemkayeva, R. Zhumadilov, T. Ramazanov, B. Alpysbayeva, M. Gabdullin. Morphological characterization of carbon nanowalls networks using Minkowski functionals // Jpn. J. Appl. Phys. – 2021. – Vol.60. – P. 115001. https://doi.org/10.35848/1347-4065/ac26e2

21. D. Nečas, P. Klapetek. Gwyddion: an open-source software for SPM data analysis // Open Phys. – 2012. – Vol.10.-P.1. https://doi.org/10.2478/s11534-011-0096-2

22. www.gwyddion.net, (n.d.). www.gwyddion.net

23. F.M. Mwema, E.T. Akinlabi, O.P. Oladijo. Effect of Substrate Type on the Fractal Characteristics of AFM Images of Sputtered Aluminium Thin Films//Mater. Sci. – 2019. – Vol.26. – P.49–57. https://doi.org/10.5755/j01.ms.26.1.22769

24. Ş. Ţălu, R.P. Yadav, O. Šik, D. Sobola, R. Dallaev, S. Solaymani, O. Man. How topographical surface parameters are correlated with CdTe monocrystal surface oxidation // Mater. Sci. Semicond. Process. – 2018. – Vol.85. – P.15–23. https://doi.org/10.1016/j.mssp.2018.05.030

25. A. Pandey, S. Tyagi, B.P. Singh, L. Kumar. Surface Morphological and Optical Evolution of Rf Sputtered Azo Films for Optoelectronic Devices// Physica B: Condensed Matter. – 2022. – Vol. 47. – P. 414393. https://doi.org/10.1016/j.physb.2022.414393

26. C. Buchko. Surface characterization of porous, biocompatible protein polymer thin films // Biomaterials. – 2001. – Vol.22. – P.1289–1300. https://doi.org/10.1016/S0142-9612(00)00281-7

27. P. Dash, P. Mallick, H. Rath, A. Tripathi, J. Prakash, D.K. Avasthi, S. Mazumder, S. Varma, P.V. Satyam, N.C. Mishra. Surface roughness and power spectral density study of SHI irradiated ultra-thin gold films // Appl. Surf. Sci. – 2009. – Vol.256. – P. 558–561. https://doi.org/10.1016/j.apsusc.2009.08.046

28. A.K. Manna, A. Kanjilal, D. Kanjilal, S. Varma. Dynamic Surface evolution and scaling studies on TiO2 thin films by Ti ion implantation//Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms. – 2020. – Vol.474. – P.68–73. https://doi.org/10.1016/j.nimb.2020.04.031

29. J.-F. Gouyet, A.L.R. Bug. Physics and Fractal Structures // Am. J. Phys. – 1997. – Vol.65. – P. 676–677. https://doi.org/10.1119/1.18629

30. M. Hiramatsu, K. Shiji, H. Amano, M. Hori. Fabrication of vertically aligned carbon nanowalls using capacitively coupled plasma-enhanced chemical vapor deposition assisted by hydrogen radical injection // Appl. Phys. Lett. – 2004.– Vol.84. – P. 4708–4710. https://doi.org/10.1063/1.1762702

31. T. Mori, M. Hiramatsu, K. Yamakawa, K. Takeda, M. Hori. Fabrication of carbon nanowalls using electron beam excited plasma-enhanced chemical vapor deposition // Diam. Relat. Mater. – 2008. – Vol.17. – P. 1513–1517. https://doi.org/10.1016/j.diamond.2008.01.070

32. A. Giese, S. Schipporeit, V. Buck, N. Wöhrl. Synthesis of carbon nanowalls from a single-source metal-organic precursor // Beilstein J. Nanotechnol. – 2018. – Vol.9. – P.1895–1905. https://doi.org/10.3762/bjnano.9.181

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