Graphene growth on the textured copper surface

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Abstract. The effect of mechanical processing of copper foil on the single-layer graphene growth is studied. The deformation of the foil in the annealed and unannealed state is carried out by rolling between rollers with varying degrees of roughness. It is shown that the formed single-layer graphene coating on the foil deformed in the unannealed state has a larger number of defects, which is associated with the heterogeneity of the copper texture formed upon annealing. In the case of rolling the copper foil after the annealing stage, the quality of graphene coatings only slightly deteriorates in the deformed areas of foil.

1. Introduction

Due to its physical and chemical properties and very low gas permeability, graphene is a promising material for protecting various surfaces from corrosion and degradation in atmospheric conditions, low vacuum and aggressive environments [1]. An important issue within this framework is the integration of the surface with a monolayer of graphene, which allows substantially changing the properties of the surface, while ensuring effective chemical protection. Copper is actively used in various heat exchangers, elements of microwave resonators, thermo- and photocathodes, etc. Moreover, copper is an effective catalyst for the growth of a single-layer graphene coating by chemical vapor deposition (CVD). Thus, the formation of a protective graphene layer is possible on a copper surface by the method of CVD, but the formation of a graphene layer substantially depends on the crystallographic orientation of the surface grains. In the case of using copper foil, the crystallographic orientation of the grains can be controlled by preliminary heat treatment of the foil [2]. In [3], it was shown that the growth rates on the family of crystallographic copper planes with the \{100\} orientation are lower than on the planes with the \{111\} orientation. In this case, the formation of a graphene layer on \{111\} surfaces proceeds with fewer defects. The authors explain the difference in the growth dynamics by the difference in the diffusion rate of carbon atoms on the crystalline faces with different crystallographic orientations [4-5].

During the heat treatment of copper foil, processes of relaxation of defects and dislocations in the material, redistribution of impurity atoms, processes of primary, secondary crystallization and collective recrystallization occur. The speed of these processes substantially depends on the purity of the material and the annealing temperature. At temperatures used in the synthesis of graphene (close to the melting point of copper), the characteristic times of the processes of relaxation of internal stresses and primary recrystallization are significantly lower than the characteristic times of synthesis. The main process that determines the average grain size is collective crystallization, in which grains grow with the most energetically favorable crystallographic orientation, determined by the total energy of the crystal or, in the case of thin films, surface free energy [6]. Mechanical processing of surfaces can
lead to defects and dislocations on the surface and in the bulk of the material, which can also affect the kinetics of crystallization. The developed surface morphology can change the contribution of bulk and surface energy to the total energy of the crystal and thus lead to a change in the texture of the crystal surface [6-7].

The growth of graphene on copper foil occurs from carbon deposited from the gas phase during the thermocatalytic decomposition of a gas precursor. The developed roughness of the copper surface can lead to a change in the composition of the gas components in various places of this surface. The present work is devoted to studies of the effect of surface roughness on the processes of recrystallization of a copper surface during heat treatment under conditions of graphene synthesis and on the process of forming a continuous coating of a copper surface with graphene.

2. Methods
Graphene was synthesized by a chemical vapor deposition method on copper using methane as a carbon precursor. For the synthesis, Alfa Aesar 13382 copper foil was used. Five samples of copper foil were made: the size of each sample was 15x70 mm. One foil sample was without mechanical processing, 2 samples were rolled between rollers with various degrees of roughness (0.2 and 0.5 mm), then these samples were annealed in a hydrogen atmosphere for 3 hours, after which they were kept in air for at least 1 hour. Two other samples of copper foil were first annealed for 3 hours in a hydrogen atmosphere and then rolled between rollers with different roughness. Before synthesis, the samples were washed in water, alcohol, and acetone.

The stage of graphene synthesis consisted of heating the samples in argon for 0.5 hours to 1070°C, holding for 30 minutes in hydrogen at a temperature of 1070°C and the stage of growth of graphene in an Ar/H\textsubscript{2}/CH\textsubscript{4} mixture at a temperature of 1070°C for 10 minutes.

The analysis of the graphene coating transferred onto the silicon surface was carried out by optical microscopy and Raman spectroscopy on a LabRam HR Evolution Raman Spectrometer (JOBIN YVON Technology HORIBA Scientific). The orientation and grain size of copper were determined by the electron backscatter diffraction method (EBSD) on a Hitachi S-3400N scanning electron microscope. To determine the grain size on the SEM images, the average length of the line dividing the grain into two equal parts was calculated.
3. Results and discussion
Using scanning electron microscopy, we studied the copper foil surface texture obtained by annealing the initial copper foil and after processing it with rollers with different roughness levels. The data are presented in Fig. 1.

The experiments carried out on a smooth (roughness of 1 μm) copper foil show that upon annealing of the foil, large grains (5-10 mm in size) are formed (the initial foil grain size of 20 μm) with a crystallographic orientation close to (111), Fig. 1. The presence of roughness significantly affects the size and crystallographic orientation of the grains formed during annealing. On a foil with a roughness of 200 μm, grains with a size of 0.5 mm are formed, and when its roughness is 500 μm, grains with a size of 0.3 mm are formed (see Fig. 1). In this case, there is no predominant crystallographic orientation of the grains relative to the surface.

For the graphene synthesis, we used the substrates obtained by rolling the initial foil and subsequent heat treatment, Fig. 1c, d, and the substrates obtained by rolling the annealed foil Fig. 1a, b. Using Raman spectroscopy, we studied the quality of the graphene coating in the undeformed regions of the copper surface and in the depressions formed during rolling. Raman spectroscopy data are presented in Figure 2.
Figure 2. Raman spectra of samples obtained by synthesis on copper: Cu – copper without treatment. Cu annealing 500 (200) surface (deep) – processing with a roughness of 500 (200) microns after annealing, spectrum from undamaged areas of copper (spectrum from a deformed area).
Cu 500 annealing surface (deep) – processing with a roughness of 500 (200) microns before annealing, spectrum from undamaged areas of copper (spectrum from the deformed region).

It can be seen from the spectra in Figure 2 that in all cases, a single-layer graphene coating forms on the surface of copper. The number of layers in the graphene coating, determined by the ratio of the intensities of the $I_G/I_{2D}$ peaks and their FWHM, is close to the parameters of the graphene coating formed on untreated copper. The degree of defects in graphene, determined by the ratio of the intensities of the $I_G/I_D$ peaks, is higher for the areas deformed after mechanical processing than for the undamaged surface (Table 1).

Table 1. Data of Raman spectra of samples.

| №          | FWHM (2D)(cm$^{-1}$) | $I(D)$ | $I(G)$ | $I(2D)$ | $I(D)/I(G)$ | $I(G)/I(2D)$ |
|------------|----------------------|--------|--------|---------|-------------|--------------|
| Cu         | 33                   | 63     | 368    | 800     | 0.17        | 0.46         |
| Cu annealing 500 surface | 38                   | 16     | 98     | 202     | 0.16        | 0.48         |
| Cu annealing 500 deep | 64                   | 80     | 396    | 224     | 0.20        | 1.77         |
| Cu annealing 200 surface | 31                   | 13     | 110    | 297     | 0.12        | 0.37         |
| Cu annealing 200 deep | 38                   | 16     | 96     | 171     | 0.17        | 0.56         |
| Cu 500 annealing surface | 35                   | 20     | 100    | 239     | 0.20        | 0.42         |
| Cu 500 annealing deep | 38                   | 31     | 128    | 202     | 0.24        | 0.63         |
| Cu annealing 200 surface | 41                   | 20     | 76     | 171     | 0.26        | 0.44         |
| Cu annealing 200 deep | 27                   | 13     | 96     | 328     | 0.13        | 0.29         |
Thus, the roughness of the copper substrate on which the formation of the graphene coating occurs affects both the processes of copper recrystallization and the growth of the graphene coating. During recrystallization, surface defects formed during rolling stabilize the grain boundaries formed during secondary crystallization at annealing. The heterogeneity of the surface texture of copper leads to the formation of graphene coatings with a large number of defects. In the case of rolling the foil after annealing, the quality of graphene coatings only slightly deteriorates in the deformed regions, which may be due to the inhomogeneous structure of the gas stream flowing around this foil region during the synthesis stage. In this case, with an increase in the surface roughness, the influence on the processes of recrystallization and growth increases. Therefore, to cover surfaces with graphene of low defectiveness, it is necessary to perform mechanical processing and geometry formation of the samples after annealing and complete recrystallization of the surface.

Conclusion
It is shown that the surface morphology of copper foil significantly affects the processes of copper recrystallization during heat treatment. The developed surface relief leads to stabilization of grain boundaries, which in turn reduces the energy gain when the crystal orientation is changed to (111), as was shown in [9]. Moreover, the formation of (111) orientation in grains occurs at grain sizes of 1 mm or more. In addition, in the synthesis of graphene coatings, it is important to create a gas stream with a variable angle of attack to minimize the formation of regions with a nonuniform precursor gas concentration in which graphene coatings grow with a large number of defects.

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