EXPERIMENTAL STUDY OF PIB-BASED CVD GRAPHENE TRANSFER EFFICIENCY

BOUŠA Milan[1,2], KALBÁČ Martin[1], JIRKA Ivan, KAVAN Ladislav[1], FRANK Otakar[1]

[1] *J.Heyrovsky Institute of Physical Chemistry of the AS CR, v.v.i., Prague, Czech Republic,*
milan.bousa@jh-inst.cas.cz

[2] *Department of Inorganic Chemistry, Faculty of Science, Charles University in Prague, Czech Republic*

Abstract

The transfer of chemical vapor deposited (CVD) graphene from metal catalyst to target substrate is an important step in preparing desirable nanoscale structures in various fields of science, and thus searching for fast, cheap and clean method attracts great interest. Investigation of mechanical properties of graphene, which are crucial for applications in flexible electronics, performed on bendable synthetic materials, requires a transfer technique using polymers soluble in aliphatic solvents harmless for target polymer substrates. In this study we explore a dry technique using polydimethylsiloxane (PDMS) as stamping polymer and polyisobutylene (PIB) layer as graphene-support polymer. After the transfer PDMS is peeled off and PIB is dissolved in hexane, hence this method fulfils the above mentioned prerequisite. The effectiveness of this transfer was examined by scanning electron microscopy, optical microscopy and Raman microspectroscopy including micro-mapping, and finally by X-ray photoelectron spectroscopy. With all methods carried out, it was found that this sort of stamp-technique is suitable for a high precision transfer of CVD graphene onto polymer substrates with large yields and similar purity compared to PMMA-based transfer methods. However, it introduces substantial quantity of surface discontinuities, and therefore this is not a proper method for large scale applications.

Keywords: graphene, chemical vapor deposition, transfer, polymer

1.   INTRODUCTION

Graphene [1], a layer of sp^2 carbon atoms covalently bonded in an array of regular hexagons, possesses many unique properties ranging from the highest thermal conductivity, large optical transparency, extreme carrier mobility to superior mechanical properties [2-5]. However, commercial applications for high quality graphene are still in its infancy [6], since they depend on reliable methods of its large scale preparation and transfer. Chemical vapor deposition (CVD) [7] is indeed the method of choice, allowing the growth of graphene with single crystal domains with lateral sizes in millimeter range [8] and promising even larger ones on metal catalysts with uniform single crystalline surfaces [9]. Nevertheless, such kind of metal-assisted growth necessitates a transfer step onto a desired, usually dielectric substrate for the final application. At least, until a proper growth method directly on the dielectric substrate is found. Most of the currently utilized transfer methods employ a sacrificial polymer layer, usually polymethylmetacrylate (PMMA) [10]. In general, a thin polymer layer is spin-coated onto the graphene resting on the metal sheet, which is subsequently etched away, the graphene-polymer stack is washed in water and left floating on its surface, scooped up from it with the target substrate ("fished"), and finally the polymer is dissolved in an appropriate solvent (in the case of PMMA usually by acetone) and/or cleaned thermally (~300°C). While this method is simple and capable of transferring large-area samples, there are several drawbacks. Firstly, PMMA reacts slightly with the metal etchants leaving insoluble residues which plague the transferred graphene [11]. Secondly, the fishing method is inappropriate for transferring onto hydrophobic substrates. And finally, some applications require polymeric substrates – however, thicker than the sacrificial layer, or processed in a different way – and hence the final step of sacrificial polymer dissolution/annealing has to be modified in order not to damage the target polymer. To this end, a transfer technique using a thermal-release tape can be used [12], but its price is too large to be used commercially on a large scale at the moment. An alternative solution

consists in employing a different polymer than PMMA, which could be soluble in less aggressive solvents, like short aliphatic or alicyclic hydrocarbons or alcohols. In this way, the problems with PMMA residues can be solved simultaneously [11]. Regarding the wet "fishing" technique, which is not suitable for hydrophobic substrates, a dry "stamping" method can be used instead. There, a chunk of PDMS is placed on the graphene-sacrificial polymer stack before the metal-etch step and then peeled off mechanically after the placement onto the target substrate.

In the present work, we have tested a dry procedure using a PDMS stamp and polyisobutylene (PIB) as the sacrificial polymer to transfer graphene grown on Cu foil onto polymeric substrates (PMMA with a thin layer of SU8 photoresist for a better optical contrast). The transferred samples were characterized by optical and scanning electron microscopies, Raman spectroscopy and X-ray photoelectron spectroscopy. The results show a viability of this method, however, with a set-back of fragmentation of the transferred samples into smaller grains.

2. EXPERIMENTAL

Graphene was grown on copper foils as detailed in [13]. In brief, a copper foil was heated to 1273 K and annealed for 20 min under a flow of 50 sccm of H_2. Then, 1 sccm of methane was introduced into the chamber for 3-30 min. Afterwards, the sample was cooled down to room temperature.

Figure 1 shows a scheme of the of the dry transfer method using PIB as support polymer. Initially, CVD graphene on Cu was treated in oxygen plasma (100 W, 40 s, 30 ml.min^{-1} O_2 flow) from one side to remove any unwanted carbon, i.e., mostly the underside graphene layer. Afterwards, PIB (M_w ~ 500000, Sigma Aldrich) dissolved in hexane (HPLC grade, Sigma Aldrich) drop was spincoated (2700 rpm, 30 s, concentration 60 mg.ml^{-1} PIB in hexane) on the top of graphene-copper sample. After several minutes of hexane evaporation, PDMS (Sylgard 184 silicone elastomer) stamp was attached to the support polymer and gently pressed to remove all remaining air from bellow it. Copper was than etched by FeCl$_3$ (Sigma Aldrich) water solution, several times washed in DI water, dried, stamped on a target substrate and heated up to 333K under vacuum to increase an adhesion between the graphene and the substrate . The PDMS stamp was peeled off carefully and the remaining PIB layer was dissolved in hexane at 323 K.
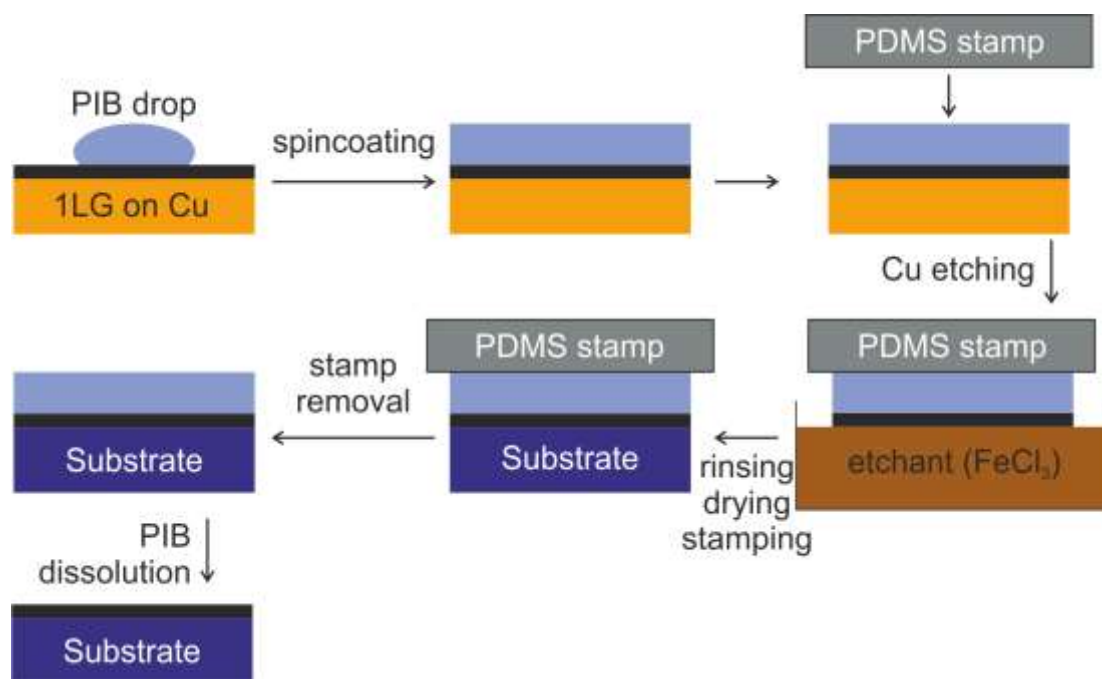

Fig. 1 Scheme of the PIB-assisted transfer procedure.

Raman spectra were measured by Labram HR spectrometer (Horiba Jobin-Yvon) interfaced to an Olympus BX-41 microscope with a 100x objective. Ar-Kr (Coherent Innova 70C Spectrum, 514 nm) laser was used for the excitation. The Raman spectrometer was calibrated by the F_{1g} line of Si at 520.5 cm^{-1}. The G and 2D peaks were fitted by Lorenzian lineshapes. Scanning electron microscopy (SEM) images were obtained using a Hitachi field-emission-scanning electron microscope S-4800 and optical images were acquired by industrial microscope Arsenal. The XPS experiments were carried out using an ESCA 3 Mk 2 spectrometer (VG) with a hemispherical analyzer in fixed transmission mode, using a pass energy of 20 eV. The photoelectrons were excited by the Al $K\alpha_{1,2}$ radiation (1486.6 eV). The pressure during an experiment was of the order of 10^{-9} mbar. The spectra were approximated by a weighted sum of Gaussian and Lorentzian functions.

3. RESULTS AND DISCUSSION

Examples of CVD graphene samples with different growth times, transferred onto a PMMA substrate using the PIB-assisted method are shown in Figure 2. The transfer obviously preserves the general grain shapes (*cf.* Fig.2a and b – before and after transfer, resp.), however, it leads to a marked fragmentation of the grains (*cf.* Fig.2c and d). Statistical analysis of the grains after transfer gives their average lateral dimensions of ~ 9.7 ± 4.1 µm.
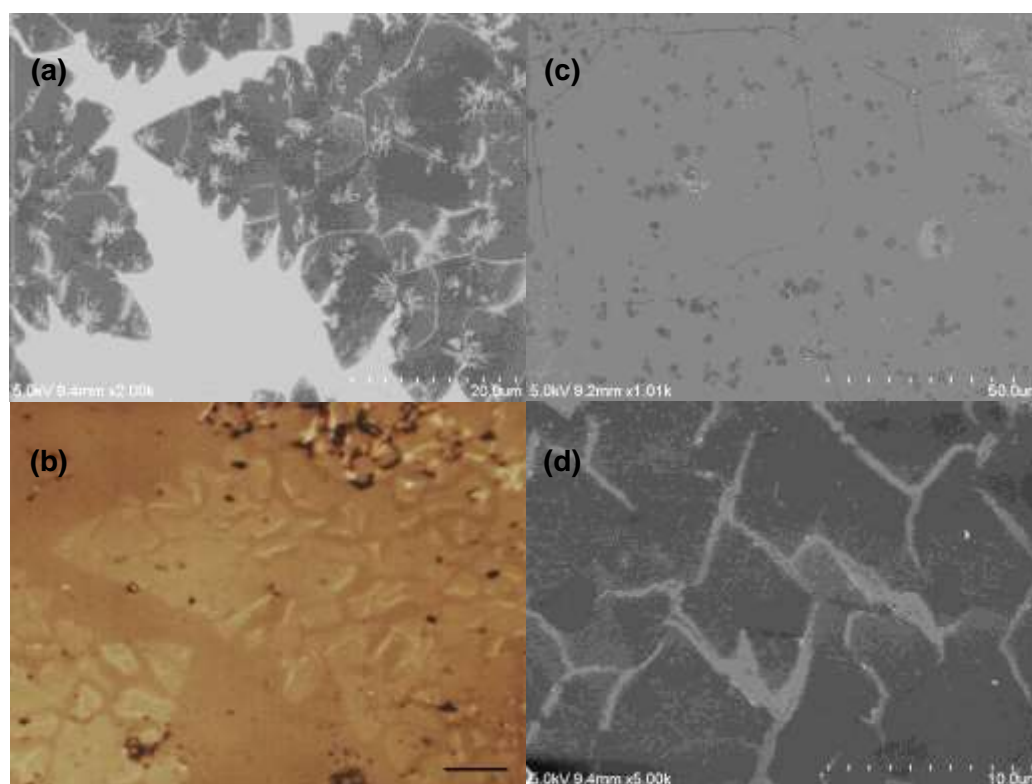

Fig. 2 Scanning electron microscope (a), (c), (d) and optical image (b) of graphene on copper (a), (c) and after transfer (b), (d) on PMMA polymer.

More detailed information about the transferred graphene samples can be provided by Raman spectroscopy, especially measured as spatial maps to obtain enough data for statistical treatment. Figure 3a shows an example of a Raman spectrum after the transfer to a PMMA substrate. The main Raman features of graphene, the G and D modes are clearly visible and they correspond to a monolayer graphene, as evidenced by the narrow, single lineshape 2D mode, and the large ratio between 2D and G mode intensities [14]. The potential defect-induced D mode is overlapped by a Raman mode of PMMA, but upon a careful subtraction of pure PMMA spectra (not shown) we found that the D mode is barely visible even for the highly

fragmented samples. It means that apart from the edges visible in the optical microscope, which might or might not give rise to a D band depending on their orientation and light polarization [15], the interior of the grains is essentially defect-free. Raman maps of one representative grain are shown in Figure 3b and selected correlations of the fitted G and 2D band parameters from the map pixels are shown in Figure 3c.
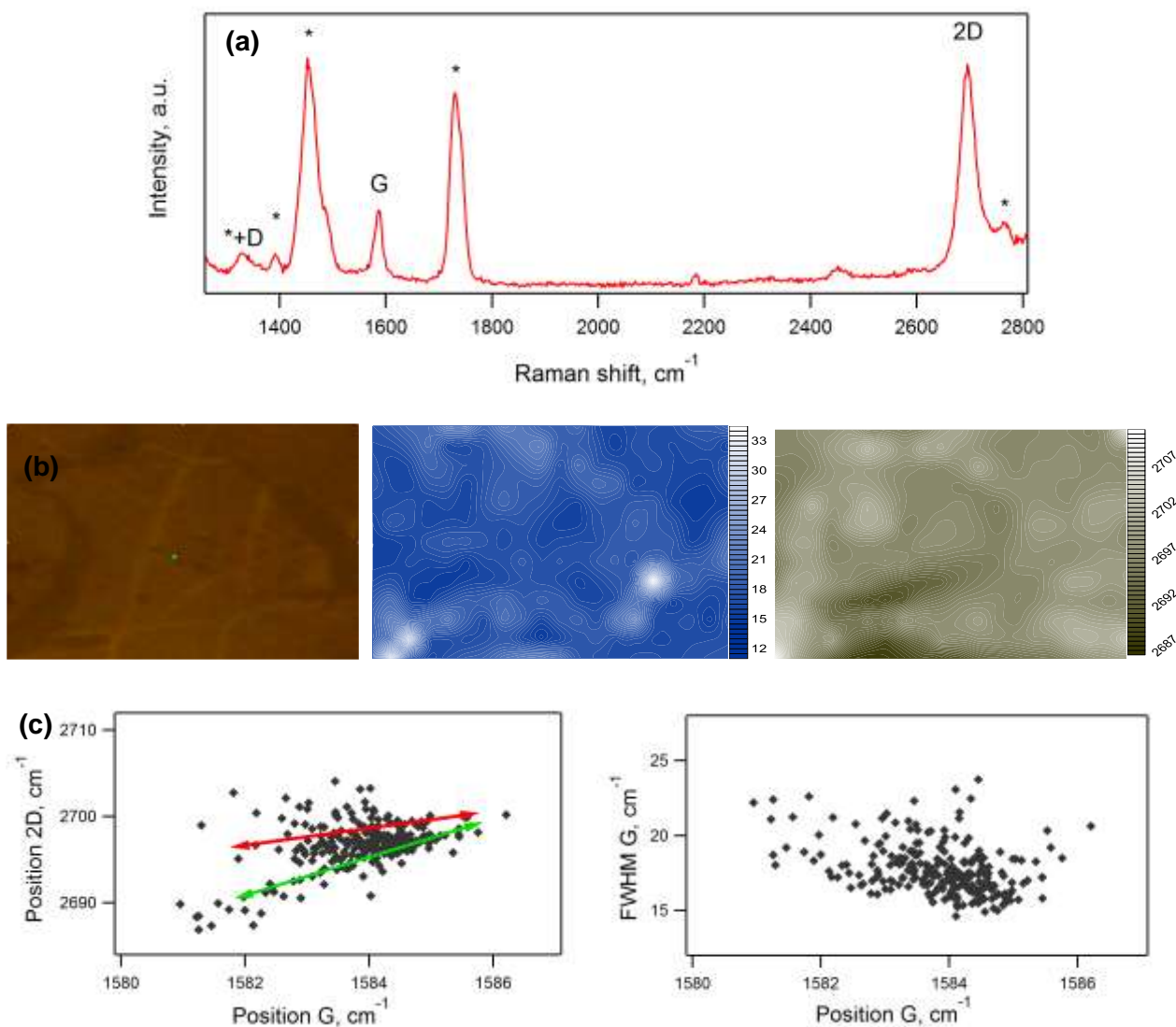

Fig. 3 (a) Raman spectrum of graphene transferred onto the PMMA substrate. G band at ~1580 cm^{-1} and 2D ~2700 cm^{-1} band are labeled, a possible D band at ~1350 cm^{-1} is overlapped by a mode belonging to the PMMA and is barely visible due to low amount of defects in the graphene structure. All other bands (marked by asterisks) belong to subjacent polymer. **(b)** Optical image (left, 100x objective) of the mapped graphene flake and maps (20x12.8 μm) of the full width at half maximum (FWHM) of the G mode (middle) and position of the 2D mode (left). **(c)** Correlations of fitted parameters of the G and 2D bands of the flake shown above. Red and green arrows indicate theoretical directions of values' distribution caused by doping and strain, respectively.

An important finding from Figures 3b and c lies in a quite high homogeneity of the parameters of the Raman features (see also Table 1). Both the G and 2D band positions (~1584 and 2697 cm^{-1}, resp.) are close to frequencies found for almost strain- and doping-free suspended graphene (1582 cm^{-1} for the G band) [16] and their dispersion is even lower than 1 and 3 cm^{-1} for the G and 2D bands, respectively. Similarly the width of the G band (17.7 ± 1.65 cm^{-1}) shows a homogeneous layer with low charge doping [17]. The correlation of

the G and 2D band positions confirms the relatively low scatter of the values with a slightly more pronounced effect of doping than strain on their dispersion, *cf.* the red and green arrows in Figure 3c [18,19], however, the influence of either one is not large.

Table 1 Statistics of selected fitting parameters from the Raman mapping from Fig.3.

Fitted parameters, cm⁻¹	Position G	FWHM G	Position 2D
Average value	1583.9	17.7	2696.8
Standard deviation	0.88	1.65	2.73

According to the photoelectron spectroscopy (XPS) there are some differences between the spectra of the graphene transferred by various techniques (including dry transfer) on silica and highly ordered pyrolytic graphite (HOPG, not shown here). The line shape of C 1s spectrum of dry-transferred graphene (full width at half maximum, asymmetry of the spectrum) is very close with the shape of C 1s spectra of HOPG. The C 1s spectra of graphene transferred by other methods are much broader and more asymmetric. This difference can be explained by (i) polymer remnants, (ii) occurrence of sp^2 defective carbon atoms [20] and (iii) the C 1s binding energy shifts with increasing number of graphene layers [21] (*cf.* distribution of wrinkles and folds, which are clearly visible on SEM and optical images), respectively. These possible effects are difficult to separate. However, together with observed lowest O/Si ratio in the stamped graphene, XPS results point to a very small amount of oxidized carbon atoms and in the same time to a very high amount of ordered carbon atoms forms in the sample.

4.   CONCLUSION

In this work the graphene dry stamp transfer technique was examined through the use of various characterization methods. By optical and scanning electron microscopy it was monitored that it is possible to transfer graphene grains by this process but with a fragmentation of the product, which is mainly due to applied pressure on the graphene/support polymer "sandwich" during the transfer. Distribution of fragmented grain sizes in the sample is relatively narrow and during larger set of transfer experiments minor differences showed up, thus the grain size can be adjusted and optimized. Also, by the XPS measurements, it can be presumed that this method does not contaminate the product by the remnants of polymers from the transfer process and resulting graphene consists from well ordered and minimally oxidized carbon atoms. An analysis of the Raman maps of the transferred graphene flakes showed a significant homogeneity in position and width of the main (G and 2D) Raman modes, as well as low number of the defects inside the grains. Finally, low influence of the strain could be explained by the presence of a higher number of the large cracks and wrinkles as well. This method can be used in the case when fast, cheap and relatively clean transfer of the graphene is needed, however, it is a very limited technique for the use in the large-scale applications.

ACKNOWLEDGEMENTS

REFERENCES

[1]   NOVOSELOV, K.S., GEIM, A.K., MOROZOV, S.V., JIANG, D., ZHANG, Y., DUBONOS, S.V., GRIGORIEVA, I.V., FIRSOV, A.A. Electric field effect in atomically thin carbon films. *Science*, 2004, vol. 306, nr. 5296, p. 666-669.

[2]   BALANDIN, A.A. Thermal properties of graphene and nanostructured carbon materials. *Nature Materials*, 2011, vol. 10, nr. 8, p. 569-581.

[3]   DU, X., SKACHKO, I., BARKER, A., ANDREI, E.Y. Approaching ballistic transport in suspended graphene. *Nature Nanotechnology*, 2008, vol. 3, nr. 8, p. 491-495.

[4]   NAIR, R.R., BLAKE, P., GRIGORENKO, A.N., NOVOSELOV, K.S., BOOTH, T.J., STAUBER, T., PERES, N.M.R., GEIM, A.K. Fine structure constant defines visual transparency of graphene. *Science*, 2008, vol. 320, nr. 5881, p. 1308-1308.

[5]   GALIOTIS, C., FRANK, O., KOUKARAS, E.N., SFYRIS, D. Graphene Mechanics: Current Status and Perspectives. *Annual Review of Chemical and Biomolecular Engineering*, 2015, vol. 6, p. 121-140.

[6]   ZURUTUZA, A., MARINELLI, C. Challenges and opportunities in graphene commercialization. *Nature Nanotechnology*, 2014, vol. 9, nr. 10, p. 730-734.

[7]   LI, X.S., CAI, W.W., AN, J.H., KIM, S., NAH, J., YANG, D.X., PINER, R., VELAMAKANNI, A., JUNG, I., TUTUC, E., BANERJEE, S.K., COLOMBO, L., RUOFF, R.S. Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils. *Science*, 2009, vol. 324, nr. 5932, p. 1312-1314.

[8]   YAN, Z., LIN, J., PENG, Z., SUN, Z., ZHU, Y., LI, L., XIANG, C., SAMUEL, E.L., KITTRELL, C., TOUR, J.M. Toward the Synthesis of Wafer-Scale Single-Crystal Graphene on Copper Foils. *Acs Nano*, 2012, vol. 6, nr. 10, p. 9110-9117.

[9]   AGO, H., OGAWA, Y., TSUJI, M., MIZUNO, S., HIBINO, H. Catalytic Growth of Graphene: Toward Large-Area Single-Crystalline Graphene. *The Journal of Physical Chemistry Letters*, 2012, vol. 3, nr. 16, p. 2228-2236.

[10]   LEE, Y., BAE, S., JANG, H., JANG, S., ZHU, S.-E., SIM, S.H., SONG, Y.I., HONG, B.H., AHN, J.-H. Wafer-Scale Synthesis and Transfer of Graphene Films. *Nano Letters*, 2010, vol. 10, nr. 2, p. 490-493.

[11]   SONG, J., KAM, F.-Y., PNG, R.-Q., SEAH, W.-L., ZHUO, J.-M., LIM, G.-K., HO, P.K.H., CHUA, L.-L. A general method for transferring graphene onto soft surfaces. *Nature Nanotechnology*, 2013, vol. 8, nr. 5, p. 356-362.

[12]   BAE, S., KIM, H., LEE, Y., XU, X.F., PARK, J.S., ZHENG, Y., BALAKRISHNAN, J., LEI, T., KIM, H.R., SONG, Y.I., KIM, Y.J., KIM, K.S., OZYILMAZ, B., AHN, J.H., HONG, B.H., IIJIMA, S. Roll-to-roll production of 30-inch graphene films for transparent electrodes. *Nature Nanotechnology*, 2010, vol. 5, nr. 8, p. 574-578.

[13]   EK-WEIS, J., COSTA, S., FRANK, O., KALBAC, M. Heating Isotopically Labeled Bernal Stacked Graphene: A Raman Spectroscopy Study. *The Journal of Physical Chemistry Letters*, 2014, vol. 5, p. 549-554.

[14]   FERRARI, A.C., BASKO, D.M. Raman spectroscopy as a versatile tool for studying the properties of graphene. *Nature Nanotechnology*, 2013, vol. 8, nr. 4, p. 235-246.

[15]   CASIRAGHI, C., HARTSCHUH, A., QIAN, H., PISCANEC, S., GEORGI, C., FASOLI, A., NOVOSELOV, K.S., BASKO, D.M., FERRARI, A.C. Raman Spectroscopy of Graphene Edges. *Nano Letters*, 2009, vol. 9, nr. 4, p. 1433-1441.

[16]   BERCIAUD, S.P., LI, X., HTOON, H., BRUS, L.E., DOORN, S.K., HEINZ, T.F. Intrinsic lineshape of the Raman 2D-mode in freestanding graphene monolayers. *Nano Letters*, 2013, vol. 13, nr. 8, p. 3517–3523.

[17]   FRANK, O., DRESSELHAUS, M.S., KALBAC, M. Raman Spectroscopy and in Situ Raman Spectroelectrochemistry of Isotopically Engineered Graphene Systems. *Accounts of Chemical Research*, 2015, vol. 48, nr. 1, p. 111-118.

[18]   LEE, J.E., AHN, G., SHIM, J., LEE, Y.S., RYU, S. Optical separation of mechanical strain from charge doping in graphene. *Nature Communications*, 2012, vol. 3, p. 1024.

[19]   FRANK, O., VEJPRAVOVA, J., HOLY, V., KAVAN, L., KALBAC, M. Interaction between graphene and copper substrate: The role of lattice orientation. *Carbon*, 2014, vol. 68, nr. 0, p. 440-451.

[20]   YANG, D.-Q., SACHER, E. Carbon 1s X-ray Photoemission Line Shape Analysis of Highly Oriented Pyrolytic Graphite: The Influence of Structural Damage on Peak Asymmetry. *Langmuir*, 2006, vol. 22, nr. 3, p. 860-862.

[21]   KIM, K.-J., LEE, H., CHOI, J.-H., YOUN, Y.-S., CHOI, J., LEE, H., KANG, T.-H., JUNG, M.C., SHIN, H.J., LEE, H.-J., KIM, S., KIM, B. Scanning Photoemission Microscopy of Graphene Sheets on SiO$_2$. *Advanced Materials*, 2008, vol. 20, nr. 19, p. 3589-3591.