The effect of grains crystallographic orientations of copper substrate on graphene growth

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Abstract. The influence of orientation of copper crystal on the processes of methane decomposition and the growth of graphene layers is studied in this paper. It is shown that crystal nucleus growth rate and coating formation rate are different on copper grains with different crystal orientation. Maximum coating formation rates are recorded for 110 planes. Maximum crystal growth rate and maximum size of graphene single crystals in a film are observed for 100 plane. The difference in the growth rates of the graphene coating is explained by the difference in the kinetics of decomposition of methane and the diffusion rates on surfaces with different crystal orientation.

1. Introduction

Graphene with a unique two-dimensional hexagonal carbon structure is one of the most promising materials in various fields of materials science. It has excellent charge carrier mobility, thermal conductivity [1-2] and optical transmission, which may open the way for unexpected technical solutions when creating various electronic devices. For the production of such graphene-based electronics, a chemical vapor deposition (CVD) method was developed for the synthesis of graphene on various metal substrates [3]. Copper foil is used as the most common material of the substrate due to the low cost of its processing and the possibility of obtaining a monolayer graphene coating of a large area [4]. In the chemical vapor deposition method, various physical parameters such as gas flow rate, substrate material and thermodynamic variables play an important role in the processes of graphene synthesis [5, 6]. A large number of parameters allows for very fine control of the synthesis process. However, there are a number of difficulties associated with the graphene growth stage.

The surface of the substrate has many peculiar properties, such as roughness, defects, impurities, size and orientation of the crystals - all these parameters may strongly influence the nucleation and growth of graphene domains. For example, flat and homogeneous regions lead to the formation of monolayer or bilayer graphene domains, while impurities and Cu nanoparticles on the surface of the substrate contribute to the formation of multilayer graphene domains [7, 8].

The above-described phenomena formed the basis of [9], in which a group of researchers studied the development of an approach to controlling the orientation of Cu crystals to obtain graphene domains of the desired shape (tetragon and hexagon shapes). In addition, the influence of the orientation of Cu crystallites on the size, number of layers, and the quality of the graphene domain was recently studied, which further demonstrates that the topography / morphology of the metal substrate has a significant effect on the uniformity of graphene. This was demonstrated in [10], where, using an ultra-flat and
electropolished copper substrate, it was possible to achieve the uniform graphene growth at low concentrations of methane.

Graphene grown by CVD is polycrystalline due to the presence of many nucleation centers on Cu substrates. The grain boundaries in polycrystalline graphene can have a negative impact on the unique properties of graphene. The dynamics of nucleation and growth of graphene play a crucial role in determining the quality of the resulting film.

The nature of the formation of nucleation centers, the growth rate, and the uniformity of graphene strongly depend on the crystallographic structure of the metal substrate. When polycrystalline copper was used, the growth of the most uniform graphene with a low number of defects on the Cu (111) planes was observed in [11]. Similar results were obtained by Wood et al. and published in [12]. The studies were performed using electron backscattering diffraction (EBSD); it was found that a defect-free graphene sheet is obtained only in the case of growth on the family of Cu (111) planes. However, another paper [13] describes the opposite picture: the (100) planes were identified as more preferable for graphene growth; in addition, the authors showed that the quality of graphene is controlled by active nucleation centers, rather than the atomic structure of the copper substrate. Such differences in the results can be explained by different conditions of CVD synthesis, such as pressure, gas concentration and temperature. The growth of defect-free graphene on Cu substrates with different crystallographic orientations in the Cu (100) or Cu (111) plane is still largely discussed. For example, in [14], the influence of the orientation of Cu crystallites was studied: it was demonstrated that graphene forms a uniform hexagonal structure on Cu (111) and, at the same time, a linear structure on Cu (100).

This research is aimed at studying the mechanism of controlled growth, as well as determining its various parameters, such as nucleation density and their growth rate on various crystallites of copper.

2. Experimental section
Synthesis was carried out on AlfaAesar copper foil, 99.8% Cu, 25µm thick. The synthesis chamber is a quartz tube placed in a furnace; the tube can be shifted to quickly remove the sample from the hot zone. The mixture of gases (Ar+H₂+CH₄) is fed through flow-regulators, creating a flow in the synthesis chamber. The copper substrate is placed to the synthesis chamber. Next, the chamber is evacuated, filled with Ar, and heated to the annealing temperature of 1070 °C. The substrate is annealed in the flow of H₂ during 30 min. Immediately after annealing, the working mixture Ar(95 sccm) + H₂(15 sccm) + CH₄(0.022 sccm) is fed into the chamber, the synthesis time was 10 min. The procedure is terminated with rapid cooling in an atmosphere of synthesis gases. Raman spectroscopy (RS) was used to determine the number of layers. The Raman spectrometer T64000 Horiba Jobin Yvon with a wavelength of exciting radiation of 514.5 nm was used for the research. To determine the crystallographic orientation of copper substrate grains, Electron backscatter diffraction (EBSD) was used with a Hitachi S-3400N scanning electron microscope. Analysis of the size of graphene domains and the degree of coverage of copper was carried out by the method of optical microscopy. For this, the copper substrate was heated to 190 °C and held for 10 minutes in air. Due to the annealing, the copper substrate has a color contrast caused by the presence of interfering phenomena in a thin oxide film. However, since graphene is impermeable to most gases, copper areas covered with graphene sheets (domains) do not oxidize and are present as light yellow areas against oxidized copper [15]. Optical images of the surface were obtained using an Olympus BX51M optical microscope. For analysis, we converted the image to monochromatic one, and using the ImageJ program, we estimated the degree of coverage of individual crystallites of copper with graphene as the ratio of the area of white areas, which corresponded to graphene domains, to the total area of copper crystallite. For copper grains with different orientations, the following parameters were determined: the average size of graphene domains, the number of domains per grain area (nucleus density), the percentage of grain area covered by graphene.
3. Results and discussion

The crystallographic map of the grains of copper substrate used in the synthesis of graphene by the method of chemical vapor deposition is shown in Figure 1a. The polycrystalline surface of metal substrate of the catalyst consists of many different crystallites, among which the dominant crystallographic plane with Miller indices (100) can be distinguished. The characteristic crystallite size is about 200 microns. Such a crystallite size distribution is typical for copper substrates that have passed the stage of annealing in a hydrogen atmosphere for 30 minutes. Longer annealing can lead not only to a change in the crystallite size, but also to a change in the dominant crystallographic plane. For example, in [16] annealing for 10 hours leads to the formation of a copper surface consisting mainly of crystallites with the (111) crystallographic direction.

![Figure 1](image-url)

**Figure 1.** (a) EBSD map of copper substrate; (b) The optical images of an annealed copper substrate with graphene domains.

The optical images of an annealed copper catalytic substrate with graphene domains synthesized on it (the area indicated by a frame in Fig. 1a) are shown in Figure 1b. To study the influence of crystallographic orientation on the growth dynamics of graphene domains, 4 sites were selected, three of which correspond to the main crystallographic directions (100), (110) and (111), as well as the site with intermediate orientation (438). The lateral size of the sites is 100-200 microns. The average diameter of graphene spots is 5 microns and varies in the range from 4 to 11 microns. Analysis on various grains of copper showed that the degree of coverage with graphene domains varies from 18 to 35%. The obtained data are present in table 1.

| Miller indices for copper grains | The area covered by graphene, % | The density of graphene domains on the grain, \( \mu m^2 \) | The average area of graphene domains, \( \mu m^2 \) | The average growth rate of graphene domains, \( \mu m^2/min \) |
|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| G(110)                          | 34,9                            | 0,007038                        | 49,6                            | 6,21                            |
| V(438)                          | 33,3                            | 0,006227                        | 53,4                            | 6,68                            |
| B(111)                          | 25,4                            | 0,004205                        | 60,4                            | 7,55                            |
| R(100)                          | 18,4                            | 0,002793                        | 65,9                            | 8,23                            |
Taking into account the synthesis time, which was 10 minutes (including 2 minutes spent on the transition process [17]) and the average size of graphene domains of 49.6 - 65.9 μm², the average growth rate will be 6.21 - 8.23 μm²/min for selected copper crystallites. Since all the sites were under the same synthesis conditions (temperature 1070°C, gas mixture H2/Ar/CH4), the difference in growth rates can be explained by the difference in graphene growth kinetics on different crystallographic planes of the metallic grains of the copper catalytic substrate.

On the SEM image (Fig. 2a), it can be seen that some of the graphene domains have a hexagonal shape. RS analysis (Fig. 2b) showed that all domains are a single-layer graphene. Line D in RS is at the noise level, which indicates an extremely low concentration of defects in the graphene domains obtained.

![Figure 2](image.png)

**Figure 2.** (a) SEM of copper substrate; (b) RS of graphene domains.

In the process of foil production, rolling lines remain on the surface. During the annealing stage, they are significantly smoothed [18]. It has been observed that the nucleation of graphene is concentrated along such lines. For example, this is clearly seen in the G(110) section. Also the characteristic sites of nucleation may be the boundaries of the cross-linking of copper crystalline grains, which is observed in section B(111). This phenomenon may be associated with an increased concentration of defects in the crystal structure of the copper substrate in these positions. Carbon clusters prefer to adsorb to certain sites, such as point defects, surface kinks, lattice vacancies, and steps [19].

The growth rate of the coating is determined by the flow of hydrocarbon fragments to the crystalline nucleus from the surface of copper, on which the adsorption and decomposition of methane fragments take place. As shown in [20], the growth of graphene on the copper surface occurs from the CH radicals and C2 dimers formed on the surface. The kinetics of decomposition of methane on different surfaces can vary significantly, which will affect the total flow of carbon fragments and, accordingly, the growth rate of the graphene coating. For our conditions, the maximum growth rates are achieved for surfaces G(110) and V(438), thus, the decomposition of methane on these planes is most effective, which may be due to the high surface energy (Es) of these planes [21]. For a group of metals with a face-centered cubic lattice, the surface energy value was calculated in the article [22]. For the main crystallographic orientations, it correlates as Es (111) < Es (100) < Es (110), in particular, for copper, these values are 938.67 ergs/cm², 1005.81 ergs/cm² and 1106.11 ergs/cm², respectively. For a surface with orientation (438), the closest surface is indicated by indices (211); it is characterized by a surface energy value 1114.53 ergs/cm², close to (110).

During the growth of a graphene crystal, the area from which the carbon fragments flow to the graphene nucleus is determined by diffuse processes on the surface, and the higher the diffusion rate, the larger the area and, accordingly, the lower the concentration of nuclei. For the studied regions, the
minimum concentration of nuclei and the maximum growth rate of a single nucleus are observed for the R(100) plane.

In the process of forming a continuous graphene film of graphene crystals, they are combined into a uniform layer, with the formation of lines of defects along the boundaries of the crosslinking. The concentration of these defects depends on the relative orientation of graphene crystals. From Fig. 1 it can be seen that the presence of the hexagonal shape of graphene fragments and their single relative orientation is characteristic for (111) regions. This effect is associated with the coincidence of the hexagonal symmetry of the graphite plane and the location of the atoms of the copper surface in the (111) plane. For (100) regions, the disorientation of growing graphene crystals is observed (Fig. 1). Thus, despite the larger average size of graphene single crystals on the (100) plane, their crosslinking leads to the formation of a larger number of defects [23], which makes it preferable to synthesize graphene structures on the (111) planes, characterized, among other things, by a higher growth rate of the graphene coating, table 1 [12].

G(110) and intermediate V(438) planes are characterized by high growth rates of the coating and small size of graphene crystals in the final graphene coating, which is a consequence of the high concentration of nuclei during growth. Graphene crystals not having the hexagonal shape and having the hexagonal shape but rotated relative to each other are also observed for these regions. The combination of such crystals into a uniform layer leads to the formation of a more defective coating than in the case of the (111) plane [23].

Conclusion
It is shown that the concentration of nuclei on different planes is different, which is associated with different scales of the regions from which the diffuse flow comes to the boundary of the forming graphene crystal. The growth rate of the graphene coating is determined by the flow of carbon fragments, which depends on the kinetics of the decomposition of methane on different planes, and is maximum for planes with high surface energy.

The highest growth rate of the coating, and the highest concentration of graphene crystals per unit area was observed on copper crystallites with an orientation of (110) and (438), which leads to the formation of structures with a large number of defects in comparison with the (111) and (100) planes.

The maximum growth rate of graphene crystals is observed for the (100) plane. However, the coincidence of the symmetry of the graphite plane and the structure of the (111) copper plane leads to epitaxial growth of graphene crystals oriented in the same direction. The combination of these crystals leads to the formation of a higher quality film than for the (100) plane.

Acknowledgements
This research was financially supported by the Russian Ministry of Education and Science. Project Identifier: RFMEFI60417X0157.

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