Modification of crystal structure of copper surface during graphene synthesis

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Abstract. The influence of annealing dynamics on the size and orientation of copper foil grains used for graphene synthesis at chemical deposition from the gas phase was studied. Annealing was carried out in argon and hydrogen atmospheres setting a constant temperature profile on the processed substrate and temperature gradient along the substrate. The temperature range and times were chosen in accordance with the regimes effective for graphene synthesis. It was shown that hydrogen has a significant effect on the growth of grains. Orientation of large grains, formed on the copper surface due to secondary crystallization, was random in the studied regimes.

Introduction
In connection with active development of applications using graphene to create transparent electrodes, sensory devices, solar cells, etc. [1], there is a need to develop the methods for synthesis of single-layer and multi-layer graphene for obtaining graphene crystals of a large area. The methods of chemical deposition from the gas phase, and especially methods using the Roll-to-Roll technology are the most promising now [2]. These technologies use foil, where the graphene planes are formed, as a substrate. The size and degree of graphene defectiveness depends essentially on the structure of the substrate surface. Graphene layers, formed on the grains with different crystallographic orientations, combine to form a large number of defects. In addition, the rate of graphene formation on different faces of the crystal lattice differs [3, 4], and this can lead to uneven covering of copper by graphene layers. The most popular substrate material in CVD technologies is copper. The standard procedure for preparing a copper substrate is washing in various solvents and annealing in the atmosphere of buffer gases, most often containing hydrogen, to ensure oxide layer etching from the surface. Annealing of copper foil is usually carried out at temperatures corresponding to the synthesis temperatures or higher. Often, the copper substrate surface has regular defects associated with the production technology (rolling) of copper foil. When annealing, the copper grains become larger, and their surface is smoothed.

It has been recently shown in [5] that copper foil annealing at the temperature of 1030°C in the argon atmosphere leads to formation of common orientation of the crystal structure of grains (misorientation is no more than 1°). Accordingly, graphene grown on this substrate, as shown by the authors, has the parameters close to graphene formed on a single crystal. The authors explain this effect by dynamics of substrate annealing. During annealing, a temperature gradient is generated on the substrate, and this thermal wave moves along the substrate. This heat wave leads to rearrangement of grain orientation and formation of a single-crystal copper surface (111).
This work aims at studying the effect of atmosphere and annealing dynamics on the crystalline structure of copper foil formed during annealing. To analyze the effect of gas on formation of a single-crystal surface, inert argon and chemically active hydrogen are chosen.

**Experimental section**
The experiments were carried out at a facility for CVD synthesis of graphene, described in detail in [6]. The copper foil AlfaAesar13382, 25 μm thick was used; this foil is often used by researchers for graphene synthesis. The substrates were annealed at the temperatures of 1030 and 1070°C in argon and hydrogen atmospheres. The samples were heated in various ways. In the first case, copper foil was drawn through the chamber at a speed of 1 cm/min (GradT). In the second, copper foil was abruptly put into the central zone of reactor and heated uniformly to the annealing temperature for about 2 min, and then it was held there for 30 min (ConstT).

The EBSD (Electron Backscatter Diffraction) analysis was carried out using a scanning electron microscope Hitachi S-3400N.

**Results and discussion**
A map of copper surface orientations is presented in Figure 1 for the samples annealed at different temperatures with and without drawing. It is seen that even after annealing, all copper orientations (111, 001, and 101) are available on the surface. Coarsening of the copper grains during annealing can be clearly seen with increasing temperature, Figure 1.
Figure 1. Inverse pole EBSD map of annealed copper foil.

Distribution of misorientation angles is shown in Figure 2 for copper samples annealed under different conditions. It can be concluded from the analysis of data on misorientation angles that the grains of initial foil have random orientation; then, during annealing, grains with similar orientations merge, and this leads to an increase in the small-angle part of the function of misorientation angles distribution. In the case of annealing at 1030°C with foil drawing in argon, the neighboring grains change their orientations more than in hydrogen. Under the regimes without drawing, redistribution of misorientation angles towards the region of large and small angles is more intense than in the case with drawing, Figure 2.
Figure 2. Misorientation angles distribution of annealed copper foil.

The function of size distribution of grains is shown in Figure 3. It can be seen that the character of dependence does not change, except for the samples annealed at high temperatures. In this case, the sample size is already insufficient to ensure smooth distribution. The diagrams in Figure 3 show the grain size distribution from the area of 3.5 mm$^2$. At copper annealing, there are formation and growth of large grains, which do not make a strong contribution to the distribution function because of their small number. The number of fine grains decreases from 18000 to 30 pieces with an increase in the annealing temperature. At that, a more pronounced drop is observed in the case of annealing in hydrogen.
Figure 3. The function of size distribution of grains in annealed copper foil.

According to data presented, it can be concluded that when annealing the copper foil, the outer atmosphere and duration of annealing are more important than the annealing dynamics. Long annealing leads to the fact that the grains, rotated at angles of up to 30°, combine. Nevertheless, even at the temperatures close to melting, a surface with single crystal orientation of grains does not form, as shown in [5]. The difference can be caused by the use of different foils: perhaps, initial orientation of grains in the foil in [5] was not random. The main constraint to the grain growth during annealing is accumulation of defects at the grain boundaries associated with impurities in metal. The main admixture for copper is oxygen, which reacts with hydrogen during annealing, forming water vapors that escape into the outer atmosphere. The maximal grain size achieved is about few millimeters. Probably, this size cannot be increased by longer annealing because the large-angle part of the angular scattering (misorientation angles) tends to grow, in all the cases, except the experiment in Figure 2h, where the sample size is insufficient for analysis.

Conclusion
In this work, modification of copper surface during thermal treatment in the atmosphere of hydrogen and argon at various temperatures has been studied. It is shown that thermal treatment leads to coarsening of the copper grains. Orientations of large grains, formed on the copper surface due to secondary crystallization, are random. A change in dynamics of sample heating with the use of the wave profile of temperature does not cause predominant orientation.
Acknowledgements

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

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