The influence of the crystallographic orientation of the copper catalytic substrate crystallites on the mechanical transfer of graphene

Evgeny Victorovich Boyko1,2, Ilya Alexeevich Kostogrud1, Ivan Andreevich Bezrukov1, Alexander Sergeevich Krivenko1 and Dmitry Vladimirovich Smovzh1,2

1 Kutateladze Institute of Thermophysics SB RAS, Novosibirsk, Russia
2 Novosibirsk State University, Novosibirsk, Russia
3 Epos-engineering, LLC, Novosibirsk, Russia

E-mail: renboyko@gmail.com

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Abstract

In this paper, we studied the dependence of adhesion between CVD graphene and copper substrate on different crystallographic orientations of copper grains. It was determined that the adhesion between graphene and copper surface increases for grains with low-index crystallographic orientations. This phenomenon is explained by the surface microrelief formation during the crystallization of the copper surface layer, molten at the stage of annealing and graphene growth. During the liquid layer cooling and crystallizing, partial exfoliation of graphene from the copper surface occurs. Graphene exfoliation leads to an increase in defectiveness of the graphene layer. However, graphene peeling from copper grains with high-index crystallographic orientations can significantly reduce damage to graphene during the transfer process to a polymer surface.

1. Introduction

Graphene is one of the allotropic modifications of carbon and has a number of interesting properties: impermeable to standard gases, significant thermal conductivity, high charge carrier mobility, excellent strength [1, 2].

The chemical vapor deposition method allows to synthesize large-area graphene with a low defect density [3]. In this method, the synthesis occurs on a catalytic metal substrate, for instance on a copper foil. In this regard, for the potential use of graphene in electronics as transparent electrodes [4–6], biotechnology as flexible sensors [7–9], or in energy as batteries or solar cells [10, 11], it is necessary to develop graphene transfer methods. To date, graphene transfer is most often carried out by removing metal substrate with chemical etching, for instance using nitric acid [12]. There are more resource-efficient transfer methods: electrochemical [13] and mechanical exfoliation of graphene [14]. The latter transfer method is the most interesting one since it allows us to save the substrate, which accounts for the main part of graphene production technology cost. At present, mechanical transfer of graphene allows to obtain samples with electrical resistance 10 times worse than using other methods of graphene transfer: for example, chemical [15–18] or electrochemical [19–21]. The main factors leading to damage to graphene sheets during mechanical transfer are described in [22]. During such a transfer, mechanical damage to the samples upon separation of graphene from the copper substrate becomes the stumbling block. To minimize damage during graphene mechanical exfoliation, a deep understanding of the interaction mechanisms between the metal substrate and graphene is necessary.

Considerable attention has been devoted in the scientific literature to the processes of graphene growth on metal substrates with different crystallographic orientations [23–27]. At the same time, such an important point as adhesion between graphene and a metal substrate has been studied and presented in the scientific literature poorly. Among the existing publications devoted to the study of this topic, may be highlighted [28–31]. This is
due to the difficulties of experimental observation and measurement of the adhesion energy between the catalytic substrate and the graphene layer. Commonly, adhesion measurements between graphene and a metal substrate are carried out using double cantilever beam method. Such a procedure was first described in [28], where the adhesion energy for a copper foil was 0.72 $\pm$ 0.07 J m$^{-2}$. In later studies [29], using the same measurement method, an adhesion energy of 1.54 $\pm$ 0.07 J m$^{-2}$ was reported for the graphene/copper system. The difference in the results can be explained by different approaches to using the double cantilever beam method or by the difference in the properties of the copper substrate. For instance, the surface treatment of copper with ultraviolet radiation and oxygen leads to an increase in the adhesion energy up to 2.10 $\pm$ 0.27 J m$^{-2}$ [32].

However, all these works have a common drawback - the role of crystallographic orientation of the metal substrate grains is not mentioned anywhere. We have noticed that this factor has a strong influence on the result of the mechanical transfer of graphene. In turn, this can explain the differences in the obtained values of the adhesion energy in the scientific literature.

The aim of this work is to study the effect of the crystallographic orientation of copper substrate grains on damage to graphene during mechanical transfer. In the present work, a qualitative analysis of adhesion between graphene and a copper substrate was performed. The study was conducted based on the analysis of the amount of graphene remained on the copper substrate after the mechanical transfer procedure. Graphene was transferred from copper grains with different crystallographic orientations.

2. Methods

In all experiments, we used graphene synthesized by the CVD method—detailed description can be found in [33].

Graphene samples were studied using Raman spectroscopy immediately after the synthesis stage and after the transfer procedure to the polymer using a T64000 Raman spectrometer (manufactured by Horiba Jobin Yvon) with a wavelength of exciting radiation of 514.5 nm. Spectra were recorded at several points on the sample surface, in the range from 100 to 3000 cm$^{-1}$. D, G, and 2D bands, characteristic of graphite structures, were analyzed in the obtained spectra. D, G, and 2D bands were approximated using a Gaussian distribution. In the resulting bands, the following parameters were determined: intensity, center position, FWHM. By the ratio of D band, responsible for structure defectiveness, to G band, the degree of graphene structure defectiveness was determined. The number of graphene layers on the substrate was determined from the shape of 2D band and the ratio of 2D and G band intensities. The spectra obtained after graphene transfer, in all cases, contain characteristic D, G, and 2D bands, however, the analysis of graphene parameters is difficult due to the strong overlap of its spectrum with the polymer’s one, which has a significantly higher intensity. Typical Raman spectra of graphene after the transfer stage can be found in [22]. After the transfer procedure, the presence of graphene was detected in all studied samples by Raman spectroscopy by the presence of D, G, and 2D bands in the spectrum.

The size of copper grains and their crystallographic orientation were analyzed using the method of electron backscatter diffraction (EBSD) on a Hitachi S-3400N scanning electron microscope.

After mentioned above procedures, graphene was transferred using polyethylene terephthalate/ethylene vinyl acetate (PET/EVA) polymer. The PET/EVA polymer was deposited using a heat press printing method. In this case, PET played the role of a carcass, and EVA played the role of an adhesive. The copper substrate with synthesized graphene was laminated with these two polymer sheets at a temperature of 190 °C. After that, the copper substrate was removed mechanically by separating the polymer coating from the substrate. To avoid graphene deformation [22] the samples were mechanically stabilized. After the transfer stage, the copper substrate was oxidized in air at 200 °C for 10 min and then examined using an Olympus BX51M optical microscope to determine the amount of graphene remained on the copper substrate.

To get the quantitative data on the amount of transferred graphene, the obtained optical images were processed (figure 1) using the 'ImageJ' software package.

To simplify the search for graphene spots, the images were pre-processed: the color depth and contrast were changed, an FFT (Fast Fourier Transform) filter was applied. The procedure of graphene spots distinguishing was controlled manually, in order to avoid the capture of bright areas that were not the graphene spots. The areas of the marked regions were summed up, then the resulting value was divided by the area of the entire site and multiplied by 100%.

3. Results

Data obtained by the EBSD analysis are shown in figure 2.
Five regions with different crystallographic orientations were selected on polycrystalline copper foil (Alfa Aesar 13382, purity of 99.8%, the thickness of 25 μm) used in the experiment, figure 3.

The regions with low-index crystallographic orientations of the elementary face-centered cubic copper cell and with high-index crystallographic orientations relative to the surface of copper were selected. The standard stereographic triangle with dots, corresponding to five picked regions, is shown in figure 4. Regions 1, 4 and 5 with Miller’s indices (001), (607) and (557) are close to the families of the main crystallographic planes {100}, {110} and {111}, while regions 2 and 3 correspond to the high-index crystallographic planes (209) and (438).

For each of five regions, the Raman spectrum of graphene on copper was obtained and the amount of remained graphene as a result of mechanical transfer was calculated. The data obtained are combined in a table, figure 5.

The obtained Raman spectra correspond to multilayer graphene with different degrees of defectiveness. Regions 2, 3, and 5 have the highest defectiveness ($D/G = 0.05$), and region 1 ($D/G = 0.01$) demonstrates the lowest defectiveness. Regions with minimal defectiveness correspond to orientation close to the low-index one — (001), all other regions have similar D/G ratios. Analysis of the areas of remained graphene on the substrate for different grains showed that graphene transfer from regions 1, 4 and 5 was the worst. Much fewer graphene residues in regions 2 and 3 were observed.

Analysis of substrate microrelief, figure 6, showed that the surface has a step-like structure with different characteristic sizes depending on the crystallographic orientation of the grain [34].

4. Discussion

The main goal of development of mechanical graphene transfer methods is to achieve the minimal electrical resistance in the graphene films, corresponding to the electrical resistance of original synthesized graphene samples. Thus, the development of technological procedures comes down to minimization of graphene sheets damage at the stages of polymer and graphene conjunction and the stage of substrate separation. The influence of the described effects depends directly on the adhesion between graphene and the copper substrate. If the graphene transfer procedure involves etching the substrate [35], the question of the interaction force is not as important as in the case of mechanical or electrophoretic [21] separation.
If graphene grows on copper, the interaction of a graphene sheet with a copper surface occurs due to the dipole-dipole (Van der Waals) interaction without consideration of the effects of graphene crystal passivation by hydrogen or substrate atoms, discussed in [36]. In this case, it should depend on the configuration of atoms, which differs for different crystallographic orientations. This interaction changes the configuration of atoms of a graphene structure and discussed in [26].

The strong influence of interaction on mechanical transfer can be used for the experimental analysis of the adhesion between graphene and various crystal faces of copper. This analysis was proposed to be carried out on a polycrystalline foil, since in this case the question of the identity of synthesis conditions and subsequent effects during the transfer for different samples, is automatically removed. EBSD mapping the orientations of copper grains and analyzing polymer-graphene composites allows us to unambiguously identify the areas of copper from which graphene was transferred.
Thermal treatment of the copper substrate before the growth stage leads to the increase of grains size and their reorientation [37]. In this work, we selected the annealing conditions, when the size of copper grains is sufficient for analysis and measurement, and at the same time, they have different crystallographic orientations. When copper is annealed at the temperatures close to the melting point, the surface morphology changes. At temperatures above 800 °C, a pseudo-liquid layer is formed on the copper surface [38, 39], which leads to smoothing the surface defects and formation of a step-like structure during subsequent cooling, whose planes correspond to the crystallographic planes of copper. With orientation corresponding to the low-index crystallographic orientations of copper grains, the steps are formed only in places with a developed surface relief and also there are areas with surfaces that are close to atomically smooth [40]. In the case when crystallographic orientation is high-index one, the steps can be formed even in the areas with poorly developed relief. The presence of peaks in figure 6 may be due to the presence of nanoparticles on the surface, or it can be explained by a change in the phase volume of the surface during copper oxidation in air at the sites of defects in graphene.
Thus, the catalytic surface has the relief associated with surface roughness and microrelief caused by crystal faceting. With the growth of graphene crystals, the microrelief is smoothed due to the formation of a pseudo-liquid layer on the substrate surface. Nevertheless, growth kinetics, as shown by many authors [23–26, 36], depends essentially on crystallographic orientation, which is apparently determined not by the surface morphology, but by the energy of interaction of carbon with the substrate, depending on the surface configuration of atoms. When the substrate is cooled, after the synthesis stage, a step-like structure forms from the pseudo-liquid layer, which should lead to the deformation of graphene crystals lying on the copper surface. According to data obtained from AFM analysis, graphene copies the step-like shape of copper, but the curvature radius of graphene sheets cannot be equal to zero. Hence, at the points of bending, graphene should peel off from the catalytic substrate. The more developed the step-like structure of the surface, the stronger the described effect.

Graphene growing on copper grains with different crystallographic orientations has different degrees of defectiveness, which is associated with a change in the force of interaction with the surface. Therefore, the defectiveness should be associated with the diffusion rate, processes of sorption and desorption of carbon atoms. It is shown in the scientific literature that the highest quality of graphene is achieved on the crystallographic plane (111) which has minimal free surface energy, and, accordingly, minimal strength of interaction with graphene. Further, this energy increases for the plane (100) and it is maximum for (110). When forming a step-like structure, additional damage of graphene layers occurs, and this leads to the fact that graphene growing on the high-index faces have higher defectiveness. In our case, only one region (region 1) has the low-index crystallographic orientation—(100), the rest of the analyzed regions are rotated relative to the low-index crystallographic planes. According to the data of Raman spectroscopy, defectiveness of graphene at region 1 is minimal (D/G = 0.01), while for all other regions the D/G ratio is 4–5 times higher.

An increase in the degree of graphene defectiveness during deformations associated with crystallization of the copper surface layers is compensated by partial exfoliation of the graphene layer from the copper substrate, which in turn leads to less defective transfer by mechanical methods. According to data in figure 5, the percentage of graphene remained on copper is higher for the regions with low-index crystallographic orientations and lower for high-index one. At the same time, in region 4, which crystallographic orientation close to (110), the degree of transferred graphene is lower than for region 1. This phenomenon is consistent with the idea, that the interaction with various basic crystallographic orientations stronger comparing to the interaction with high-index crystallographic planes.

5. Conclusion

In the present paper, the methodology for analyzing the adhesion between graphene and copper during the mechanical transfer was proposed.

It is shown that during the mechanical transfer, the degree of transferred graphene depends on the crystallographic orientations of copper grains.

The obtained data of graphene adhesion are consistent with the ideas of an increase in the interaction for the (111) - (100) - (110) planes, respectively.

It is shown that the adhesion decreases for crystallites with low-index crystallographic orientations. This effect is explained by the formation of a microrelief during crystallization of the pseudo-liquid copper surface layers during sample cooling, after the stage of synthesis, and partial separation of the graphene sheets from the substrate surface.

The obtained data can be used to develop technologies for the mechanical transfer of graphene from a catalytic substrate, which is essential for the development of low-cost production of functional devices based on graphene CVD.

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ORCID iDs

Evgeny Victorovich Boyko © https://orcid.org/0000-0001-8782-9193
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