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CALCULATION OF THE SURFACE POTENTIAL OF NANOSTRUCTURED CARBON FILMS USING MULTIFRACTAL ANALYSIS METHOD

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In this paper surface potential of diamond-like carbon nanostructured film is studied. Fractal form of the surface of this film is discussed. Fractal parameters and surface potential as a function of them are calculated theoretically. Then obtained results are compared with the results measured by Kelvin probe method. The evolution of the surface topology and related surface potential during the deposition time is studied also. The dependence of multifractal parameters on the deposition duration was revealed.

Key words: *Surface potential, nanostructured film, multifractal analysis.*

1. Introduction

The process of forming the semiconductor layers for modern electronic devices is accompanied by a process of self-organization at the nano and micro levels. A promising approach to describe such self-similar state to the surface is the multifractal analysis [1, 2, 3]. Introduced by Benoit Mandelbrot general pattern of geometric properties of the physical world, which is manifested in the self-similarity of its structure, has found numerous applications in materials science and has provided new opportunities for describing disordered materials microstructures using rigorous quantitative terms, such as fractal dimension. To date, found that to describe the self-similarity of natural materials is not enough just to use one of the fractal dimension, and in the works of different authors [1-7] show that the multifractal formalism provides such an opportunity. One of the important physical parameters of the nanostructured films is surface potential, which we can calculate using the results obtained by multifractal analysis. These results allow us to propose a mathematical expression that gives an opportunity to evaluate the surface potential of the film, due to the presence of fractal structure on its surface. The methodology of multifractal parameterization of structures of materials is based on the fundamental principles of self-similarity, stochastic and fractal broken symmetry structures of natural materials [4, 5, 6]. It uses a set of self-similar measures in Euclidean space, so can more accurately describe the characteristics of the material [7, 8]. The property of self-similarity quantitatively expressed using the concept of fractal dimension. To determine the fractal dimension of the fractal and other parameters, we used obtained atomic force microscopy images for chemical vapor deposited diamond-like carbon nanostructured films.

2. Theory

2.1. Multyfractal Analysis

In materials science and allied areas in the majority of cases studied structure is presented in the form of flat images. In the modern computer technology and bitmap processing programs such flat images presented in the so-called digital (digitized) form - a matrix of discrete elements of the same size images - pixels. Each pixel is attributed to three numerical characteristics (coordinates): two of them (i, j) define the position of the pixel on the image plane (x, y), third characteristic defines its

color z (i, j). The color characteristics of pixels are given by integers. Coordinates of the pixels on the plane are numbers of rows and columns of pixels in the matrix (by which the image represented in digital form) and also are set of integers. Thus, using the color characteristics of pixels as the usual number, we can imagine a flat image of the surface topography in three dimensions [3, 7, 15, 16]. Examples of such structures may be three-dimensional digital images of the surface of materials obtained by atomic force microscope (AFM) (Figure 1).

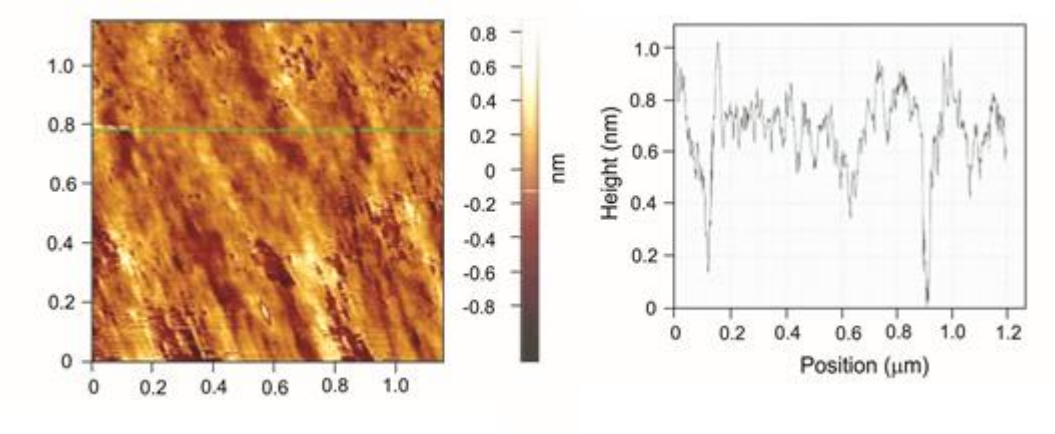

Figure 1. **AFM image of a sample of DLC grown on Ge substrate (upper panel) and cross sectional profile of thickness across the green line on the image (lower panel).**

Generated by the color characteristic or height *z* (*i*,*j*) measure [7,14,18,20]

$$\lambda_{0ij} = \frac{z(i,j)}{(\sum_{ij}(z(i,j))} \tag{1}$$

on the set of elementary cells - pixels can be directly used for multifractal analysis of images. The sum of two indices for all the pixels on a square matrix (*i*, *j*) can be represented as the sum of one index *i*, if renumber the pixels using one index.

Thus, when the partition of space covering, which contains the object being studied, it is possible to generate a measure $\{\lambda_i\}$, ($\sum_{i=1}^{N}\lambda_i = 1$) - some effective distribution does not change its sign value. For anyway constructed (generalized) measure *Pi* the generating function is constructed:

$$\Gamma(q,\tau,l) = \sum_{i=1}^{N}\frac{(p_i)^q}{(l_i)^\tau}, \tag{2}$$

where the summation is only for not empty cells measure *pi* >0, q and τ are arbitrary real numbers ($-\infty \le q, \tau \le \infty$).

In the case of the singular behavior of measure, taking place in many situations [13],

$$p_i \cong (l_i)^\alpha, l \to 0, \tag{3}$$

where α is positive real number, it has been shown [22, 23] that there is a unique function of τ(q), in the limit $l \to 0$, such that $\Gamma(q, \tau(q), l \to 0)$ is finite.

For generalized correlation function χ and its exponent τ we have [1, 7, 16, 19]

$$\chi(q) = \sum_{i=1}^{N} (p_i)^q \sim l^{\tau(q)}, l \to 0 \tag{4}$$

$$\tau(q) = \lim_{l \to 0} \cdot \frac{\ln(\chi(q))}{\ln(l)} \ . \tag{5}$$

By summing over the cells by expression (4) we can for χ(q) go to the integral form [19]

$$\chi(q) = \int d\alpha \cdot p(\alpha) \cdot l^{-f(\alpha)} \cdot l^{q\alpha}, \tag{6}$$

where $\rho(\alpha')l^{-f(\alpha')}d\alpha'$ is the probability that a randomly selected α singularity in the equation (3) for p_i has a value in the range (α′, α′+dα′), and ρ(α) is not singular function. In this way, studied self-similar set is modeled by a set of interpenetrating set of singular α, each of which has a corresponding fractal dimension f (α). In the $l \to 0$ limit the integral (6) is determined by some α, at which $q\alpha - f(\alpha)$ = min, obtained from the relationship between the function of τ(q) and the spectrum of singularites f (α) [1,12,16, 19]:

$$\tau(q) = q\alpha - f(\alpha), \ \alpha = \frac{d\tau}{dq}, q = \frac{df}{d\alpha} \tag{7}$$

From the last relations can be seen, the normalization condition is this τ (1) = 0. This fact can be expressed explicitly, putting [21]

$$\tau(q) = (q-1)D_q \ \text{ or } \ D_q = \frac{\tau(q)}{q-1} \ , \tag{8}$$

where Dq is generalized Renyi dimension, at that $D_0 \geq D_1 \geq D_2$. Here D_0, D_1 and D_1 are fractal (q=0), informative (q=1) and correlative (q=2) dimensions, respectively.

Similar results for $\tau(q)$, $f(\alpha)$ and Dq are obtained in works [1, 5, 8, 14, 16], but our work contains mathematical approach differing from their formalism.

In the study of multifractal properties of regular fractal structures acts as *D*o fractal dimension. Strictly speaking, the term "dimension" is only applicable to the D_0, as the value of q = 0 removes the distinction of cells of different measures, and we have to deal with the media configuration "in its purest form".

2.2 Surface Energy Calculation

Excess component of free energy of system, associated with the appearance of the interfaces, can be calculated from the expression [8]

$$dG_S^{ex} = dA_s = \alpha dS \, , \tag{9}$$

where dG_S^{ex} is the change in free excess Gibbs energy, due to the emerging of separation boundary, dA_s is the work on the formation of the section area of the surface dS, α is the specific surface energy of the separation boundary. In this case, the component of the excess chemical potential, associated with the emergence of new geometric shapes on the surface, can be calculated by the classical expression of thermodynamics [8]:

$$\mu_s = \frac{dG_s}{dn} = \frac{\alpha M}{\rho} \cdot \frac{dS}{dV} \ , \tag{10}$$

where ρ and M are density and molecular weight of solid phase, dV and dn are changes of the volume and the number of moles of the solid phase, providing change of surface of the section with area dS.

To formally obtain the desired expression for the surface energy associated with the fractal shape of the surface of the system, it is necessary in the formula (10) enter the expression for the surface area and volume nanoforms. To implement this approach, it is necessary to take advantage of the fundamental dependencies between the parameters, characteristic of fractal approximations:

$$S = N_s \cdot r^{D_{os}} \quad \text{and} \quad V = N_V \cdot r^{D_{0v}} \ , \tag{11}$$

where N_s and N_V are constant proportionality factors depending on the geometry of the system and taking into account the fractal dimension of the described parameters.

Then, forming the differentials for the area and volumes of fractal surfaces in accordance with (10), we obtain the following expression for the surface components of the phase chemical potential:

$$\mu s = \frac{\alpha M}{\rho} \cdot \frac{N_s D_{0s}}{N_v D_{0v}} \cdot r^{D_{0s} - D_{0v}} \ , \tag{12}$$

where r is the characteristic (length) size of the analyzed space.

The obtained expression is used to estimate the magnitude of the surface energy of the thin DLC film deposited on Ge substrate. As the input data to perform calculations AFM image is used.

3. Experiment and Numerical Nalculation

For more concrete investigation, we examined diamond-like carbon (DLC) layers deposited by CVD method on Ge substrate. Films were deposited from dc-plasma excited by the vapor of mixture of carrying gases and hydrocarbon (in our case toluene C**7**H**8**) in crossed electric and magnetic fields. In the technological process ion and magnetron sources (or both of them simultaneously) were used [9, 10, 11, 17].

It is possible to study the surface transformation of these nanolayers upon deposition time by examining them with AFM system Solver Nano-NT-MDT (Fig.2a,b,c). Also, it is possible to sketch out their boundary line (Fig. 3a,b) which enables one to draw an idea of peculiarities of formation these layers.

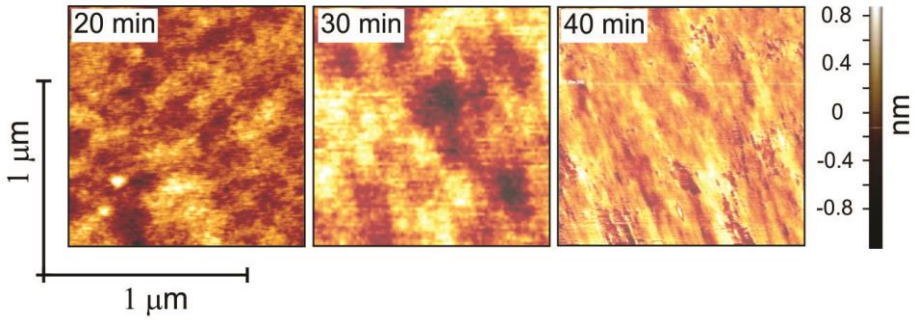

Figure 2 : AFM images of DLC samples with different CVD deposition time.

During the initial stage of layer formation, grained structures, granules, which combine and form granules of the same type but bigger and so on. The granules are shown on Fig. 3. Since when these

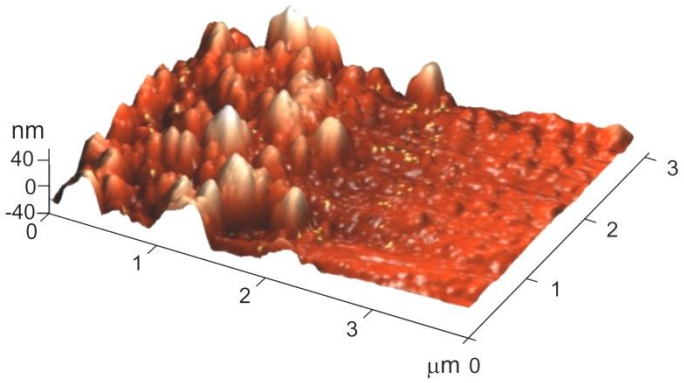

Figure 3. The border line between Ge substrate and DLC film.

granules begin to overlap each other a layer is formed. On the shaped layer, another fragmented layer is formed and so on. As the measurements reveal the topmost fragmented islet-like layers have thickness of 0.34 nm, which indicates that an atomic layer of carbon exists there. These results, as well as the cross-sectional and statistical analysis allow us to state that our layers can be subjected to fractal analysis. Applying already considered to be classical mathematical formalism of multifractal analysis together with computational programs the fractal parameters are deduced which makes possible to present some specific physical properties, in particular the surface energy of the layer, as a function of these parameters. Accordingly, the Regne's fractal coefficient decreases with the deposition time, which is the result of fact that the surface becomes more even and ordered. A software was developed by us to calculate Regne coefficients for surface and the bulk. Thus, for 10 min, 20 min, 30 min and 40 min deposition time Regne's fractal coefficients of D_{0S} we respectively obtained the following values: 2.75, 2.62, 2.54 and 2.5 and or D_{0S} : 2.9, 2,88, 2.86, 2.86. Introducing these values into equation 12 we obtained the following relations for surface energy:

$$\mu_{S1} : \mu_{S2} : \mu_{S3} : \mu_{S4} = 1 : 1.49 : 2.15 : 2.32$$

On the other hand, similar relation for surface potential can be obtained also by using data measured by Kelvin probe method. The Kelvin probe technique relies on the detection of an electric field between a sample material and probe material. The electric field can be varied by the voltage that is applied to the sample relative to the probe. Although the Kelvin probe technique only measures

a work function difference, it is possible to obtain an absolute work function by first calibrating the probe against a reference material (with known work function) and then using the same probe to measure a desired sample. The Kelvin probe technique is used to obtain work function maps of a surface with extremely high spatial resolution, by using a sharp tip for the probe.

$$\mu_{S1} : \mu_{S2} : \mu_{S3} : \mu_{S4} = 100 : 150 : 225 : 240$$

The results of the calculations obtained by the method of multifractal analysis and measurements are very similar.

Conclusions

- DLC film as a self-organized system can be analyzed by the method of multifractal analysis.
- In the process of forming of the DLC film some different fractal regularity are maintained.
- Range parameter decreases with increasing deposition time.
- Investigation made by multifractal analysis method gives similar results with experimental data.

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Սույն աշխատանքում ուսումնասիրված է ալմաստանման ածխածնային նանոկառուցվածքային թաղանթի մակերևույթային պոտենցիալը: Քննարկված է այդպիսի թաղանթի մակերևույթի ֆրակտալ ձև: Տեսականորեն հաշվարկված են ֆրակտալ պարամետրերը և մակերևույթային պոտենցիալը՝ որպես վեջիններից ֆունկցիա: Այնուհետ ստացված արդյունքները համեմատված են Կելվինի զոնդի մեթոդով չափումների արդյունքների հետ: Ուսումնասիրված է թաղանթի մակերևույթի տոպոլոգիայի և մակերևույթային պոտենցիալի էվոլուցիան նստեցման ժամանակի ընթացքում: Արտածված է ֆրակտալ պարամետրերի կախվածությունը նստեցման ժամանակից:

Բանալի բառեր. Մակերևույթային պոտենցիալ, նանոկառուցվածքային թաղանթ, մուլտիֆրակտալ անալիզ

РАСЧЕТ ПОВЕРХНОСТНОГО ПОТЕНЦИАЛА НАНОСТРУКТУРИРОВАННЫХ УГЛЕРОДНЫХ ПЛЕНОК МЕТОДОМ МУЛЬТИФРАКТАЛЬНОГО АНАЛИЗА

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В данной работе исследован поверхностный потенциал алмазоподобной углеродной наноструктурированной пленки. Обсуждается фрактальная форма поверхности этой пленки. Теоретически рассчитаны фрактальные параметры и поверхностный потенциал как функция от них. Затем полученные результаты сравниваются с результатами, измеренными методом зонда Кельвина. Изучается эволюция поверхностной топологии и связанного с ней потенциала поверхности в течение времени осаждения. Выявлена зависимость мультифрактальных параметров от продолжительности осаждения.

Ключевые слова: Поверхностный потенциал, наноструктурированная пленка, мультифрактальный анализ.