Graphene transfer from a copper surface to a silicon substrate

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Abstract. The article presents a comparison of two methods of transferring single-layer graphene onto silicon substrates using poly (methyl methacrylate) (PMMA) and thermo-adhesive tape. The continuity of the transferred coating and the quality of the graphene film after the transfer stage were investigated. An analysis of the contaminants formed during the transfer of the graphene surface is carried out. It is shown that when using PMMA for transfer, heating of the samples leads to their damage due to thermal expansion and the formation of indelible impurities on the surface.

1. Introduction
Currently, the most promising method for the production of graphene materials is CVD growth on the surface of various metal substrates. An important advantage of the CVD method is its scalability. For instance, in [1, 2], techniques for the continuous synthesis of graphene coatings on copper foil using roll-type facilities were proposed. However, most modern applications of graphene materials require the transfer of graphene from a metal substrate to substrates with specified optical and dielectric properties. The most popular and proven methods include transfer technologies with the use of various polymers [3]. Particular attention should be paid to the transfer of graphene using poly(methyl methacrylate) (PMMA); this technique is the most common in the scientific literature. The transfer of graphene using PMMA is based on applying PMMA to graphene, subsequent etching of the metal substrate, transfer of the PMMA/graphene film to the target substrate, and dissolution of PMMA. Despite the extensive testing of the method in the literature, it has a number of significant drawbacks. Removing PMMA residues after transfer from the graphene layer is not an easy task; in the literature, high-temperature annealing of graphene in inert atmospheres and in atmospheres of hydrogen [4] and oxygen [5] is used for this. Obviously, these effects cannot occur without damage to graphene layers. In addition to the purity of the transferred graphene, the continuity of the transferred coating also plays an important role, which becomes the most important parameter when transferring large-area samples. The stage of transfer of graphene to the polymer does not cause technical difficulties; various regimes allowing the production of polymer-graphene composites of high uniformity have been worked out. The transfer of graphene from a polymer material to silicon is a more difficult task. When polymer solutions are applied to graphene surfaces, the polymer shrinks during drying, which can lead to its peeling. In order to avoid delamination, the polymer is applied in thin layers in several stages, however, graphene is in a mechanically stressed state and its deformation occurs during etching of copper. The adhesion between the deformed film and a smooth crystalline surface of silicon is low, which leads to the fact that the amount of transferred graphene from PMMA to the silicon substrate is not high. A number of methods are used to improve adhesion: transfer of the PMMA-graphene film
with the use of water [3, 6] and heating the graphene-PMMA composite on a silicon substrate to temperatures above the melting temperature. The thermal expansion coefficients of graphene and polymer differ significantly. When the polymer is heated, its thermal expansion occurs, which leads to the straightening of strained graphene regions and a more tight fit to the silicon substrate, which positively affects the uniformity of transfer of graphene layers. A method that is also actively gaining popularity in the scientific literature is the transfer of graphene through a thermo-adhesive tape [7].

In this article, we compared the methods of transferring a single-layer graphene coating using the PMMA technology and using a hot-melt adhesive tape on single-crystal silicon substrates with a layer of natural SiO$_2$ and evaluated the prospects of their use for large-area samples.

2. Methods
The synthesis of graphene was carried out in a tube furnace on a copper surface, using methane as a carbon source, at the atmospheric pressure. In order to synthesize single-layer graphene Alfa Aesar copper foil 13382, 25 micron thick, pre-annealed at 1070°C for 30 minutes in hydrogen was used. The synthesis was carried out at a temperature of 1070°C in a mixture of gases Ar/H$_2$/CH$_4$ = 90.8/20/0.2 for 10 minutes.

Transfer to PMMA was carried out by the spincoating method. PMMA was dissolved in acetone in a weight ratio of 1:10, after which a drop of the solution was applied to the surface of copper coated with a graphene layer. After that, the copper sample was accelerated with 300 rotates/s$^2$ to 1500 rpm and maintained a speed of 1500 rpm for 1 minute. Then the sample rotation was stopped and the polymer application procedure was repeated twice more.

After applying the polymer layer, the sample was heated to a temperature of 190°C, to prevent peeling of the polymer, after which copper was etched in a 40% nitric acid solution. The sample was washed in distilled water.

The PMMA-graphene composite was placed in degassed distilled water on a silicon substrate, then it was dried at a temperature of 60°C for 1 hour, after which the silicon wafer was heated to 190°C. The PMMA was removed by dissolution in acetone, followed by washing in distilled water.

During transfer using a heat release tape (Revalpha 3198LS), the protective layer was removed from the tape, it was applied to the graphene surface, after which copper was removed by a method identical to the procedure described above. The heat release tape-graphene composite was placed on a silicon substrate and heated to a temperature of 120°C; upon heating, the tape peels off from the surface.

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).

3. Results and discussion
Figure 1a shows the Raman spectra of synthesized graphene on a copper surface before and after subtracting the luminescent background of copper. On the spectra, D, G, 2D graphite bands are observed, the ratio 2D/G = 1.6 and FWHM is 34 cm$^{-1}$, which corresponds to single-layer graphene. Figure 1b shows the Raman spectrum of graphene transferred to PMMA polymer; in addition to graphite G and 2D bands, the spectra also exhibit a set of peaks related to PMMA polymer, the main of which are situated in the range of 1430-1485 cm$^{-1}$, 1715-1735 cm$^{-1}$ and characteristic peaks of CH$_3$ vibrations situated in the range of 2800-3200 cm$^{-1}$. 
Figure 1. Raman spectra of synthesized graphene coatings on copper (a) and transferred to PMMA (b).

Figure 2 shows optical images of a silicon substrate with a graphene layer transferred to it. In both cases, the coating appears to be fairly uniform except for the presence of particles probably associated with dust from the atmosphere. On the samples transferred using the PMMA polymer, regions with a contrast are visible (marked with dotted lines). These areas are associated with imprints of copper grain boundaries.

Figure 2. Optical images of graphene samples on silicon substrates.

The Raman spectra of graphene coatings transferred onto Si/SiO$_2$ substrates are shown in figure 3. Graphite bands D, G, D’, D + D”, 2D are observed in all spectra [8], the ratio 2D/G = 1.5 and the FWHM is 31 cm$^{-1}$. In addition, peaks of 1514 cm$^{-1}$, 1393 cm$^{-1}$, 1285 cm$^{-1}$, and 1252 cm$^{-1}$ are observed on graphene transferred using PMMA polymer.
Figure 3. Raman spectra of single-layer graphene on single-crystal silicon substrates with a natural oxide layer.

The Raman signal peaks (figure 3a) of 1393 cm\(^{-1}\), 1285 cm\(^{-1}\) and 1252 cm\(^{-1}\) can be associated with vibrations of a single C–O bond. The peak of 1514 cm\(^{-1}\) has an unobvious nature and can be associated with silicon carbide or asymmetric vibration aromatic C–C bond [9]. This peak was also observed by other authors using a similar technology for the transfer of graphene, but its nature has not been explained [10]. To study the nature of the 1520 cm\(^{-1}\) peak, the Raman spectra of graphene coatings on copper coated with single-layer graphene were measured after the following treatment:

1) a solution of PMMA in acetone was applied, which was washed off with acetone after drying;
2) a solution of PMMA in anisole was applied, which was washed off with acetone after drying;
3) a solution of PMMA in acetone was applied, which, after drying, was heated at a temperature of 190°C, then it was washed off with acetone;
4) a solution of PMMA in anisole was applied, which, after drying, was heated at a temperature of 190°C, then it was washed off with acetone. The Raman spectra obtained are presented in figure 4.
Figure 4. Raman spectra of single-layer graphene on copper a) PMMA/acetone-Washing
b) PMMA/anisole-Washing c) PMMA/acetone-Heating 190°C-Washing
d) PMMA/anisole-Heating 190°C-Washing.

It can be seen from the spectra that when using the PMMA polymer with acetone, a plateau of 1480-1530 cm⁻¹ forms after the peak characteristic of PMMA 1453 cm⁻¹ after annealing and, accordingly, observed in the spectrum, figure 3a; the peak of 1514 cm⁻¹ corresponds to the products of thermal degradation of PMMA after dissolution in acetone. As it can be seen from the spectra in figure 4e, when using PMMA dissolved in anisole, the Raman spectrum does not change upon heating.

An analysis of the graphene coating in the region of the imprint of the grain boundaries in figure 2 showed that the graphene signal is absent in the Raman spectra of these regions. The reason for this observation may be the thermal expansion of the polymer upon heating, during which the graphene crystals formed on different grains of copper are separated. The formation of this gap leads to a significant increase in the electrical resistance of graphene films (from 0.8 kOhm×sq.⁻¹ on the polymer to 30 kOhm×sq.⁻¹ on Si/SiO₂). The absence of such gaps when using a thermal adhesive tape is apparently due to a lower coefficient of thermal expansion.

Thus, it can be concluded that the use of thermo-adhesive tape for transferring single-layer graphene from copper is more preferable due to the fact that there are no additional contaminants resulting from thermal decomposition of the PMMA polymer with acetone residues in air during heating of the samples. The thermal expansion of the PMMA polymer during heating leads to the gaps occurring between the crystals in the graphene film. The transfer using the PMMA polymer can be used to obtain local regions of transferred graphene with a size of the order of the copper grain size. In this case, it is most preferable to use anisole as a solvent during application using PMMA polymer.
Conclusions

Studies of the efficiency of transferring single-layer graphene onto silicon (or other smooth surfaces) performed in the work show that the transfer method that is actively developing in the scientific literature using thermo-adhesive tape is more effective in comparison with the traditionally used transfer method applying a PMMA polymer. The use of PMMA polymer can be used if it is necessary to implement the transfer of graphene, which excludes the stage of heat treatment. Moreover, the use of anisole as a solvent for the PMMA polymer instead of acetone leads to less pollution of the graphene surface.

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