Comparing the methods of copper substrate polishing for CVD graphene synthesis

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Abstract. This paper presents a comparison of chemical and plasma electrolyte polishing methods for preparing a copper substrate for graphene synthesis by chemical vapour deposition. It is shown that in order to achieve the most uniform morphology of the surface of the copper substrate, it is preferable to use the electrolyte-plasma polishing method. With its help, the proportion of multilayer regions in the graphene coating obtained as a result of CVD synthesis decreases. The obtained results may serve a recommendation for creating a graphene coating with specified parameters.

1. Introduction
The flexibility, transparency, mechanical strength and electrical conductivity of graphene make it an attractive material for a wide range of applications: solar cells, supercapacitors, touch screens, joule heaters, and gas sensors. Chemical vapor deposition (CVD) on a metal substrate seems to be the most promising method for the production of large continuous graphene sheets. In the process of graphene CVD synthesis on the copper surface, during the carbon precursor decomposition, nuclei of a new phase, graphene, are formed at the initial stage; after that they grow, coalesce and cover the copper surface with a continuous polycrystalline film. The surface structure of a copper substrate is one of the most important parameters affecting the synthesis of graphene. The developed morphology of the copper substrate surface leads to the formation of a large number of graphene nucleation centers, which in turn results in the formation of a multilayer graphene coating [1, 2]. In order to obtain a single-layer coating with a simultaneous increase in its homogeneity, various methods of preliminary treatment of the catalytic substrate surface, on which the graphene coating grows, are used. Particular cases of pretreatment are polishing methods: mechanical using abrasive materials, chemical, electrolyte-plasma, etc. [3, 4, 5]. In addition, the resolidified method is used to smooth the surface [6]. Plasma Electrolytic Polishing is a relatively new method that is successfully used for processing metals and alloys due to a number of advantages, which include high quality of the polished surface, the use of environmentally friendly and inexpensive aqueous solutions, high processing speed, etc. [7, 8]. Plasma electrolytic polishing is a reliable method used for various technologies; however, in our case, after polishing, the substrate is annealed and graphene grows. Our goal is not to maximize surface smoothing, but to maximize the quality of the grown graphene coating. We assume these things are related.

This work presents a comparison of the chemical and plasma electrolytic methods of preparing a copper substrate prior to the CVD procedure for graphene synthesis.
2. Methods

We used 25 μm thick copper foil Alfa Aesar 13382 (99.8% Cu) and 50 μm thick copper foil M00B (99.999% Cu). For M00B foil, two polishing methods were used: 1) chemical polishing in a solution of H3PO4 (60 vol.%) + HNO3 (20 vol.%) + CH3COOH (20 vol.%) for 10 min [9]; 2) Plasma electrolytic polishing in an aqueous solution (NH4) 2SO4 (3 vol.%) + NH3 (6 vol.%) at a solution temperature of 87 °C and a voltage of 280 V. After polishing, all samples were washed in distilled water and ethyl alcohol in an ultrasonic bath. All samples were subjected to CVD synthesis of graphene under identical conditions. The synthesis procedure began with heating up to 1070°C in an Ar (95 sccm) + H2 (5 sccm) gas flow. This was followed by annealing for 30 min in an H2 flow (100 sccm) at a temperature of 1070 °C. It was followed by synthesis: for 10 min a mixture of gases Ar (91 sccm) + H2 (20 sccm) + CH4 (0.2 sccm) was fed into the chamber at a temperature of 1070°C. The procedure ended with rapid cooling (from 1070°C to 100°C for ~ 2 min) in the synthesis gas mixture. The samples obtained were examined using optical microscopy and Raman spectroscopy (RS) directly on the copper surface. In addition, graphene was transferred from copper to silicon substrates and studied by scanning electron microscopy. Graphene transfer was done by dissolving a copper substrate.

A copper substrate was lowered onto the surface of a (NH4) 2S2O8 solution with a concentration of 0.044 g/mol (1 gram of ammonium persulfate per 100 ml of water) to place the graphene on top. The etching time for Alfa Aesar copper substrate and chemically polished M00B was 26 hours, and for M00B and M00B with electrolytic-plasma polishing it took 50 hours. After the copper dissolution, the graphene film remained floating on the solution surface. To rinse the graphene film, the solution was partially evacuated several times and replaced with distilled water. After that, the graphene film located on the water surface was removed using a silicon wafer. Then the resulting sample was dried.

The analysis of the graphene coating synthesized on the copper surface was carried out by optical microscopy (Olympus BX51M) and Raman spectroscopy on a LabRam HR Evolution Raman Spectrometer (JOBIN YVON Technology HORIBA Scientific). Roughness measurements were carried out on a scanning nanohardness meter (NanoScan-3D).

3. Results and discussion

As a result of the experiment, optical images and profilometry data of copper substrates of various types (M00B and Alfa Aesar) were obtained before and after the synthesis procedure of graphene coating by chemical vapor deposition (CVD), which is shown in Figure 1 and Table 1.

Table 1. Profilometry data of the obtained samples.

| Sample name                  | Rms, nm | Ra, nm |
|------------------------------|---------|--------|
| AA (Alfa Aesar №13382)       | 104     | 77     |
| M00B                         | 163     | 130    |
| AA + Gr                      | 215     | 161    |
| M00B + Gr                    | 171     | 126    |
| M00B chem. polishing + Gr    | 112     | 89     |
| M00B plasma-el. polishing + Gr | 82     | 64     |
Figure 1. Optical images and profilometry data of unpolished copper surface: a) Alfa Aesar 13382; b) Alfa Aesar 13382 after the stage of graphene synthesis; c) M00B; c) M00B after the stage of graphene synthesis (lighter areas correspond to a single-layer graphene, darker ones – to a multilayer graphene).

Figures 1 A and C illustrate a pronounced relief, consisting of submicron roughness and regular stripes left during the production process after rolling. The surface of M00B copper foil has a more pronounced relief in comparison with Alfa Aesar foil. This can be seen from the profilometry data in Table 1.

The difference in the surface morphology (A and B, C and D) is due to the fact that during the synthesis, annealing stage occurs in a hydrogen medium at a temperature (1070°C) close to the melting point of copper (~ 1083°C) and, thus, the copper surface is smoothed with accompanying recrystallization process. However, profilometry data show that the roughness of M00B copper practically does not change, while the roughness of Alfa Aesar copper increases. In Figures B and D, residual surface irregularities can be observed in the form of stripes.

Using optical analysis, as well as analysis by Raman spectroscopy, it was determined that, in comparison with copper foil Alfa Aesar, a multilayer coating on M00B foil occupies a larger percentage of the total substrate area. The graphene coating formed on the M00B foil has the same level of defectiveness as in the case of comparison with the graphene coating synthesized on the Alfa Aesar copper substrate.

To improve the uniformity of the M00B copper foil surface, it was decided to preliminarily polish the surface of the copper substrates by two methods: chemical and plasma-electrolytic methods. The comparison results are shown in Figure 2 and Table 1.
Figure 2. Optical images and profilometry data of the copper surface: a) M00B with chemical polishing; b) M00B with chemical polishing after the stage of graphene synthesis; c) M00B with electrolytic-plasma polishing. d) M00B with electrolytic-plasma polishing after the stage of graphene synthesis (lighter areas correspond to a single-layer graphene coating, darker ones – to a multilayer coating).

During chemical polishing, there is a simultaneous decrease in surface irregularities as a result of the surface layer dissolution and the oxide film formation when the components of the solution interact with the processed material, which is observed in Figure 2a in the form of a change in the color of the copper foil surface. An opposite picture (Fig. 2c) is specific for the case of plasma electrolytic polishing: surface irregularities are smoothed out, but the oxide film is virtually not formed. In both cases, during the annealing stage of the graphene coating synthesis, the formed oxide film is reduced in a hydrogen atmosphere.

In addition to all of the above, it should be noted that the thickness of the M00B copper substrate decreased 3.2 times in the case of using the method of chemical polishing, and 1.4 times after the plasma electrolyte-one. Rolling strips are smoothed in both cases, but an additional humpy relief is formed on the surface of the chemically polished foil.

The analysis has shown that the sample surfaces have a continuous graphene coating. The surfaces contain both single-layer and multi-layer graphene regions. After electrolytic-plasma polishing, the area of single-layer graphene regions increases significantly (Fig. 2d). Annealing of the copper foil leads to a smoothing of the microrelief in all cases, however, a coarser relief remains; thus, the conditions for the growth of graphene on different surfaces differ and the quality changes. Chemical polishing does not smooth the macro-relief as much as electrolytic-plasma polishing; therefore, after chemical polishing, the growth conditions are less uniform: a larger number of nucleation sites for graphene nuclei appear, which leads to the formation of a graphene coating with higher layering.
For a detailed analysis of the morphology of the graphene coating, the procedure of its transfer to a silicon substrate was carried out. The analysis was performed using scanning electron microscopy, Figure 3.

As a result of the analysis of SEM images, it was determined that the most homogeneous graphene coating is observed when using plasma electrolytic polishing. The characteristic size of the homogeneous regions, in this case, is about 10 \( \mu m \). The opposite picture can be seen in Figure 3a, which shows a graphene coating synthesized on Alfa Aesar copper foil. In this case, a strong heterogeneity of the surface morphology is observed. The formation of developed surface morphology as a result of the sequential action of chemical polishing and annealing procedure manifests itself in the form of a larger number of graphene nucleation centers, compared to the second method. The increased number of nucleation centers, in turn, forms a polycrystalline coating with a large number of multilayer islands, which is clearly seen in Figure 3c.

Thus, we can conclude that the most uniform coating can be obtained using plasma electrolytic polishing.

**Conclusions**

It is shown that in order to achieve the most uniform morphology of the copper substrate surface, it is preferable to use the plasma electrolytic polishing method. With the use of this method, the proportion of multilayer regions in the graphene coating obtained as a result of CVD synthesis decreases.
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