

Graphene growth from the metal/carbon/SiO₂ structure

Petr Machac^{*}, Jan Pajtai^{**}

The paper presents results related to graphene growth by the method of precipitation on the boundary between a transition metal (nickel or cobalt) and a dielectric (SiO₂). The source of graphene is a thin evaporated carbon layer. Carbon in the annealing process diffuses through the transition metal and precipitates on the surface of the dielectric substrate as the structure cools down. Relatively thick layer of copper, which is evaporated over carbon as a cover, prevents carbon to diffuse to the surface of the metallization. The structure of the metallization for graphene forming is then Cu/C/(transition metal)/SiO₂/Si. We consider the utilization of the diffusion barrier to be the contribution of our work to graphene formation using this method. Even though both transition metals are of similar features, the necessary conditions for growth of high-quality graphene are different. In case of nickel, long annealing times within the whole range of annealing temperatures are necessary, while in case of structures with cobalt annealing time of 20 minutes at 900 °C is enough for graphene growth. By annealing the Cu(300 nm)/C(20 nm)/Ni(50 nm)/SiO₂ structure at the temperature of 800 °C for 60 minutes we obtained single-layer graphene (SLG).

Key words: graphene, transfer-free process, nickel, cobalt, Raman spectroscopy, XPS, SEM

1 Introduction

Graphene, allotrope of carbon, has attracted scientists for ages due to its favourable properties. Graphene is a 2D form of carbon (a monolayer or few layers of sp² hybridized carbon atoms) with significant perspective of use in many branches of technology, thanks to its interesting properties [1]. Currently, graphene can be prepared by different methods [2] — chemical vapour deposition, epitaxial growth on SiC, synthesis on the structure metal/SiC and so on.

Frequently used methods of graphene preparation are so-called transfer-free methods [3, 4]. These methods utilize metallization deposited on a dielectric substrate. The metallization contains carbon in various forms, which serves as a source for graphene formation. The metallization further contains catalytic metal, which ensures formation of the crystalline graphene film on the surface of the dielectric layer during the process of annealing and consequent cooling of the structure. An essential step of the preparation process is etching-off of the metallization. This way the structure of graphene/dielectric is directly obtained without the necessity to transfer prepared graphene layer onto a dielectric. The resulting structure can be then used for a number of applications.

The above-described growth of graphene films can be divided according to the used material into groups of similar methods based on different physical principles. The first division is based on the carbon-containing layer. Here, three materials are used: a thin layer of amorphous carbon [5], a polymer [4] and the layer of the metal, which contains certain quantity of dissolved carbon [6]. Second division of the methods for graphene growth is based on

the metal used. These are mainly transition metals; most frequently nickel [7] or cobalt [8], but also iron [6]. Precious metals, such as platinum [9] or palladium [10], are used as well. In such a case, the costs of the preparation are considerably higher. All the metals have the same role; carbon atoms diffuse through them and precipitate on the metal-dielectric boundary in the form of graphene. Different physical principle takes place when copper is used within the base structure [11]. Copper shows minimal solubility for carbon; graphene is formed by a catalytic process on the copper-dielectric boundary.

In our work, we have used a combination of the above-mentioned methods. The source of carbon is a thin layer of amorphous carbon. The contribution of our work is utilization of both transition metal and a copper layer. The metallization is of the structure Cu/C/(transition metal)/SiO₂/Si, where nickel or cobalt are used as transition metals. The base of the metallization is of the bi-layer C/(transition metal), which forms graphene as a result of carbon diffusion through the metal and its precipitation on SiO₂ surface at cooling-down of the structure. The upper cover layer of copper prevents to carbon diffusion on the surface of the metallization. The principal advantage is the used method of graphene growth is its simplicity.

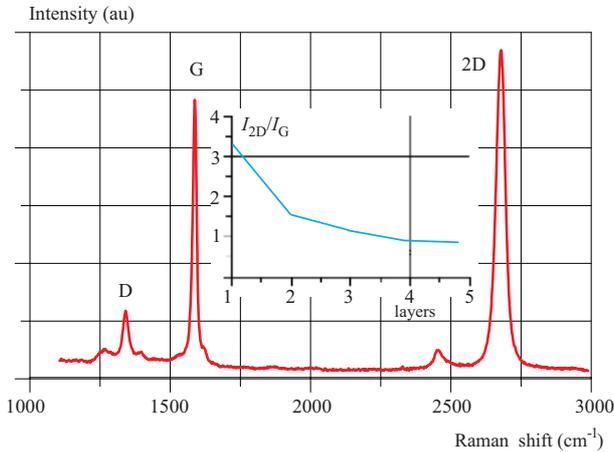
2 Experimental

The substrate for graphene formation was a SiO₂ layer 300 nm thick, prepared by thermic oxidation — this structure had been purchased from ON Semiconductor, Rožnov p. Radhoštěm, Czech Republic. Prior to exposition, the SiO₂ plates were carefully cleaned using the process described in [12]. Metals were deposited by means of

^{*} University of Chemistry and Technology, Prague, Technická 5, 166 28 Prague 6, Czech Republic, petr.machac@vscht.cz, ^{**} CVP Galvanika, 261 01 Příbram VI/550, Czech Republic, pajtai.jan@gmail.com

Table 1. Applied chemicals for the etching

	Chemical compound	Concentration
Ferric chloride	FeCl ₃	10 % wt
Marbles etchant	CuSO ₄ *5H ₂ O+HCl	5 g+25 ml
Nitride acid	HNO ₃	22 % vol
Ammonium peroxodisulphate	(NH ₄) ₂ S ₂ O ₈	0.2 mol/l

**Fig. 1.** Typical example of bilayer graphene raman spectrum prepared from the structure Cu(300)/C(10)/Ni(50)/SiO₂/Si

e-gun evaporation in vacuum of 2×10^{-6} mbar. Standard layer thickness of transition metals was 50 nm, for copper it was 300 nm. Carbon layers were prepared by the flash evaporation method, by burning of carbon filament with current impulse of 16 A in vacuum of 10^{-2} mbar. The plates with individual deposited structures were cut to pieces of approx. 5×5 mm for partial experiments. The structure annealing was done in a small vacuum chamber equipped with a resistively heated ceramic boat Boralectric Heating Element HTR-1001. The range of operational temperatures was 800–950 °C, annealing time was changed within the 5–60 min range. The last operation of graphene layer preparation was etching-off of the metalization. We tested four standard etchants that are used in production processes for etching of copper — Tab. 1. There is a number of such etchants [13], we selected the most frequently used ones and compared their efficiency and usability in the process of graphene preparation.

Raman analysis was carried out using the Thermo Scientific DXR Raman Microscope spectrometer equipped with confocal Olympus microscope. Nd: YAG laser was used as the excitation source with the following measurement conditions: $\lambda = 532$ nm, laser power = 7 mW, 10 accumulations of 10 sec scans, grating with 900 lines/mm and 50 μm slit aperture. The multichannel thermoelectrically cooled CCD camera (magnification 50 \times) was used as a detector, providing measurement spot-size of approximately $1 \mu\text{m}^2$. Raman spectra were measured in the range of 1000–3000 cm^{-1} . Evaluation of the spectra was done using OMNIC for Dispersive Raman software (Thermo Fisher Scientific). Scanning Electron Microscopy (SEM) technique was carried out on LYRA3

GMU microscope (Tescan, Czech Republic). The applied voltage was 10 kV with installed Everhart-Thornley SE detector at the chamber pressure 2.15×10^{-2} Pa. X-ray Photoelectron Spectroscopy (XPS) measurement were performed in an ultra-high vacuum (10^{-8} Pa) using an ESCAProbe apparatus (Omicron Nanotechnology Ltd.) equipped with an Al anode as an X-ray source with energy of 1486.7 eV. The X-ray source was monochromatized. Size of the analysed area was approximately 1 mm^2 . Photographs of the structures were made using the optical microscope Jenavert.

3 Results and discussion

The goal of the experiments was to compare the influence of the transition metal, thickness of the carbon layer and type of the etchant onto graphene preparation. Layer thickness of the transition metals (50 nm) and layer thickness of copper (300 nm) were kept constant within the experiments; their value was not changed. Unpublished experiments showed that influence of these parameters onto graphene quality is minimal. Taking this fact into consideration, graphene growth was studied on four basic structures: Cu(300)/C(10)/Co(50)/SiO₂/Si, Cu(300)/C(20)/Co(50)/SiO₂/Si, Cu(300)/C(10)/Ni(50)/SiO₂/Si, Cu(300)/C(20)/Ni(50)/SiO₂/Si.

Graphene preparation consisted in a search for optimal parameters of the annealing process, in order to obtain graphene with as few carbon monolayers as possible (optimally the SLG) and as low failure rate as possible. Raman spectroscopy was applied for determination of quality of the prepared graphene films, for this technique is fast and simple. Figure 1 shows an example of Raman spectrum of graphene, which has been prepared from the Cu(300)/C(10)/Ni(50)/SiO₂/Si structure (annealing temperature 900 °C and time 60 min). Within the spectrum, typical bands D(1350 cm^{-1}), G(1580 cm^{-1}) and 2D(2700 cm^{-1}) are visible. From the size of these bands, we can judge for graphene quality – the ratio of intensities I_D/I_G gives the failure rate and the I_{2D}/I_G ratio gives number of carbon monolayers in graphene. Such dependence is shown in the inset of Fig. 1, [14]. Quality of graphene layer increases with the increasing I_{2D}/I_G ratio in the Raman spectrum (the number of carbon monolayers in graphene decreases) and at the same time with the decreasing I_D/I_G ratio (the crystallite size L_a increases). This motivated us to introducing a criterion for

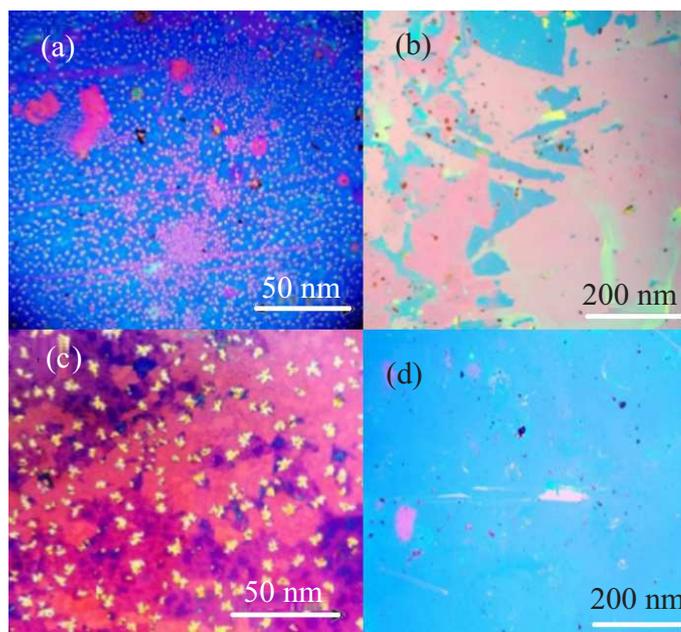


Fig. 2. Photo of structures etched in various etching agents: (a) – nitric acid, (b) – marble etching agent, (c) – ammonium, peroxodisulphate, (d) – ferric chloride

evaluation of graphene layers quality in the form of the parameter [15]

$$\delta = \frac{I_{2D} - I_D}{I_G} \quad (1)$$

which should be as high as possible.

3.1 Structure etching – surface quality

As already discussed above, the last step in the graphene preparation was etching-off of the metallization after its annealing. Within the study, we tested selected etchants used in technical practice for etching of copper – see Tab. 1. The etchants were applied in concentrations as shown in the table. Etching was carried out at room temperature without its stabilization temperature was ranging approx. from 20 to 24 °C, each sample was etched in freshly mixed etchant. It was proved that etching time and proper choice of etchant has significant influence onto quality (namely homogeneity) of prepared graphene. Generally, we can say, that samples with thinner carbon layer were etched-off better. For samples with thicker carbon layer not insignificant carbon segregation on the metallization surface took obviously place and also more carbon remained scattered within the volume of the metallization itself. Residual carbon complicated then the etching process and it took a longer time. An experiment was carried out with the aim to remove surface carbon before etching by burning it with oxygen plasma. The etching process however was not any faster, which bears witness to the principal influence of carbon scattered within the metallization itself instead of on its surface.

The influence of the individual etching agents onto homogeneity and quality of graphene layer on the SiO₂ substrate is shown at Fig. 2. There is the surface of the

Cu(300)/C(20)/Co(50)/SiO₂/Si structure in all examples (annealing temperature 900 °C and time 20 min). Fig. 2(a) shows the surface after etching-off with nitric acid for the period of 190 min. It is obvious from the picture that the etching agent has left residues of metallization on the surface of the structures even after the long period of etching and thus it is not suitable for graphene preparation. At Fig. 2(b), there is the surface etched with Marble's etching agent for 30 minutes. This etching agent is relatively fast and more suitable for structures with nickel. This etching, however, provided unrepeatable results and it often removed even the carbon layers, as evident from Fig. 2(b). Therefore, this etching agent, too, was not used for the experiments. Figure 2(c) represents the surface etched-off with ammonium peroxodisulphate for the period of 24 hours. This etching agent is very slow and it again has left residues of metallization on the surface, so that it was not suitable for the experiments. Finally Fig. 2(d) shows the surface after etching in the solution of FeCl₃ for the period of 60 min. This etching agent provided the best results, the etching period for the individual structures reached 60–120 min. In further text, only the results obtained for structures etched-off with this etching agent are described.

For determination of graphene layers quality, the SEM technique was used. Figure 3 shows a detail of graphene layer surface prepared from the Cu(300)/C(20)/Ni(50)/SiO₂/Si structure (annealing temperature 900 °C, time 60 min, etching in FeCl₃) visualized by this technique. At the picture, traces of boundaries of the individual graphene crystals are visible; these could be, however, also the imprints of the boundaries of metallization grains. Right at the boundaries of these grains carbon diffuses much easier, precipitation takes place, and therefore they are more distinct. At the graphene surface, further irregular impurities are visible. These are most probably

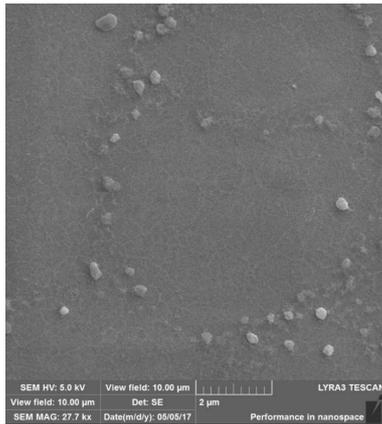


Fig. 3. SEM micrograph of graphene prepared from the structure Cu(300)/C(20)/Ni(50)/SiO₂/Si

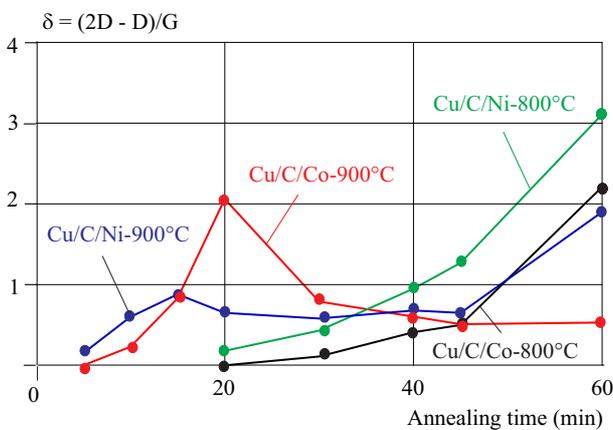


Fig. 5. Dependence of the δ parameter on annealing time: black line - Cu/C/Co, 800°C, red line - Cu/C/Co, 900°C, green line - Cu/C/Ni, 800°C and blue line - Cu/C/Ni, 900°C

impurities that come from the fact, that we do not have at disposal clean rooms.

3.2 Optimization of the annealing process available

In this paragraph, optimization of the annealing process is described with the aim to prepare highest quality graphene layers. This optimization was based on measurement of basic parameters of graphene by means of Raman spectroscopy. Parameter δ defined by (1) was taken for the principal measure of graphene layer quality. In the following graphs, the individual points represent average values of the parameter δ measured in 5 points randomly chosen at the samples' surface. The experiments were based on a search for optimal annealing conditions for four said structures, where the annealing temperature was changed within the range of 800–950 °C and for the individual temperatures; the annealing times were set within the range of 5–60 min. Other annealing conditions were kept constant — temperature ramp rate 17.5 °C/s and cooling rate 15 °C/s. As already stated above, etching-off of the metallizations was carried out using FeCl₃.

First, the influence of annealing temperature onto quality of prepared graphene was followed. At Fig. 4, the

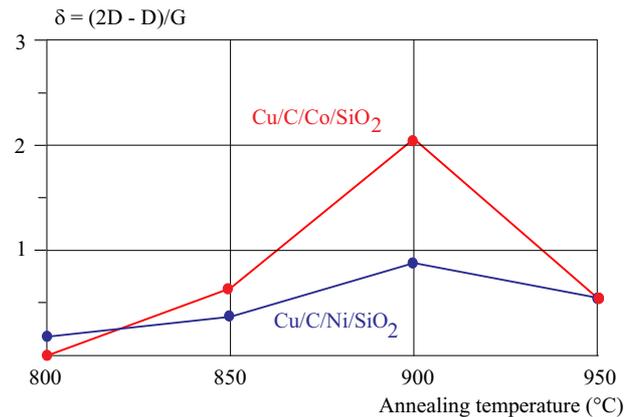


Fig. 4. Dependence of the δ parameter on annealing temperature: red line - Cu/C/Co/SiO₂, blue line - Cu/C/Ni/SiO₂ structure

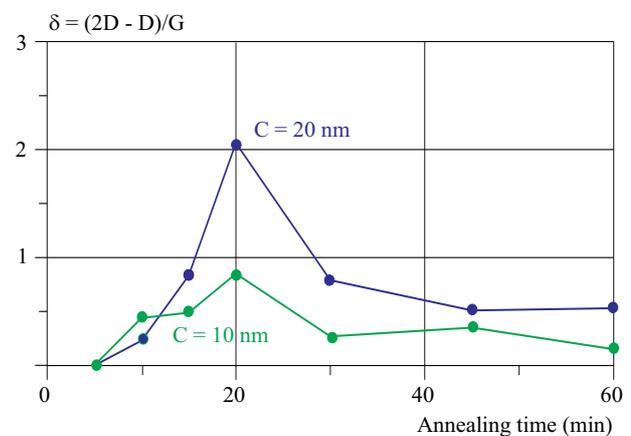


Fig. 6. Dependence of the δ parameter on annealing time for various thicknesses of carbon layer in the metallization with cobalt: blue line 20 nm, green line 10 nm

parameter δ is shown as function of annealing temperature for structures with both cobalt and nickel. Carbon thickness is in both cases 20 nm and annealing time 20 min. From the diagram, it is obvious that graphene shows the best parameters at annealing temperature of 900 °C for both structures with cobalt and nickel. The graphene film formed from the structure with cobalt gets by its parameters close to SLG, it consists of one to two carbon monolayers. In case of the structure with nickel, graphene was formed that consists of 2–3 carbon monolayers.

Figure 5 illustrates dependence of quality of prepared graphene layers on annealing time. The individual dependences belong to structures with nickel and cobalt at annealing temperatures 800 and 900 °C. The experiments show that for 800 °C short annealing times are insufficient. The highest quality graphene was formed at the annealing time of 60 min for both basic metals. In case of nickel, SLG was prepared, in case of cobalt graphene shows slightly worse parameters, as more two-layered graphene (BLG) is contained in the prepared layer. Annealing to 900 °C resulted in quite more complicated dependences of the δ parameter. For the structure with cobalt, the highest quality graphene was prepared with

Table 2. Survey of basic parameters of chosen graphene layers

Structure	Annealing process		Etching time (min)	Graphene parameters		
	temperature (°C)	time (min)		I_{2D}/I_G	I_D/I_G	number of monolayers
Cu(20)/Co	800	60	120	2.32	0.11	1
	900	20	130	0.74	0.25	3
Cu(10)/Co	850	10	60	0.23	0.67	> 5
	900	20	60	1.05	0.26	2–3
Cu(20)/Ni	800	60	120	3.55	0.41	1
	850	40	90	1.49	0.11	2
	900	60	120	2.11	0.21	1–2
Cu(10)/Ni	900	15	60	1.15	0.27	2
	950	15	60	0.91	0.43	2–3

Table 3. Element representation on surface of the structures

Structure	Composition (at %)				
	C	O	Si	Fe	Cl
Cu(20)Ni	78.31	16.81	1.71	1.79	1.4
Cu(20)/Co	90.09	7.62	0.67	0.85	0.77

annealing time of 20 min. Graphene prepared from the structure with nickel within the range of annealing times 15 to 45 min was of roughly constant quality, the highest quality graphene corresponds to the longest time (SLG with large representation of BLG).

The last dependence shown at Fig. 6 represents graphene quality as function of thickness of carbon layer in the metallization. The graph illustrates dependence of the δ parameter on annealing time. Thickness of carbon layer is a parameter of the individual curves. In the graph there are plotted data belonging to the structure with cobalt annealed at 900 °C. From the dependences, it is obvious that higher quality graphene was prepared from the structure with thicker carbon layer. Similar results were obtained for structures with nickel.

From the results that are represented in this paragraph following conclusions can be done:

- for the structure with nickel, SLG was prepared, long annealing times were necessary; however, temperature of 800 °C suffices, the structure with thick carbon layer was more advantageous; ferric chloride suited for etching, etching time is about 120 min
- for the structure with cobalt, graphene on the boundary of SLG-BLG was prepared, long annealing times were necessary for annealing at 800 °C; for 900 °C 20 min were enough. Conclusions related to etching and thickness of carbon layer, were identical as for the nickel structure

For information, the best results obtained from all metallizations at chosen temperature were summarized in Tab. 2. The table contains the following information:

- the column “structure” gives the type of metallization – C(xx)/Ni represents metallization with nickel and layers of appropriate thickness of carbon; marking C(xx)/Co has similar meaning,
- information on the annealing process (temperature and time),
- ratios I_D/I_G and I_{2D}/I_G ,
- estimated number of carbon monolayers.

3.3 XPS spectroscopy

XPS spectroscopy was used for verification, whether Raman spectroscopy truly detected graphene. The analysis was carried out with the sample of Cu(300)/C(20)/Ni(50)/SiO₂/Si that had been annealed at 800 °C for 60 min and subsequently etched-off in Ferric chloride. Figure 7 shows a detail of XPS C1s core level spectrum taken off the surface of the graphene layer made on the given structure. C1s spectrum contains just two dominant bands on binding energy roughly within the range of 284.4–284.75 eV and 288.6–288.7 eV. The first one relates to the C=C – sp² bounds of graphitic carbon (graphene) and the second one belongs to an unspecified bound C–O [16–17]. Table 3 contains the proportional ratio of elements detected on the surface of graphene layers prepared from the structures containing nickel and copper. These are carbon, oxygen, silicon, iron and chlorine. Carbon originates from the prepared graphene, oxygen is once bound to the carbon layer, but also to silicon, which forms the basic substrate of the structure. Chlorine and iron represent the residua of the used etching agent. It is important, that in neither structure any of the elements from the metallization (nickel and copper) were detected, which testify on their perfect etching-off.

4 Conclusion

The work summarizes results of graphene preparation by so-called transfer-free method, which is simple, usable in practice, not demanding on complicated equipment and thus capable of forming graphene with low

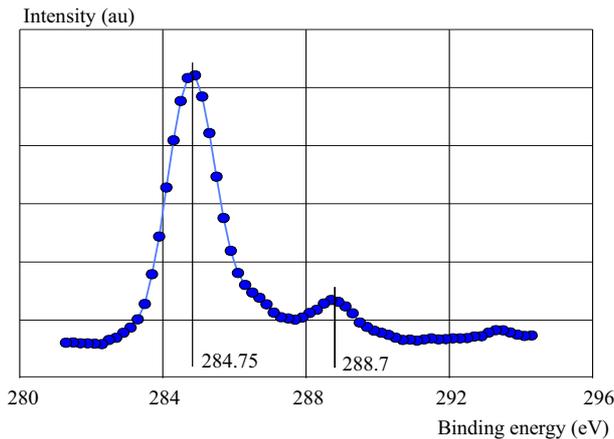


Fig. 7. XPS C1s core level spectrum

costs. The paper has been dedicated to graphene growth from the Cu/C/(transition metal)/SiO₂ structure. A set of structures containing cobalt or nickel and two different thicknesses of carbon was prepared. Several etching agents were tested for the necessary etching-off of metallization; Ferric chloride proved to be the most suitable one. Even though both transition metals are of similar features, the necessary conditions for growth of quality graphene are different. In case of nickel it is necessary to use long annealing times within the whole range of annealing temperatures, while in the case of the structure with cobalt suffices for graphene growth at 900 °C annealing time of 20 min. The metallization with nickel produces graphene films with better parameters. By annealing the Cu(300 nm)/C(20 nm)/Ni(50 nm)/SiO₂ structure at 800 °C for 60 min we obtained SLG with very low failure rate, which is given by the I_D/I_G ratio obtained from Raman spectra.

Verification, whether the prepared layers truly consist of graphene, was carried out by means of XPS analysis. The measurement confirmed that in the carbon layers there are the sp² bounds, which form the structure of graphene. Macroscopic homogeneity of the prepared layers, however, was not really good; it is probably affected by the unavoidable final etching-off of metallization. Further research will have to be focused on the problem.

Acknowledgements

This study was supported by the Czech Science Foundation, Project No. 17-00607S.

REFERENCES

- [1] W. Choi, I. Lahiri, R. Seerlabozina and Y. S. Kang, "Synthesis of Graphene and its Application: a Review", *Cri. Rev Solid Mater. Sci.* vol.35, 2010, pp. 52–71.
- [2] K. E. Whitener and P. E. Sheehan, "Graphene Synthesis", *Diamond Rel. Mater.* vol. 46, 2014, pp. 24–34.
- [3] K. Katakura *et al.*, "Surface Morphology of Multilayer Graphene Synthesized Directly on Silicon Dioxide", *Phys. Status Solidi C*, vol. 10, 2013, pp. 1628–1631.
- [4] H. K. Seo and T. W. Lee, "Graphene Growth from Polymers" *Carbon Lett.* vol. 14, 2013, pp. 145–151.
- [5] G. Pan *et al.*, "Transfer-Free Growth of Graphene on SiO₂ Insulator Substrate from Sputtered Carbon and Nickel Films", *Carbon*, vol. 65, 2013, pp. 349–358.
- [6] M. Kosaka, S. Takano, K. Hasegawa and S. Noda, "Direct Synthesis of few- and Multi-Layer Graphene Films on Dielectric Substrates by "etching-precipitation" method", *Carbon*, vol. 82, 2015, pp. 254–263.
- [7] W. C. Yen *et al.*, "Ultra-Fast Synthesis of Graphene and Highly Oriented Graphite by Rapid Microwave Heating Process", *Sci. Adv. Mater.*, vol. 6, 2014, pp. 1–8.
- [8] M. E. Ayhan *et al.*, "Synthesis of Transfer-Free Graphene by Solid Phase Reaction Process in Presence of a Carbon Diffusion Barrier", *Materials Letters*, vol. 129, 2014, pp. 76–79.
- [9] J. H. Gao *et al.*, "Graphene Growth on a Pt(111) Substrate by Surface Segregation and Precipitation", *Nanotechnology*, vol. 23, 2012, 055704.
- [10] J. H. Gao, N. Ishida, I. Scott and D. Fujita, "Controllable Growth of Single-Layer Graphene on a Pd(111) Substrate", *Carbon*, vol. 50, 2012, pp. 1674–1680.
- [11] Z. Wu *et al.*, "A Fast Transfer-Free Synthesis of High-Quality Monolayer Graphene on Insulating Substrates by a Simple Rapid Thermal Treatment", *Nanoscale*, vol. 8, 2016, pp. 2594–2600.
- [12] P. Machac and O. Hejna, "Transfer-Free Chemical Vapour Deposition Process for Graphene Preparation", *Proceeding of IMAPS Flash Conference*, Brno, 2016, pp. 75–76.
- [13] M. Yuh *et al.*, "Wafer Size Effect on Material Removal Rate in Copper CMP Process", *J. Mech. Sci. Technol.*, vol. 31, 2017, pp. 2961–2964.
- [14] Y. Hao *et al.*, "Probing Layer Number and Stacking Order of Few-Layer Graphene by Raman Spectroscopy", *Small*, vol. 6, 2010, pp. 195–200.
- [15] P. Machac, T. Fidler, S. Cichon and V. Jurka, "Synthesis of Graphene on Co/SiC Structure", *J. Mater. Sci.: Mater. Electron.*, vol. 24, 2013, pp. 3793–3799.
- [16] S. Kim *et al.*, "Robust Graphene Wet Transfer Process through Low Molecular Weight Polymethylmethacrylate", *Carbon*, vol. 98, 2016, pp. 352–357.
- [17] R. R. Sagar *et al.*, "Growth of Graphene on Copper and Nickel Foils via Chemical Vapour Deposition using Ethylene", *Mat. Res. Innovation*, vol. 18 (sup4), 2014, pp. S4-706–S4-710.

Received 21 March 2018

Petr Machač was born in Hranice, Czech Republic in 1953. In 1977 he graduated in Electrical engineering from the Czech Technical University in Prague and received the PhD degree in electronics from the same university in 1982. From 1978 to 1984 he was with the Czech Technical University Prague. In 1991 he was appointed associate professor in electronics with the Czech Technical University Prague, being active with the University of Chemistry and Technology, Prague, from 1984 till now. His current research interests are in deposition of materials, formation of contacts on semiconductor materials (mainly SiC), and preparation of graphene layers by several methods. He is author or co-author of more than 60 articles in scientific journals and 100 contributions at international conferences.

Jan Pajtai was born in Příbram, Czech Republic in 1992. From 2007 to 2011 he was studying Masaryk Secondary School of Chemistry, Prague. In 2017 he graduated in Materials for electronics from the University of Chemistry and Technology, Prague. Theme of his final thesis was Growth of graphene film from a structure metal/carbon/dielectric. Now he is working in CVP Galvanika s.r.o., Příbram, as Chemical process technician.