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Polygraphene Coatings on Copper: Mechanisms of Nucleation and Growth

I.N. Kolupaev[1,*], A.V. Murakhovski[1], T.S. Koltsova[2], V.O. Sobol[2], Dai Yu[1]

[1] National Technical University «Kharkiv Polytechnic Institute», 2, Kyrpychov Str., 61002 Kharkiv, Ukraine
[2] Peter the Great St. Petersburg Polytechnic University, 29, Polytechnic Str., 195251 Saint-Petersburg, Russia

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Samples of polygraphene layers on a copper substrate were obtained using CVD technology. For the preparation, a gaseous mixture of methane, hydrogen and argon was used. To analyze the degree of filling and the specific area of the polygraphene formed on a copper substrate, we used optical microscopy (with specialized computer image processing) in combination with Raman spectroscopy and atomic force microscopy. It is proposed to use the approach based on the double structure model (transparent regions of graphene and copper) for evaluating the morphological parameters of the coating of polygraphene on a copper substrate. This approach is used for the primary optimization of the production process of polygraphene formation. The mechanism of initial stages of polygraphene growth on copper is proposed.

Keywords: Polygraphene coating, Optical microscopy, Surface morphology, Computer processing, Fractal dimension.

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1. INTRODUCTION

In recent years, structural engineering at the nanoscale is the most developed direction [1, 2]. Have been obtained new materials (for example, [3-5]), structural polytypes [6], single-layered [7], and multilayer [8] compositions. However, the most interesting structures conditions and properties were obtained in coating materials [9]. Carbon-based coatings are among the most popular [10]. This applies both to carbide coatings of the transition materials [11], and to various forms of pure carbon [12]. However, graphene coatings have the greatest prospects for use in modern technologies [13, 14].

The wide application of graphene and persisting prospects [15, 16] of this development require the optimization of technological methods for obtaining polygraphene coatings. They are consistently systematized in reviews [17]. The management of multilayeredness and defectiveness of coatings are presented among the main technological problems, not counting the transfer of graphene to practically attractive substrates [16, 17], in particular, copper.

The CVD coating production method is considered an optimal technology for polygraphene coatings production on metal substrates. The CVD process parameters (cooling rate, pressure in the reaction chamber during the synthesis process) obviously significantly affect the growth rate of graphene films, their thickness and defect density.

It is assumed, that in reaction zone methane diffuses from gas form to surface thru a boundary layer. Then, adsorbs to a substrate surface and defuses on the copper surface with the evolution of atomic carbon.

In the reaction zone methane from the gas phase diffuses as assumed to the surface through the boundary layer, adsorbs on the substrate surface, decomposes with the evolution of atomic carbon, which diffuses on the copper surface. The development of processes on the copper surface largely depend, even ideally, on both the substrate temperature and the rate of carbon supply to the surface, and the surface relief, not to mention the role of impurities, the appearance of which accompanies a real technological operation.

The preliminary annealing of the copper substrate [15] can be considered as the preventive measure for reducing the uncontrolled factors listed above. The prepolished copper substrate is annealed in an argon-hydrogen mixture to restore the copper grains perfection whose surfaces will interact with carbon. Such a procedure is widespread, although its effectiveness deserves a critical (but objective) discussion.

2. MATERIALS AND METHODS OF RESEARCHES

The study of the growth dynamics of graphene islands as a function of substrate temperature and deposition time base on a series of specially conducted experiments. The method of optical microscopy with computer image processing used as the main.

Copper foil of 25 μm in thickness was used as a substrate for graphene growth. It should be noted the difficulty of control the thickness of the coating. This concerns the number of layers of graphene, as well as the defectiveness of the coating. The next parameters have been varied within definite limits: the substrate temperature, holding time and system pressure [18].

The modern measuring system being used for the evaluation of graphene layers includes, in addition to optical microscopy and REM, a confocal Raman spectrometer and atomic force microscopy (AFM) [16, 19, 20]. In our opinion, Raman spectroscopy methods (Raman scattering, AFC) can be significantly supplemented by optical microscopy. Optical microscopy can be technologically attractive with the appropriate computer image processing, that makes it much more affordable than the first two methods [18].

* igor.kolupaev@gmail.com

When the analyzing the optical image of the growth surface was carried out in the work, special computer processing [21] is required to obtain the necessary information.

The basis of the multi-threshold segmentation method is the "three-dimensional" representation of the optical image, where the intensity scale is used as the Z axis. The separation of such an image on the turn number of sections (thresholds) leads to the possibility of evaluating the morphological parameters of each of the cross sections [21].

3. RESULTS AND DISCUSSION

The evaluation of the surface relief of a copper substrate as a future growth surface of GCC was carried out by optical microscopy.

M4 assumes that the substrate roughness has a "double scale": (1) the size of the sections (111) or (110) planes Cu (other crystallographic orientations are also allowed, but not detect in practice) and (2) the characteristic dimensions of polycrystalline copper blocks.

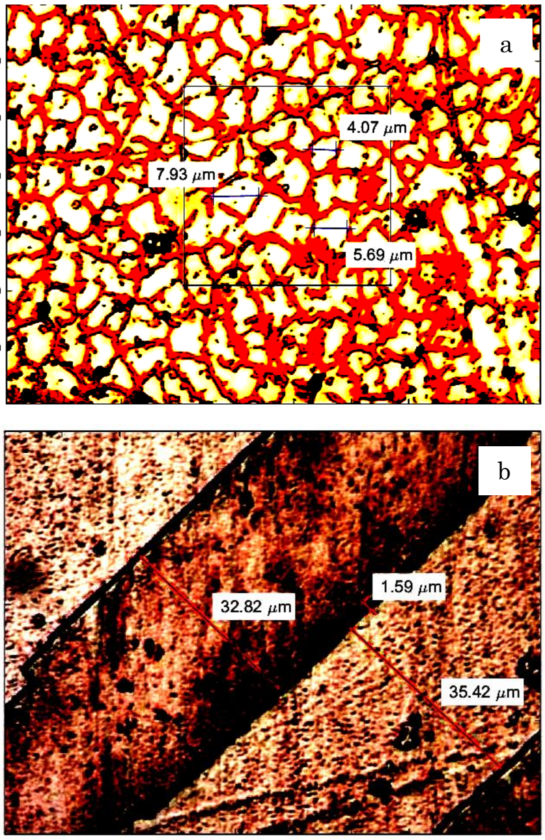


Fig. 1 – The scale of typical sizes of substrate places and polygraphene coatings under straight measurement: a) polygraphene; b) matrix of copper.

The comparison sizes characteristic in Fig. 1 does not give grounds for concluding that the scale of the grains of the polycrystalline copper (30...40 μm) after annealing play a significant role on the final size of the graphene domains (5...7 μm). This conclusion no doubt based on the data of optical microscopy and, of course, is not intended to assess the details of the nanoscale.

X-ray study of the orientation of the grains of copper at all stages of its preparation leads to ambiguous conclusions about the development of recrystallization processes. In any case, the ratio of grain orientations of (111)/(200) parallel to the surface, even though after rolling increases but does not exceed 0.5 ... 0.6.

The determination of the number of graphene domains per area unit (surface density) is no more than additional estimate of the relief influence of the substrate.

For this purpose, the computer analysis of the images was carried out on the assumption about an isotropic growth of the graphene island in the region of the perfect substrate plane. It is assumed by default that the growth of the domain occurs by attaching the carbon atoms entering the surface to the perimeter of the island. Thus, considering the "reverse evolution" of the growth process, one can draw a conclusion about the initial density of nucleation centers.

Each domain allocated as an element of the image was reduced to the point size (pixel); Its location is determined by the "center of mass" of the flat domain. After that, a part of the surface plane of the substrate was calculated. Carbon atoms according to this model were supplied to form a domain from these finite areas.

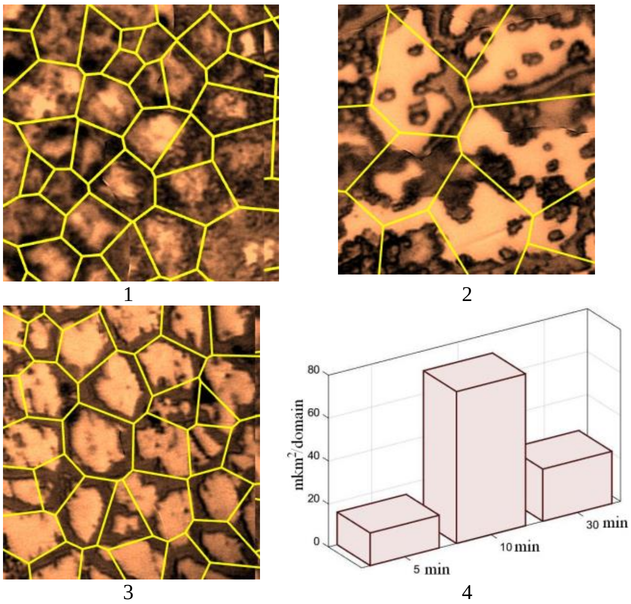


Fig. 2 – Comparison of the density of putative nucleous against the time of graphene growth, ×800. (1) exposure time 5 min, (2) 10 min; (3) 15 min; (4) the nucleation center density diagram (1, 2, 3), μm²/domain

Fig. 2 shows the comparative results of such an assessment for different exposures of the CVD regime, all other conditions being equal. The possibilities of studying GCC by optical microscopy are not limited to assessing the relief of the substrate and, in the opinion of the authors, can be extended.

Fortunately, traditional methods (electron microscopy: REM and TEM, atomic force microscopy, and of course confocal Raman spectrometry) make it possible to objectively relate to the results of processing optical microscopy images in a specific study.

The known obtained images of graphene on a copper substrate, by [16, 22, 23], show that the change in the thickness of the coating, lead to the changes of substrate contrast that we observe "through the coating".

This gives to the optical microscopy a chance for successful application in such a study.

The M4 mechanism, which proposed, includes four components: actually, a copper substrate and three "phases" of the coating. These include monographene (1..3 layers), multigraphene (more than three layers) and amorphous carbon, which, according to the proposed model, is primary.

The following procedure for computer processing of optical microscopy images is proposed to this end to identify a polygraphic coating on a copper substrate. An object is selected on the image (segmentation), then it transformed into the color space of four levels, each of which corresponds to one of the GCC phases.

The number of levels of color space determines the same model mechanism of coating formation (M4), which was discussed above. Fig. 3 shows all four phases (the contrasting colors are chosen for clarity). Such a technique allows to discuss the morphology and the ratio of the volumes of each phase, which exists as the M4 mechanism assume, in order to visually assess its adequacy.

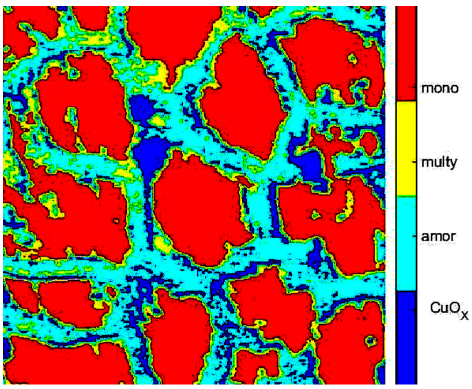


Fig. 3 – The relative arrangement of the phases of the coating, which are assumed by the M4 mechanism

This data processing was performed for a series of GCC samples. As a result, it becomes possible to construct and examine the histogram of the arrays of the area of each of the phases of the coating, depending on the process time or substrate temperature, Fig. 4. Such a diagram is expected to have technological value.

4. GROWTH MECHANISM

Growth patterns and homogeneity control of graphene coatins on copper (GCC) are considered by software processing of surface relief images. The aim of such studies is as possible the modeling of physical mechanisms of the graphene layers growth on a copper substrate and the proposing on this basis the practical recommendations.

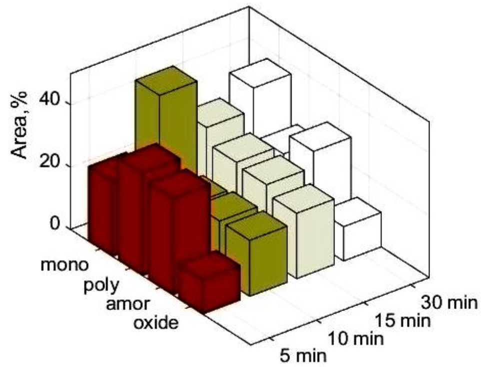


Fig. 4 – Comparison of the relative area occupied by the prospective M4 phases of the graphene coating on copper

Such mechanisms of GCC formation, even with obvious simplifications, should take into account the following assumptions:

1. Formation of nucleus of amorphous carbon and graphene domains is carried out at the same time;
2. The filling of the surface of a copper substrate with amorphous carbon and graphene domains, as elements of the structure of the coating, must take into account their competitive interaction in the growth process;
3. Surface (relief) defects of a substrate of structural and chemical nature affect the formation of the GCC coating;
4. With the increase of the coating thickness due to the increase of exposure time of the technological process, the number of layers of graphene in the area of the multigraphne changes.

Such a mechanism (M4) of GCC coating formation, despite generally ordinary assumptions (1...4), is the basis for a comparative study of the structure of graphene (polygraphene) coatings obtained by different exposures on a copper substrate in the state provided by CVD technology.

5. MODEL OF RELIEF CHANGES

The development of events in the formation of a graphene coating occurs, as suggested by the M4 mechanism, as follows.

Islets of amorphous carbon form on the surface defects of the copper substrate. On the one hand, this leads to a decrease in the surface energy of the substrate, on the other the metastable amorphous phase (amor) of carbon is kinetically more attractive when adsorbed carbon atoms form a macroscopic phase.

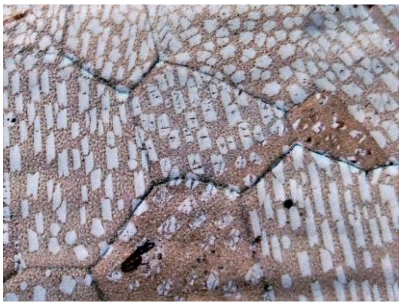
The monolayer of graphene (mono) begins to grow according to a favorable crystallographic orientation relative to the substrate. The beginning of growth occurs from the perimeter of amorphous islets. The growth of the graphene layer is controlled by the diffusion of carbon atoms along the domain boundary Such a process can be inhibited by a number of factors: chemical contamination of the substrate, relief defects, effects of the plasma, and others. The growth of the multilayered domain (multi) in this case begins by building up layers of graphene, starting from the amorphous layer.

As a result, the graphene coating on copper consists of four components, which are provided by the M4 mechanism and are detected by optical microscopy.

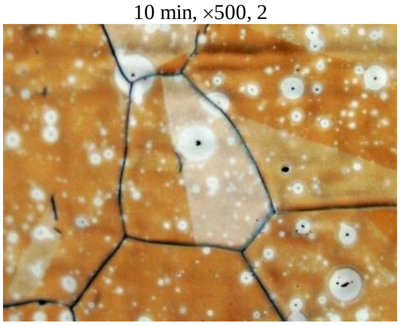
These include the remains of islets of amorphous carbon as the boundaries between domains, areas of mono- and multigraphene, as well as areas of a copper substrate without carbon coating. In the latter case, it may be a surface of a layer of copper oxide (oxide).

The reasonableness of the M4 mechanism's predictions was checked on samples obtained at as possibly low temperature. These studies were carried out by the same method and showed that the graphene islets are elongated and have the same direction of the larger axis, Fig. 5.

5 min, ×500, 1



10 min, ×500, 2



20 min, ×500, 3

Fig. 5 – Growth of graphene islands on a copper substrate (minimum time)

The growth rate in the substrate plane is not the same. There is a growth hindrance to the small islands near the large ones and so the hardness to fill the whole grain of the substrate. There are no islands of "intermediate" size (shape).

The texture of the substrate look like if the face (111) comes to the surface: this is indicated by the characteristic triple joints of the grains (Fig. 6, yellow). The rolling bands of the foil are also found after annealing, but they have little effect on the nucleation of graphene domains. The islets have a rectangular shape, right angles presented (Fig. 6, green). They are stretched in one direction in one grain, the ratio of the sides is 1:3 ... 1:4 (Fig. 6, white arrows on the islets). Dark spots in the middle of domains are not observed everywhere.

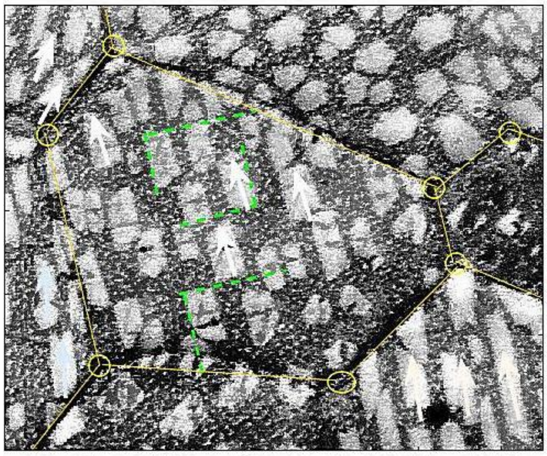


Fig. 6 – Scheme of estimation of morphology of graphene islets (Fig. 5, sample 2).

The growth process of the different area domains fractions as show may be different. Such conclusion directly link with the M4 mechanism's predictions. The statistics (clustering) of the three groups of graphene islets is only a first step in a long way to check and prove real relation between surface profile and graphene growth kinetic. The number of clusters (1...3) been used as parameter (Fig. 7).

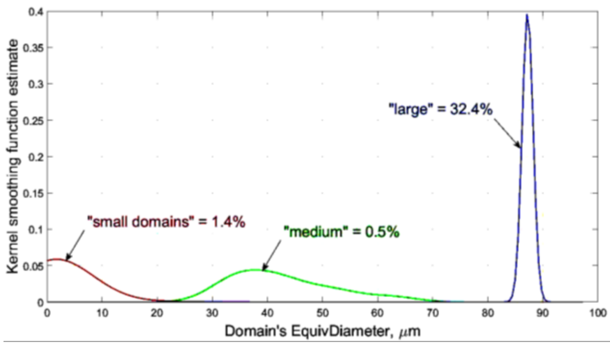


Fig. 7 – Statistics of the three groups of graphene islets (Table 1, sample 2). The results of approximation the experimental data of an array of the equivalent diameter of graphene islands by a smoothed distribution kernel function are presented

Part of the image area occupied by "small domains" = 1.4 %, "medium" = 0.5 %, "large" = 32.4 %. The average area of one image element is "shallow domains" = 1.8 μm^2, "medium" = 38.0 μm^2, "large" = 87.1 μm^2.

6. CONCLUSION

Computer image processing allows the quantitative description of a system of graphene islands on a copper substrate. The color's analysis provides an additional opportunity for segmentation of an inhomogeneous graphene coating on copper.

An M4 mechanism for the GCC formation remains the basis for the discussion of surface defects influence.

The relief of the substrate plays a significant role in the sequence of growth processes of the graphene layer. The proposed mechanism basis of its own data and does not contradict known concepts. It assumes the formation of islets of amorphous carbon as the first phase in the defective places of the relief of the substrate. The next graphene layers of different degrees of perfection are subsequently formed.

Поліграфенові покриття на міді: механізми зародження та росту

І.Н. Колупаєв[1], А.В. Мураховський[1], Т.С. Кольцова[2], В.О. Соболь[2], Dai Yu[1]

[1] *Національний технічний університет «Харківський політехнічний інститут», вул. Кирпичова, 2, 61002 Харків, Україна*
[2] *Санкт-Петербурзький державний політехнічний університет Петра Великого, вул. Політехнічна, 29, 195251 Санкт-Петербург, Росія*

Зразки поліграфенових шарів на мідній підкладці були отримані за технологією CVD. Для отримання використовували газоподібну суміш метану, водню і аргону. Для аналізу ступеня заповнення і питомої площі поліграфії формованого на мідній підкладці використовувалася оптична мікроскопія (зі спеціалізованою комп'ютерною обробкою зображення) в поєднанні з методами спектроскопії комбінаційного розсіювання та атомно-силової мікроскопії. Запропоновано використовувати підхід на основі моделі подвійної структури (прозорі області графена і міді) для оцінки морфологічних параметрів поліграфенового покриття на мідній підкладці. Цей підхід використовується для первинної оптимізації виробничого процесу формування поліграфена. Запропоновано механізм початкових стадій росту поліграфену на міді.

Ключові слова: Поліграфне покриття, Оптична мікроскопія, Морфологія поверхні, Комп'ютерна обробка, Фрактальна розмірність.

Полиграфеновые покрытия на меди: механизмы зарождения и роста

И.Н. Колупаев[1], А.В. Мураховский[1], Т.С. Кольцова[2], В.О. Соболь[2], Dai Yu[1]

[1] *Национальный технический университет «ХПИ», ул. Кирпичова, 2, 61002 Харьков, Украина*
[2] *Санкт-Петербургский государственный политехнический университет Петра Великого, ул. Политехническая, 29, 195251 Санкт-Петербург, Россия*

Образцы полиграфеновых слоев на медной подложке были получены по технологии CVD. Для получения использовали газообразную смесью метана, водорода и аргона. Для анализа степени заполнения и удельной площади полиграфена формируемого на медной подложке использовалась оптическая микроскопия (со специализированной компьютерной обработкой изображения) в сочетании с методами спектроскопии комбинационного рассеяния и атомно-силовой микроскопии. Предложено использовать подход на основе модели двойной структуры (прозрачные области графена и меди) для оценки морфологических параметров покрытия полиграфена на медной подложке. Этот подход используется для первичной оптимизации производственного процесса формирования полиграфена. Предложен механизм начальных стадий роста полиграфена на меди.

Ключевые слова: Полиграфеновое покрытие, Оптическая микроскопия, Морфология поверхности, Компьютерная обработка, Фрактальная размерность.

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