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Express Method for the Analysis of the Morphological Parameters of Graphene Coatings on a Copper Substrate

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CVD method in a gas mixture of methane, hydrogen and argon was used for condensation of graphene layers on copper substrates. Along with traditional methods of studying growth morphology, such as Raman spectroscopy and atomic force microscopy, the method of multi-threshold cross-sections with a 3*D* representation of the optical microscopy image, where the intensity scale acts as the third *Z*-axis, was used in the work for the rapid assessment of the degree of filling and the specific area of the graphene. Based on the results obtained, conclusions are drawn about the regularities of the formation of graphene layers. The presence of the most probable areas of formation of graphene domains (~ 13 μm^2) is revealed with a small time (10-20 minutes) of the production process. An increase in the process time to 30 minutes is accompanied by an increase in the uniformity of the distribution of areas of graphene domains to 200 μm^2 at their high fractal dimension in the range of HD values of 1.82 ... 2.0.

Keywords: Graphene coatings on copper, CVD method, Raman spectra, Optical microscopy, Morphology of the coatings, Computer processing, Multi-threshold analysis, Nucleation conditions.

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1. INTRODUCTION

Currently, the great interest in graphene as a functional material is associated with a number of its unique properties (electronic, optical, mechanical, etc. [1]). The synthesis of graphene on a copper substrate by the chemical vapor deposition (CVD) method is considered as one of the most promising methods for obtaining large area substrate/graphene coating system [2, 3] for practical use. The basis of the method in this case is the controlled process of decomposition of a volatile carbon-containing compound in order to create conditions for its deposition on the substrate surface and to ensure a stable growth of the layer with specified structural characteristics.

The management of the number of layers and defectiveness of the deposited graphene coatings remains the main technological problem. The solution of this problem is complicated by the absence of a direct correlation between the deposition time of graphene layers and their number, while the increase in pressure during synthesis leads to an increase in the defectiveness and thickness of the formed material. All this makes it necessary to carry out a reliable control of the graphene layer formation combining objectivity and operativeness, as well as to clarify the physical growth mechanisms of graphene domains.

The currently most used methods of Raman spectroscopy and atomic force microscopy can be significantly supplemented by optical microscopy (under appropriate software image processing), which is much more accessible compared with the first two.

This paper is devoted to the evaluation of the possibilities of using the multi-threshold cross-section method for processing optical surface images in order to determine growth regularities, as well as to control the uniformity and continuity of the coating.

2. EXPERIMENTAL

To obtain the samples, graphene layers were grown by the CVD method in a gas mixture of methane, hydrogen and argon on a copper foil substrate (Alfa Aesar, thickness of 25 μm) at temperatures up to 1000 °C. In Fig. 1 we illustrate the gas flow diagram of a mixture of gases (methane, hydrogen, argon) on the Cu catalyst surface at the synthesis temperature of (~ 1000 °C).

At this temperature, methane from the gas phase diffuses to the surface through the boundary layer, then is adsorbed on the catalyst surface and decomposed with the atomic carbon emission, which diffuses on the copper surface. The processes occurring on the surface to a large extent depend on the substrate temperature, and also on the carbon supply rate to the surface.

Preannealing of the copper substrate is a necessary operation before the synthesis (Fig. 2). A polished copper substrate is annealed in the argon-hydrogen mixture for surface restoration and the copper grain growth.

The process occurred at a reduced total pressure of 2.4 mbar. A polished copper substrate was annealed in the argon/hydrogen mixture at flow rates, respectively, of 250 and 15 cm^3/min for surface restoration and the copper grain growth. Then, the synthesis was carried out for 5...30 min, while the hydrogen flow rate was reduced to 5 and methane was supplied at a rate of 50 cm^3/min.

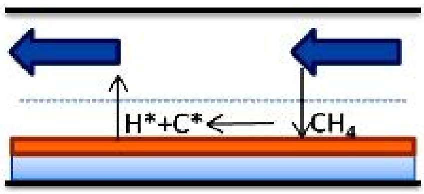

Fig. 1 – Gas flow diagram of a mixture of gases (methane, hydrogen and argon) on the Cu catalyst surface

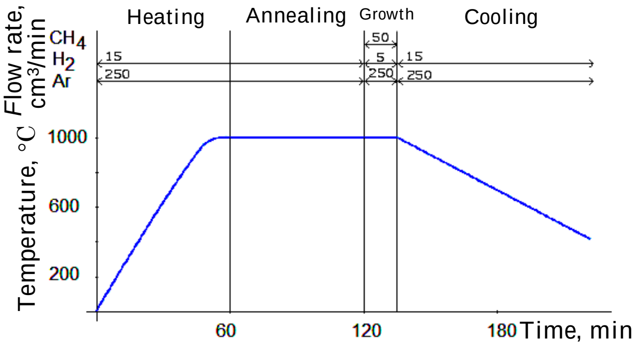

Fig. 2 – Technological synthesis of a graphene layer on a copper substrate

A comprehensive analysis of the Raman spectroscopy, optical and atomic-force microscopy data was conducted to study the manufactured graphene layers. The Raman spectra were obtained at room temperature in the back-scattering geometry on a LabRAM HR-800 spectrometer equipped with a confocal microscope. The measurements were performed under the following conditions: the excitation wavelength was 532 nm, the laser radiation power on the sample surface was equal to 2.0 mW in a spot with a diameter of ~ 1 μm.

The optical microscopy method with computer image processing was used to study the growth dynamics of graphene islands depending on the substrate temperature and deposition time.

To obtain the necessary information in the analysis of the optical image of the growth surface, we used the multi-threshold cross-section method based on a 3*D* representation of the optical image, where the intensity scale serves as the third *Z*-axis. In its division into the corresponding number of sections (thresholds), it is possible to estimate the morphological parameters of each section [4]. The results of the complex processing of optical images by the multi-threshold cross-section method given in [5] for diboride coatings in the spinodal decomposition process [6] and for multi-element (high entropy) nitrides [7] suggest that this method can be effectively used for the necessary express analysis in the growth system of graphene layers on a copper substrate.

The image processing was done in the MATLAB environment: both the segmentation procedure of graphene islands (IPT) and statistical processing (Statistics). After the selection of image regions corresponding to graphene, a data array of their areas was formed (several hundred values depending on the image region) was formed. The ProbDist function was used with the "kernel" parameters for approximation [8].

3. RESULTS AND DISCUSSION

The coatings produced by deposition for 20 minutes were chosen as the basis for a pivotal study. In Fig. 3 we illustrate the image of the graphene nucleus surface (a) and the Raman spectra obtained by scanning the sample along a line with a step of 1 μm (b).

As seen from Fig. 3b, the Raman spectra of graphene layers are represented by two lines with the positions of the maxima of ~ 1580 cm^{-1} (G-line) and ~ 2700 cm^{-1} (2D-line). The G line in the Raman spectrum corresponds to light scattering at the Γ point of the Brillouin zone by

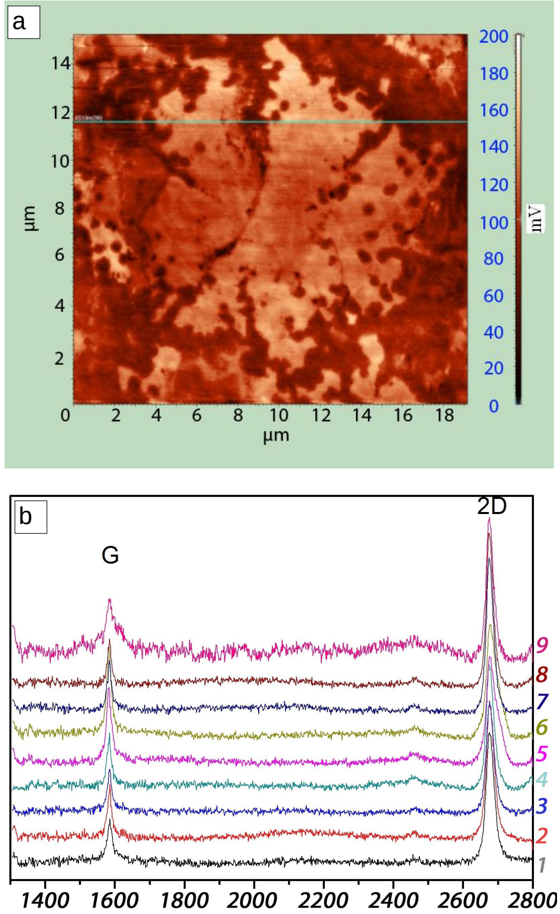

Fig. 3 – Image of the region of the "graphene/copper substrate" system obtained by atomic force microscopy (a) and a series of spectra of the graphene coating regions from the edge (the upper spectrum 9) into the interior of the graphene domain (b)

optical phonons of the *E2g* symmetry generated by planar vibrations of carbon atoms in the layer plane [9]. The 2D spectral line is caused by resonance light scattering with participation of two phonons of the same energy, but the opposite pulse direction [10].

Starting with [11, 12], there is a stable tendency to use the intensity ratio of G and 2D lines (I_G/I_{2D}) in the Raman spectra to estimate the number of monolayers in graphene. It was shown in [13] that the number of monolayers (n) in multi-graphene can be evaluated from expression $n = 10\times(I_G/I_{2D} - 0.14)$. The results of analysis of the Raman spectra of graphene layers allow to conclude that the value of the I_G/I_{2D} ratio is in the range of 0.25-0.26 for all the studied sample regions that indicates a monolayer structure of the obtained graphene.

These data give grounds to consider graphene samples as "test" ones to estimate the coating structure on the basis of optical microscopy data. Additional data on the optical properties of graphene layers [14, 15] can be used as the basis for the analysis of the "graphene coating/substrate" system under specific technological conditions. A practical study involves the identification of the graphene regions (domains) of a certain structure (number of layers). For this purpose, the color of domains of the poly-graphene coating placed on a copper substrate is chosen (Fig. 4a-c) that, in fact, is the color of a copper substrate, which varies after light transmission through the graphene coatings with *n* layers.

In a simplified case of image processing, the selection of graphene coating regions can be performed only based on the image contrast in conversion to monochrome format. Even on this basis, we can estimate the coating parameters including their fractal dimension, which is an important parameter determining the functional properties of the system. The process of selecting domains on a particular image (segmentation), in this case, proceeds from a model considering only two elements of the "substrate/coating" system: an ideal substrate and a graphene domain uniform in structure. This model, even in such a form, can be useful in evaluating the technological conditions for obtaining poly-graphene coating.

In the paper, based on computer processing of optical images of graphene layers synthesized during 10, 20 and 30 min (Fig. 4a-c), the morphological characteristics of graphene domains are obtained on the basis of data on their area and Hausdorff dimension (HD) [4]. The area covered with a graphene layer is equal to 7.3 %, 29.5 %, and 40.3% (is represented as a histogram in Fig. 5) and the number of elements amounts to 92, 173, and 115, respectively. In this case, the minimum area of a graphene domain was taken to be about 1 μm^2.

The first of these parameters (domain area) characterizes the size of a selected individual element regardless of its shape. The second parameter – HD – estimates the development of boundaries. Change in this parameter from one to two indicates a change in the structural element from a one-dimensional object (line) to a two-dimensional (plane). The data obtained as a result of such processing are illustrated in Fig. 4d and Fig. 6d.

As seen from Fig. 4d, at relatively short times of the CVD process (10-20 min), an increase in the process time leads to an increase in the number of nuclei of graphene regions, while their most probable formation size remains relatively constant (curves 1, 2). This size (critical growth

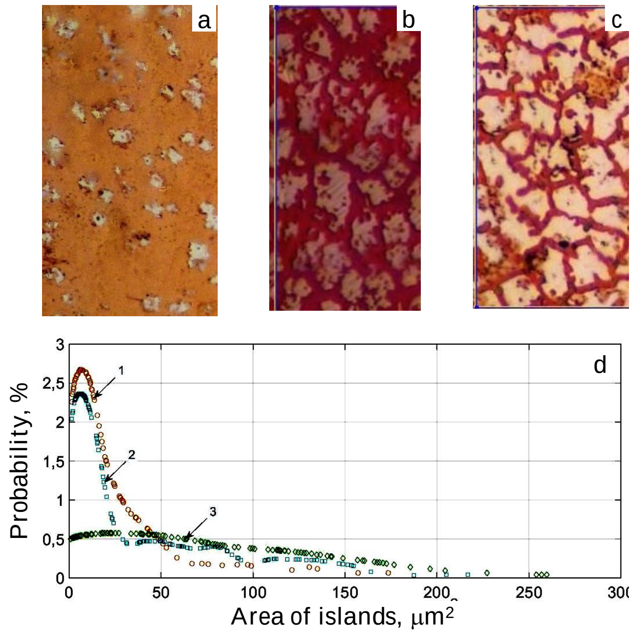

Fig. 4 – Optical images of graphene coatings synthesized for 10 min (a), 20 min (b), 30 min (c) and statistics of structural elements of a graphene coating (d)

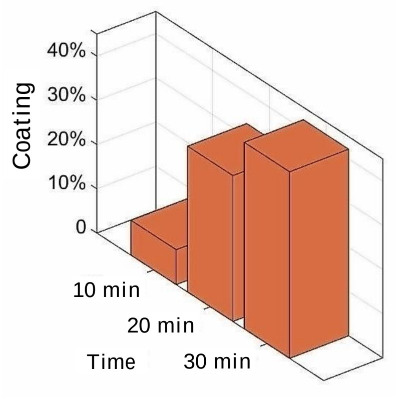

Fig. 5 – Distribution histogram of the substrate area percentage coverage by graphene formations on the deposition time

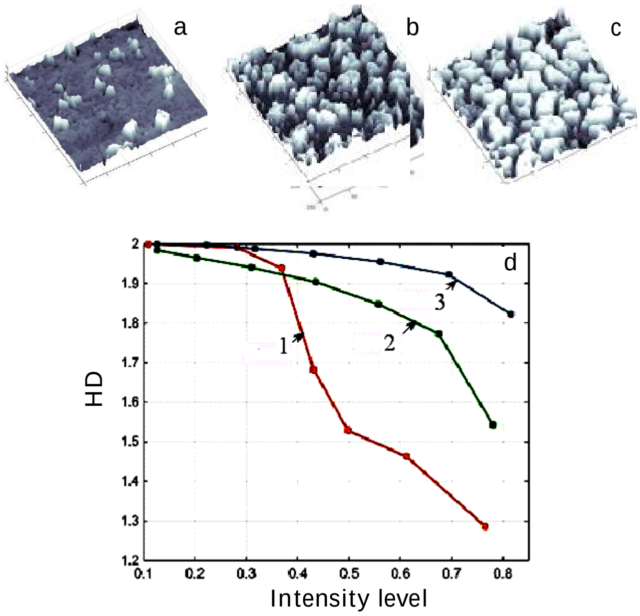

Fig. 6 – Change in the HD of image elements when changing the CVD process conditions; a-c – image intensity of the coating at different exposures: 1 – 10 min, 2 – 20 min, and 3 – 30 min; (d) HD at different intensity levels

size) is about 13 μm^2. At the same time, at longer times of the CVD process (~ 30 min), a significant increase in the filling density with graphene regions (up to 40.3 %) occurs on account of the dense filling with graphene regions of different areas that is reflected in the close to equiprobable distribution in area of graphene regions (see curve 3 in Fig. 4d).

The established regularity of formation at short times of the CVD process of a set of graphene regions (domains) with almost identical areas is an important parameter when using the "graphene/copper substrate" system as elements of electronic devices [16]. The functional properties of such devices depend even more on the characteristics of the boundaries of graphene regions determined by their fractal dimension. This characteristic can also be defined from the express data of optical microscopy by computer processing of the obtained surface photographs with the analysis of the fractal dimension for different contrast levels determined by the multi-threshold cross-section method [5, 17].

In Fig. 6 we show the results of such a processing.

At the shortest deposition time of 10 min, the formation of domains in the form of islands leads to a significant change in the dimension even for small differences in the intensity levels that can be related to the structural inhomogeneity of graphene regions, where regions with a small number of graphene layers (small change in dimension (from 2) from 0.1 to 0.4 of the intensity level, Fig. 6) are combined with regions with larger number of layers and less developed boundaries. The reason for this inhomogeneity is the insufficiency (which is most likely associated with a short time of the deposition process at the used temperature) of the diffusion mobility necessary for the formation of flat uniform graphene domains. At longer times (20 and 30 min), a more uniform decrease in the fractal dimension is noticeable that is associated with an increase in the uniformity of the formed graphene regions, as well as with a change in the filling level of the substrate as a whole.

The most homogeneous structure of the formed graphene regions corresponds to a 30 min deposition, when the change in the threshold dimension is the least, and the curve has no sharp breaks (curve 3 in Fig. 6).

4. CONCLUSIONS

Thus, the approbation of optical microscopy as an express method for studying the morphological properties of the formed "graphene/copper substrate" system allowed to reveal the presence of the most probable areas for the formation of graphene domains (~ 13 μm^2) at short times (10-20 min) of the production process, and also to establish an increase in the homogeneity of the formed structural graphene elements when they are filled with increasing fractal dimension to a relatively narrow interval of 1.82...2.0 (HD of the image element 2.0 corresponds to uniform filling of the plane) at the maximum process time (30 min).

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