В роботі методом CVD в спеціальних умовах (низька температура підкладки, малі часи зростання) одержані зразки вуглецевих конденсатів. Використання спеціальних технологічних умов дозволяє досліджувати початкові стадії росту графенових шарів. Для аналізу впливу микронеоднородностей мідної підкладки на умови росту в роботі застосовувалися різні режими її електрохімічного полірування. Структурний стан поверхні досліджувався з використанням комп'ютерної обробки цифрових зображень поверхні з колірною сегментацією. Проведено металографічний аналіз більш 70 зразків і на підставі комп'ютерної обробки виділені три основні структурні елементи початковій стадії росту графенових шарів при конденсації. Це графенові шари, ділянки мідної підкладки і скупчення атомів з відмінним від графена структурним станом (імовірно аморфноподібним). Встановлено, що підготовку поверхні підкладки слід віднести до найважливіших технологічних операцій отримання якісного графенового покриття. При цьому виявлено, що використання в процесі полірування мідної підкладки багатокомпонентних електролітів дозволяє підвищити однорідність за розмірами структурних елементів шорсткості поверхні. Це призводить до збільшення площі поверхні формування графенових шарів вже в процесі початкових стадій росту (при відносно низькій, 700 ºC, температурі процесу).

Одержані результати свідчать про перспективність використання багатостадійного аналізу зображень (з використанням методу кластеризації) для оптимізації технологічних режимів отримання систем "вуглецевий конденсат/підкладка" з урахуванням вихідної шорсткості останньої

Ключові слова: вуглецеві конденсати, система графен/мідь, CVD процес, оптична мікроскопія, комп'ютерна обробка зображень, фазовий склад

UDC 539.216.2
DOI: 10.15587/1729-4061.2018.140970

A STUDY OF INITIAL STAGES FOR FORMATION OF CARBON CONDENSATES ON COPPER

Yu Dai*
E-mail: 1042531903@qq.com
I. Kolupaev
PhD, Associate Professor*
E-mail: kolupaev@kpi.kharkov.ua
O. Sobol
Doctor of Physical and Mathematical Sciences, Professor*
E-mail: sool@kpi.kharkov.ua
*Department of Materials Science
National Technical University
"Kharkiv Polytechnic Institute"
Kyrpychova str., 2,
Kharkiv, Ukraine, 61002

1. Introduction

In recent years, structural engineering at the nanoscale is the most used method for obtaining materials with specified characteristics [1, 2]. The materials thus obtained have high functional properties [3, 4] and can have an unusual structural state [5] or form supersaturated solid solutions [6]. In the decay of such supersaturated solid solutions, a nanostructured state with a fractal dimension of the constituent elements can be formed [7].

As a result of using the method of structural engineering of the surface, it is possible to achieve uniquely high hardness [8, 9], adhesion strength [10], wear resistance [11], and electrically conductive properties [12].

One of the most promising materials obtained by nanostructural engineering is graphene [13, 14].

However, the widespread use of graphene and the prospects for further increasing the number of areas of its use [15, 16] require optimizing the technological methods for obtaining polygraphenic coatings and developing rapid control methods [17]. In most laboratories, a CVD technology for its growth on a substrate is used to produce graphene. In this case, with the growth of graphene, a “graphene/substrate” system is actually formed. This makes it essential to develop express optical methods for monitoring the state of the substrate surface before deposition, as well as controlling the growth conditions of the graphene coating.

2. Literature review and problem statement

Although graphene can exist in a stable state, its surface is not an ideal two-dimensional plane structure since some nanoscale microscopic folds may be present (Fig. 1) [18]. This is the simplest explanation of the stability phenomenon of graphene layers.

Graphene has high mechanical properties, and its measured values of tensile strength and elastic modulus reach 15 GPa and 11 TPa, respectively [19]. Graphene also has good light transmittance [20], and the permeability of single-layer graphene of electromagnetic radiation of visible and infrared wavelength ranges can reach 97.7 %. At the same time, there is practically no correlation of transmittance with wavelength [21].

When graphene is obtained by the CVD method, it is grown on a substrate, so it is very important to choose a suitable growth surface [22]. When choosing a substrate, it is necessary to take into account 3 factors [23]:

– thermodynamic (the melting point of the metal);

– catalytic (the ability to decompose molecules of a carbon source);

– chemical (whether there is a carbide phase during the growth process and whether the coating undergoes a phase change in the process of lowering the temperature from the growth temperature).

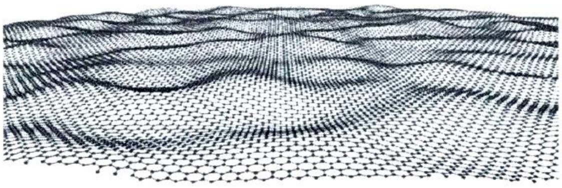


Fig. 1. A pattern of the real surface of a stable graphene layer

At present, metal substrates are mainly used [24]. Most often, Ni [25] and Cu [26] are used as metallic substrates. Data on graphene grown on a Cu substrate were originally published in [27]. It was believed that there was no appreciable interatomic interaction between the copper substrate and graphene grown on it that would require matching of the gratings. However, it was established in [28] that, in comparison with a crystallographic plane with a high index on a crystallographic plane with a low index and fewer defects, there appeared a large area of single-layer graphenes.

The authors of [29] succeeded in obtaining graphene on the surface of liquid copper. Compared with the surface of solid copper, due to the absence of defects (such as grain boundaries) on the surface of liquid copper, the rate of nucleation of graphene is lower, but the distribution is more homogeneous.

Temperature is an important factor affecting the growth of graphene. In studies [30, 31], CH_4 was used as a carbon source to study the nucleation and growth of graphene in the temperature range of 720–1050 °C. The studies have shown that as the temperature increases, the density of nucleation of graphene decreases, and the size of individual grains increases.

Three important components of the deposition process of the graphene layer from adsorbed carbon atoms have been established. The first (in importance) components are the rate and density of nucleation of graphene islands. Other important components are the diffusion mobility of carbon atoms on the copper surface and the desorption of adsorbed carbon atoms. The effectiveness of implementing all three processes during sedimentation is determined by the temperature. In particular, with a change in temperature, the activation energy of nucleation strongly changes [32]. Thus, at temperatures below 870 °C, the coating has an islet shape [33, 30]. In this case, analysis of the shape, size, and other parameters of graphene domains according to optical microscopy can be an effective way to clarify the mechanisms of growth of the coating as a whole.

In addition, at present, there remains the need to determine the fundamental parameters of the initial stages of the graphene growth process. This is the basis for creating technologies with controllable functional parameters of graphene films. Therefore, a promising task, both from the fundamental and from the practical points of view, is to study the mechanisms of nucleation and growth of graphene domains on the substrate surface (as well as other aspects of the initial stages of the formation of carbon coatings).

3. The aim and objectives of the study

The aim of the work is to study the influence of the structural state of the copper coating after different polishing regimes on the regularities of the initial stages of graphene domain formation in the "graphene/copper substrate" system.

To achieve this aim, the following objectives were accomplished:

– to test the model of color segmentation as an express method for technological recommendations determining the CVD process of formation of the "graphene/copper" system;

– to determine the effect of electrolyte compositions based on orthophosphoric acid on the distribution of micro-inhomogeneities of the surface of a copper substrate after electrochemical polishing;

– to specify the microstructural state of the copper substrate that ensures the most effective growth of graphene layers at the initial stages of formation (at a relatively low temperature of 700 °C).

4. Methods of polishing a copper substrate, deposing carbon layers, carrying out metallographic research, and performing computer image processing

Copper foil (99.9 % Cu) with a thickness of 30 μm was used as a catalyst support. The foil was washed in an ultrasonic bath of sodium laurit sulfate, acetone and propanol (10 min). To remove contaminants, the foil was washed then in distilled water.

To obtain copper coatings with different surface roughness, three electrochemical polishing technologies were used. The electrolyte compositions and the main process parameters were as follows:

– Technology <1>. Electrochemical polishing in the electrolyte of composition: H_2SO_4 (14 %) H_3PO_4 (59 %), CrO_3 (0.5 %) and H_2O (26.5 %); the current density was 20...50 A/dm^2; the process temperature was (16...25) °C;

– Technology <2>. Electrochemical polishing in the electrolyte of composition: H_3PO_4 (75 %), CrO_3 (7.5 %) and H_2O (17.5 %); the current density was 30...50 A/dm^2; the process temperature was (65...75) °C;

– Technology <3>. Electrochemical polishing in the electrolyte of composition: H_3PO_4 (37 %), CrO_3 (15 %), HNO_3 (7 %), HCl (0.5 %) and H_2O (40.5 %); the current density was 10...35 A/dm^2; the process temperature was (15...25) °C.

Foil after electrochemical treatment was transferred to the chamber for CVD deposition of carbon coatings.

Graphene-like layers were grown by the method of deposing from the gas phase onto copper substrates. Synthesis of graphene-like layers on the surface of copper foil was carried out in an apparatus schematically depicted in Fig. 2.

The parameters of the deposition process are given in [34]. When obtaining samples, a low (compared with the technologically optimal [30]) substrate temperature (700 °C) during the deposition of the carbon film was used. Also, to study the initial stages of carbon film growth, a short exposure time (10 min, 20 min, and 30 min) was applied.

Metallographic examination of the samples was carried out using the Optika XDS-3MET microscope (Italy). A series of images obtained under identical recording conditions served as initial data for further computer processing. The task of computer image processing was to segment areas of carbon coating, based on color differences. The processing was carried out while using the MATLAB system (IPT software package) [35]. The most used image processing algorithm is as follows:

– transition from the original (rgb) image format to monochrome;

– distinction of intensity by a given number of levels;

– selection of image objects by their belonging to the chosen level [36]. Separate tasks of image analysis were solved by the method of developing their own algorithm, which uses the standard functions of the IPT package.

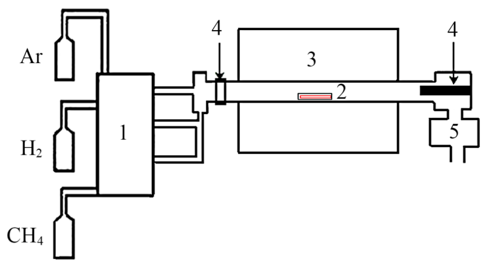


Fig. 2. The diagram of equipment for CVD synthesis of carbon condensates on a copper substrate: 1 — a chamber for supply of working gases, 2 — a copper substrate, 3 — the furnace, 4 — water cooling, 5 — a filter

For statistical processing, the use of the method of cluster analysis of color space is more informative (in terms of its processing capabilities of spectral regions with different intensity of the color spectrum). Therefore, the work was approbated using this method as an express approach to analyzing and controlling the morphology of growth of graphene layers. To use the method of cluster analysis of color space, the transition to the (L*a*b) format was first carried out [36]. This format makes it possible to quantitatively distinguish colors without taking into account the “brightness” (intensity in the color spectrum) of the image. After that, the data array was processed by the “clustering” method based on a specified number of color-coded sections (color clusters).

The image processing algorithm was tested on model samples of images having predetermined morphological parameters.

5. The results of studying the morphology of the substrate and deposed carbon condensates by computer processing of optical surface images

At the first stage of the research, the influence of different technologies of electrochemical treatment on the morphology of the surface was studied. As a comparison element, the statistical distribution of the surface roughness was chosen.

Analysis of the histogram distribution of surface microinhomogeneities by size (Fig. 3) makes it possible to determine the parameter of the statistical measure of roughness, Jbw [36, 37]. The choice of the parameter Jbw is related to its successful ([36]) application in the analysis of image areas of different intensity (texture), which is precisely related to the geometry of the real surface relief.

In view of the fact that the parameter Jbw is determined by the statistical measure, it can be used to compare the influence of the electrochemical processing regimes on the micro roughness of the copper substrate. To do this, the filtering of the structural components of the elements is performed in the source image (column on the left of Fig. 3). The resulting image is translated into a binary (in color) and a histogram of the distribution of structural elements of roughness in size is constructed. Based on the received histogram (right column of Fig. 3), Jbw is calculated.

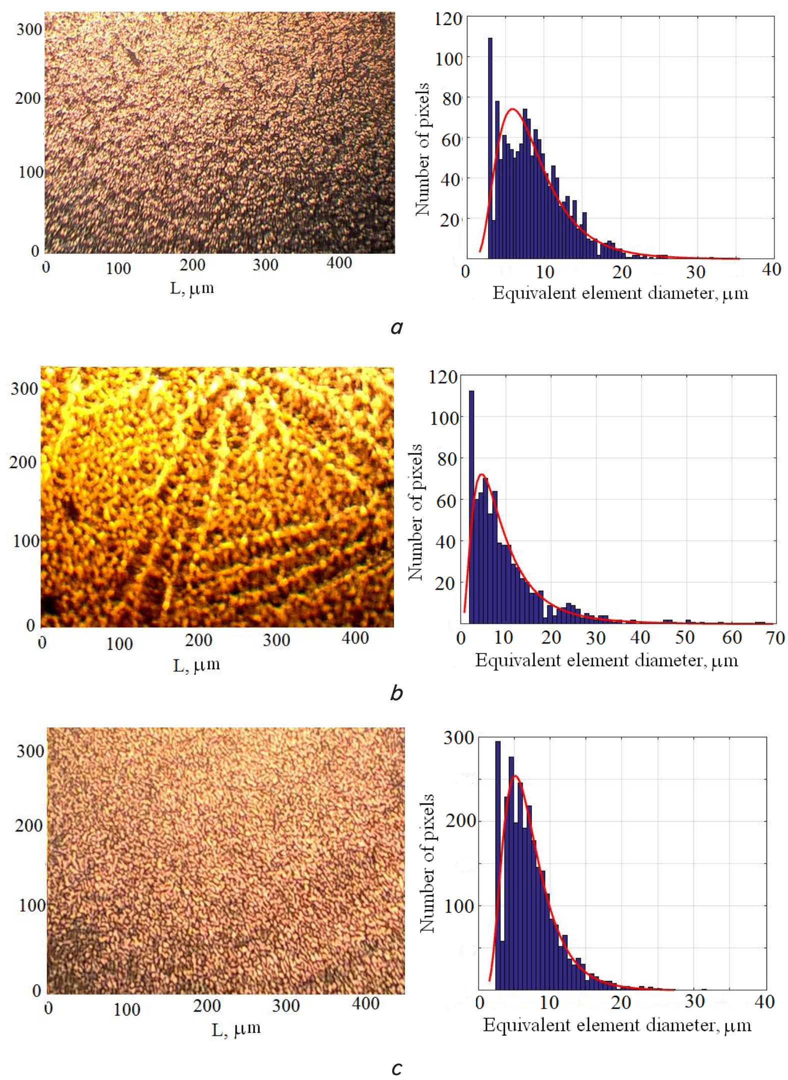
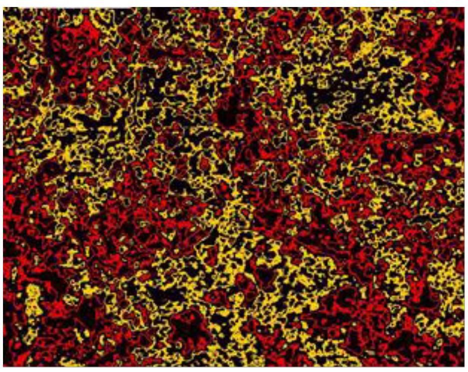


Fig. 3. The surface morphology (left) with the corresponding histogram of the distribution of the elements of this image (right) for the surface polishing modes: *a* — technology <1> (Jbw=0.9177), *b* — technology <2> (Jbw=0.8501), *c* — technology <3> (Jbw=0.9351)

The second stage of the research was aimed at the choice of informative computer processing of the image of a copper surface after the deposition of carbon layers. In this case, the study of the morphology of separately located graphene domains should be based on the assumed model of the phase composition of graphene coatings at the “island” stage when segmenting the image of optical microscopy. On this basis, the basic structural elements in the segmentation were graphene layers (referred to as "phase (Y)" or "yellow phase") and a copper substrate (referred to as "phase (R)" or "red phase"). An example of such an allocation is shown in Fig. 4.

a



b

Fig. 4. Segmentation of the image of optical microscopy: *a* – images of graphene coating on a copper substrate (substrate polishing technology <1>, deposition time 10 s, optical magnification ×1000); *b* – binary separation of the phases "(Y)" and "(R)" in the image (the relative phase content is 15 % and 21 %)

It can be seen that the division into two components leads to a total area of less than 100 %. This is due to the presence of a third component, which is presumably based on graphene-like forms of carbon (such as amorphous) and impurity aggregations of atoms. In the study, it is proposed to designate it as "phase (G)", or "green phase".

The use of this method of image processing makes it possible to compare the results of the initial stage of growth of graphene layers with previous studies of later stages (at a high deposition temperature of 1000 °C). As was shown in [34], in this case, the use of scanning Raman spectroscopy made it possible to identify the color range of the "phase (Y)" (detected from optical microscopy images) as corresponding to graphene domains.

For the analysis of a multicolor image without considering the influence of different intensity of the color spectrum, it is convenient to use the method of cluster analysis of the color space with the transition to the (*L*a*b*) format. At the same time, the specificity of the copper/graphene system in the study by optical microscopy (as was shown in a number of works [34, 38, 39]) is that when the graphene sites on the copper surface are separated, the color characteristic (*L*a*b*) is almost completely connected with the "a" axis. A preliminary experimental verification established that the addition of the remaining parameters *L*a*b* of space has practically no effect on the result, except for the obvious complication of the processing procedure.

In this study, the objects of the image were selected on the basis of proximity in the chosen color space (an example of such an allocation is shown in Fig. 5). After the allocation of the required color area on the metallographic images, statistical processing and finding of the area for each selected element were carried out. The use of such an algorithm made it possible to compare the various technological regimes for obtaining carbon coatings.

In the upper part, Fig. 5 shows the sections chosen on the image under examination as the "standard" phases of the condensate. Each of the sections is considered in the format (*L*a*b*), and the graph below shows the approximation of the data along the "a" axis: the probability density function from the conventional scale of the *L*a*b* format (–100, 100). As can be seen from the figure, the distribution of the "red phase" (1), "yellow phase" (2), and "green phase" (3) are markedly different. The method of statistical processing solved the problem of determining the proportion of each phase. The results obtained in terms of percentage are shown in Fig. 5, *b*.

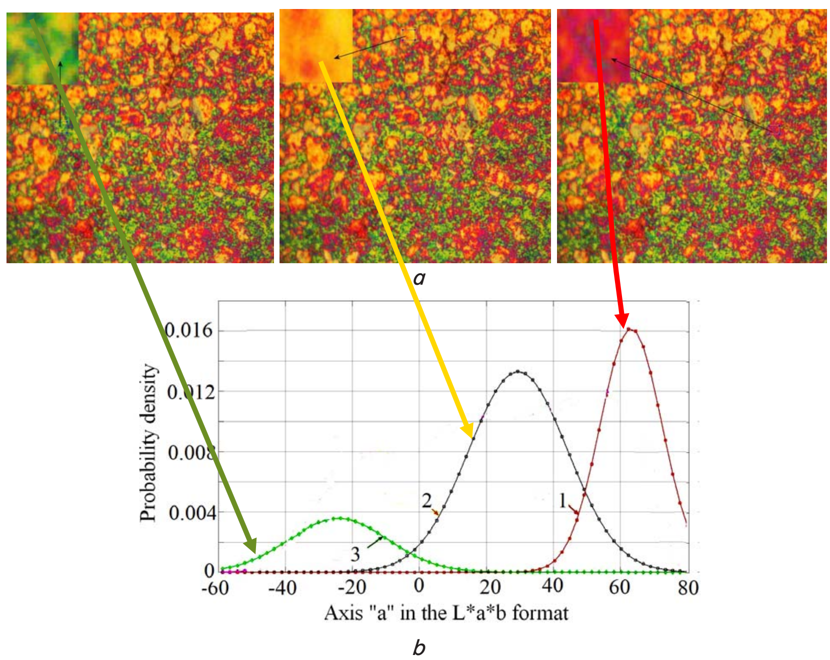
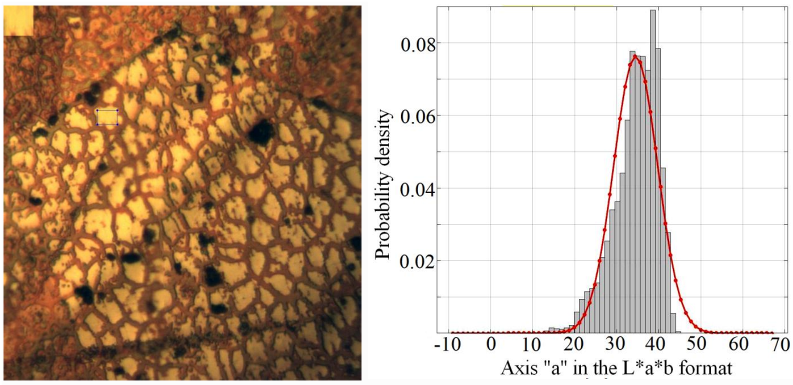
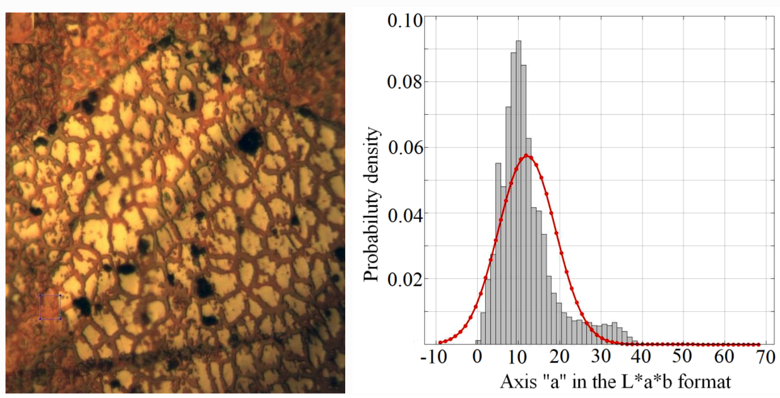


Fig. 5. Determination of the phase composition of the carbon coating on a copper substrate by statistical processing in the model of three components (different in color): *a* – selected areas of the image ("green phase", "yellow phase", "red phase"), *b* – simulation results on intensity distribution in the *L*a*b* format: 1 – "red phase" (37 % of the area); 2 – "yellow phase" (49 % of the area); 3 – "green phase" (14 % of the area)

Fig. 6 shows the results of processing the optical image of an already certified graphene coating on a copper substrate (deposition was carried out for 30 minutes at an optimum temperature of about 1000 °C). The histogram of the distribution is used as the comparison parameter (the histogram shows the frequency of the intensity levels (the “a” axis) in the conventional scale of the format L^*a^*b (–100, 100)).



a



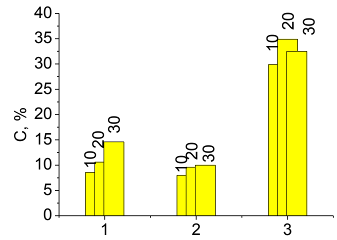
b

Fig. 6. The results of processing the optical image of a certified graphene coating on a copper substrate: *a* – the selected area corresponding to the graphene layer (on the left) and a histogram (in the L*a*b format) of this image area (right); *b* – the type of the selected area of the corresponding copper substrate (on the left) and the histogram of this section of the image in the L*a*b format (on the right)

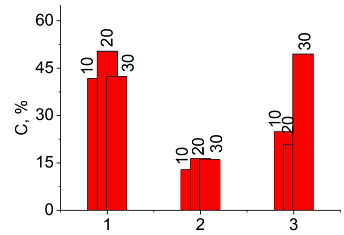
In comparison with the results of [34, 39], the areas determined by the color region as “phase (Y)” correspond to the layers of graphene (Fig. 6, *a*). The sections of the “phase (R)” (the form of which is shown in Fig. 6, *b*) are defined for the reference sample as a copper matrix [39]. After the comparison, the identified images can be used to study the more complex initial stage of graphene growth (at a low deposition temperature of carbon condensate), which is researched in this study. However, in this case, as shown in Fig. 5, the separation of the spectrum must be carried out in three components.

Thus, to analyze the initial stages of growth, according to optical microscopy, there were 3 characteristic color ranges that corresponded to “phase (Y)”, “phase (R)”, and “phase (G)”.

The results of processing optical images of the surface microstructure for different conditions of electrochemical treatment of a copper substrate and the deposition time of carbon condensates are presented in the form of histograms in Fig. 7.



a



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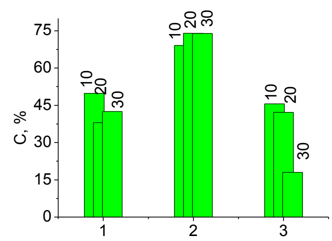

c

Fig. 7. The content of the structural constituents in the sedimentation (700 °C on the substrates <1>, <2>, and <3>) for 10 min (columns “10”), 20 min (columns “20”), and 30 min (columns “30”); *a* for “phase (Y)”, *b* for “phase (R)”, and *c* for “phase (G)”

It can be seen that the smallest content of the transition (impurity) phase (G) is observed in condensates deposed on copper substrates of series <3> (Fig. 7, *c*, columns <3>). In this case, the content of “phase (G)” decreases with increasing the process time (from 10 to 30 minutes).

6. Discussion of the results of studying the influence of substrate surface morphology and deposition regimes on the composition of deposed carbon condensates

Comparison of the results obtained under the conditions of the initial stages of growth of carbon coatings (Fig. 7) with initial surface characteristics (Fig. 3) shows that the largest relative area of graphene layers is formed on substrates of series <3>. Note that for substrates of series <3> the largest value of Jbw=0.9351 is characteristic. Thus, the more homogeneous (in terms of the dimensions of the structural elements of the roughness) becomes the distribution of the surface roughness (parameter Jbw tends to unity), the more likely the nucleation of the graphene layer, as evidenced by the increase in its relative content (Fig. 7, *a*).

For samples with preliminary electrochemical surface treatment of copper technologies <1> and <2>, the content of “phase (G)” is greater than 40 % for all the duration of the deposition process (Fig. 7, in columns <1> and <2>). It should be noted that a relatively large scatter in the sizes of the structural elements on the surface of a copper substrate after polishing for mode <2> (*Jbw*=0.8501) causes a significant increase in the relative content of transition (disorderly, containing impurity formation) in “phase (G)” (Fig. 7, *c*). Besides, the graphene component decreases (Fig. 7, *a*).

The obtained results testify to the prospects of using multi-stage image analysis (applying the clustering method) to optimize the technological regimes for obtaining the “condensate/substrate” systems, taking into account the initial roughness of the latter. The study of the initial stages of the formation of graphene domains is of interest for determining optimal technological regimes (in terms of growth rate and area of formation). It should be noted that already based on the data obtained in the work, it is clear that there is the importance of controlling the relief of the copper substrate before condensation. This concept includes not only the geometric roughness but also the distribution of the nucleation centers of graphene domains with the growth of the carbon coating. Due to this technological parameter, such as preparation of the substrate surface, great attention must be paid to all technologies for obtaining the graphene coating on copper. In this case, copper as a coating on other types of substrates can be an effective growth surface for graphene, which will be the subject of further development of this study.

7. Conclusion

1. It has been shown that the use of the color segmentation model in computer processing of the surface images of the “graphene/copper substrate” system helps identify three main components: graphene, copper substrate, and accumulation of deposited atoms in the transition state.

2. It has been established that the inclusion of nitric acid in the electrolyte during electrochemical polishing makes it possible to obtain the most uniform microstructure with the highest parameter of the statistical measure of roughness *Jbw*=0.9351.

3. It has been revealed that at the initial stages of graphene formation (at a temperature of 700 °C), the largest relative to the content of the graphene phase (more than 33 %) on the growth surface is observed when deposited on a copper substrate with the most uniform size of microstructural roughness elements (*Jbw*=0.9351).

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