

Graphene growth by chemical vapor deposition process on copper foil

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Anotace:

Příspěvek popisuje přípravu a charakterizaci grafenových filmů připravených metodou chemické depozice z plynného prostředí. Je použit reaktor se studeným pláštěm, jako zdroj uhlíku je použit metan. Grafen je vytvořen na měděné fólii při teplotě cca 1000°C. Druhým krokem přípravy je přenos grafenu na dielektrický substrát s využitím polymethylmethakrylátu. Nejlepší připravené grafenové filmy vykazují tloušťku v rozmezí jedné až dvou uhlíkových nanovrstev.

ÚVOD

Graphene, a mono or few layers of sp^2 hybridized carbon atoms, has significant perspective of use in microelectronics, due to its highly interesting features [1]. These favorable properties predestinate graphene as a possible candidate for post-silicon electronics. Graphene can be prepared in a number of technological procedures [2]. Here, we present a simple cold-wall chemical vapor deposition (CVD) method [3] for preparation of the graphene film on a Cu foil.

SAMPLE PREPARATION

The basic material for graphene preparation is copper foil by the GoodFellow company, 0.025 mm thick, of cleanness 99.95%. Before the CVD process, the foil was cleaned in acetone, isopropylalcohol and acetic acid. Graphene growth was carried out in the nanoCVD-8G apparatus by the Moorfield Nanotechnology Company (a cold-walled apparatus with low-thermal-mass heater stage, maximal substrate size 20 x 40 mm). The applied process can be divided into 4 basic stages: heating-up of the heater stage in hydrogen and argon atmosphere to the required temperature; annealing of the foil, again in hydrogen and argon atmosphere; the growth itself in atmosphere enriched in methane; cooling down of the foil in argon atmosphere. Cleanness of the gasses was as follows: argon 6.0, hydrogen 5.5 and methane 5.5.

The second - practically equally important - step of graphene preparation using the CVD method is graphene transfer onto a dielectric substrate, which is most often a SiO_2 layer on silicon. In practice, a number of various methods are being used [4]. We choose the classical procedure using polymethylmethacrylate (PMMA). A layer of PMMA (5% solution in chloroform), 0.5 μm thick, was applied onto the copper foil with graphene by the spincoating method, followed by drying of the samples at temperature of 150°C for 30 min and by etching-off of the copper foil in Marbles etchant

($CuSO_4$ 5g, HCl 25ml, H_2O 25ml). The resulting PMMA/graphene foil was then carefully washed in water and placed onto SiO_2 surface, where it was allowed to dry at temperature of 80°C. The last step was removing of the PMMA layer by diluting in boiling chloroform.

Raman analysis was performed on DXR Raman Microscope spectrometer of the company Thermo Scientific equipped with confocal Olympus microscope. As excitation source was used solid-state Nd:YAG laser (wavelength 532 nm, maximum power 10 mW). Measurement conditions were 7 mW power, 10 accumulations of 10 sec. scans, grating with 900 lines/mm and aperture 50 μm slit. As detector was used a multichannel thermoelectrically cooled CCD camera. Magnification 50x provided measurement spot-size $\sim 1 \mu m^2$.

RESULTS

The CVD process optimization was based on the data obtained from the apparatus manufacturer and from literature [3]. The basic parameters were the growth temperature (900 – 1050°C), time of the individual stages of the process (tens of seconds up to single minutes), pressure in the reactor (2 – 20 Torr), ratio of gasses in the reactor ($H_2:CH_4$ 2:35).

Fig. 1 shows an example of Raman spectra of graphene films on the Cu foil (spectrum a) and after transferring it into SiO_2/Si substrate (spectrum b). The graphene film was prepared at the following conditions: annealing at 1000°C for 10 min, the process itself was carried out at temperature of 1000°C for 5 min, flow of gasses H_2 0.4 sccm and CH_4 7 sccm. The spectrum of as growth graphene is modified by the luminescence of Cu foil. Within the spectra, 3 basic carbon bands are apparent: D (1350 cm^{-1}), G (1580 cm^{-1}) and 2D (2700 cm^{-1}). From the ratio of the I_{2D}/I_G bands, the number of carbon monolayers within the graphene can be determined, and from the ratio of the I_D/I_G bands it is possible to deduce size of crystals, from which the graphene layer consists (layer failure rate) [5]. It is obvious, that the graphene film obtain between 1 and 2

monolayer. The sample contains a large number of failures (ratio of the bands I_D/I_G is relatively high).

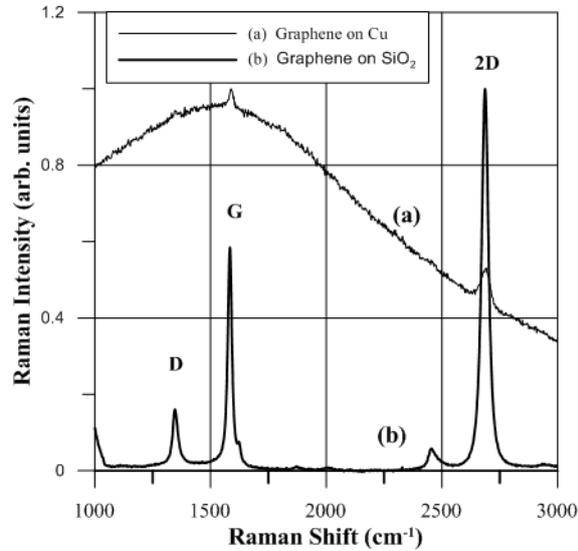


Fig. 1: Raman spectra of the graphene film on Cu foil (a) and after transferring it into SiO₂/Si substrate (b).

In Tab. 1, parameters of prepared graphene films of given ratios I_{2D}/I_G and I_D/I_G are shown for better clarity in dependence on the conditions of their preparation. The stated values were obtained from Raman spectra of graphene films after their transfer onto the SiO₂/Si substrate. The table is amended with a column, which shows the estimated number of carbon monolayers within the graphene film [5]. As far as the number of layers is concerned, graphene films prepared at the following conditions: 1025°C, 300s and 1000°C, 300s seem to be the best. The area of these films partially consists of mono-layer graphene, partially consists of two- or more-layered graphene.

Tab. 1: List of parameters of prepared graphene films.

CVD parameters		Basic parameters of graphene films		Estimated number of carbon layers
Temperature (°C)	Time (s)	I_{2D}/I_G	I_D/I_G	
1050	300	0.95	0.15	2 - 3
1025	300	1.76	0.27	1 - 2
1025	600	1.41	0.12	2
1000	300	1.56	0.25	1 - 2
1000	600	0.94	0.20	2 - 3
950	300	0.96	0.18	2 - 3
900	150	1.40	0.25	2
900	300	1.01	0.16	2 - 3
900	600	0.98	0.20	2 - 3

An important feature of graphene films is their morphology. At Fig. 2, parts of surface of a graphene film prepared at 1000°C for 300s are visualized by

various techniques. Fig. 2a shows a photo obtained from an optical microscope. There are visible cracks, which resulted from graphite transfer from Cu foil onto the SiO₂/Si substrate, as well as point defects caused by imperfect cleanness of the surrounding environment at graphene preparation or by unremoved residues of PMMA. Fig. 2b shows a selected section without macroscopic defects, visualized by the Scanning Electron Microscopy (SEM) method. The area is approx. 15x15 μm large. The surface consists of tiny flakes, which is confirmed by alternating of mono-layered and two- or multi-layered graphene monocrystals on the surface. Fig. 2c then shows a surface section of about 2x2 μm size, visualized by the Atomic Force Microscopy (AFM) method. The surface is of globular character and covered by clusters of atoms, distributed relatively uniformly over the structure surface.

For verification of existence of graphene on the SiO₂/Si substrates after transfer of graphene films, the X-ray Photoelectron Spectroscopy (XPS) method has been used. Fig. 3 shows details of binding energies for the C1 carbon band. Fig. 3a shows the dependence obtained at exciting the spectrum under the right angle, the said spectrum provides information from greater depth below the surface. At Fig. 3b, there is the measurement under the angle of 9° from the surface; this spectrum provides the data basically just from the surface of the structure.

The spectrum shown at Fig. 3a has been distributed into 6 partial peaks in the shape of the Gaussian-Lorentzian function; we have used data from literature [6, 7, 8] for their assignment. The obtained dominant peak has binding energy 288 eV, which corresponds to the C-O bonds. The peak of binding energy 284,8 eV is corresponding to the graphitic bonds sp², which originate from graphene on the SiO₂ surface. Also, the residuals of PMMA are apparent within the spectrum, with the corresponding peaks of 286,8 and 289,5 eV of binding energy. Further, the spectrum contains traces of common adsorbed carbon (bonds C-H, sp³ and some others), to whose belongs the peak of 285,7 eV of binding energy. We were unable to identify the last peak of 291,7 eV of binding energy with the available literature. From the spectrum, which was scanned under the angle of 9° (see Fig. 3b) it is obvious, that the dominant peak corresponds to the sp² bonds, i.e. to the graphitic carbon – graphene. The peak corresponding to common adsorbed carbon is not represented here; this constituent is probably bound directly to the SiO₂ surface. Other constituents have remained in the spectrum.

Based on the XPS analysis it is possible to state, that graphitic carbon is present in the surface carbon layer in the form of graphene. The layer is however contaminated with PMMA residuals, with carbon adsorbed on the substrate surface including carbon in oxidized state, and other unspecified bonds.

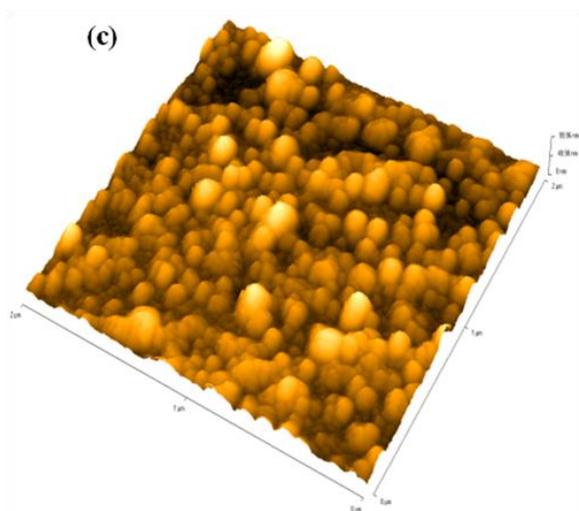
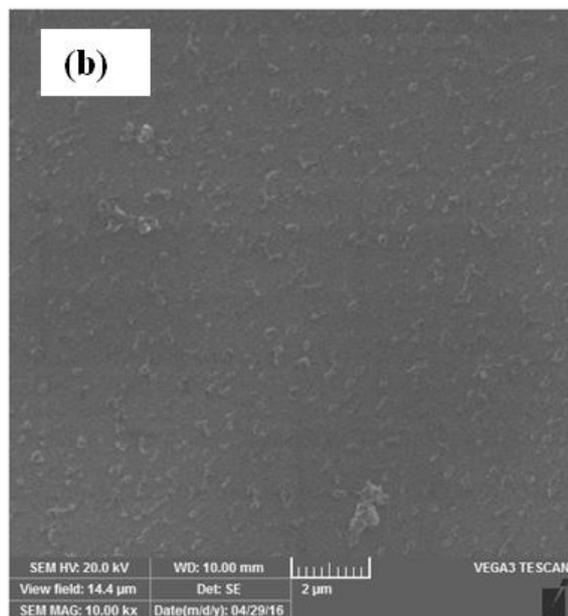
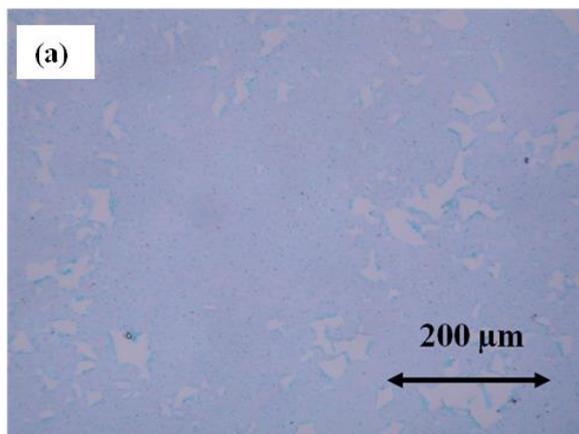


Fig. 2: Surface morphology of the graphene film: (a) – optical microscope, (b) – SEM, (c) – AFM.

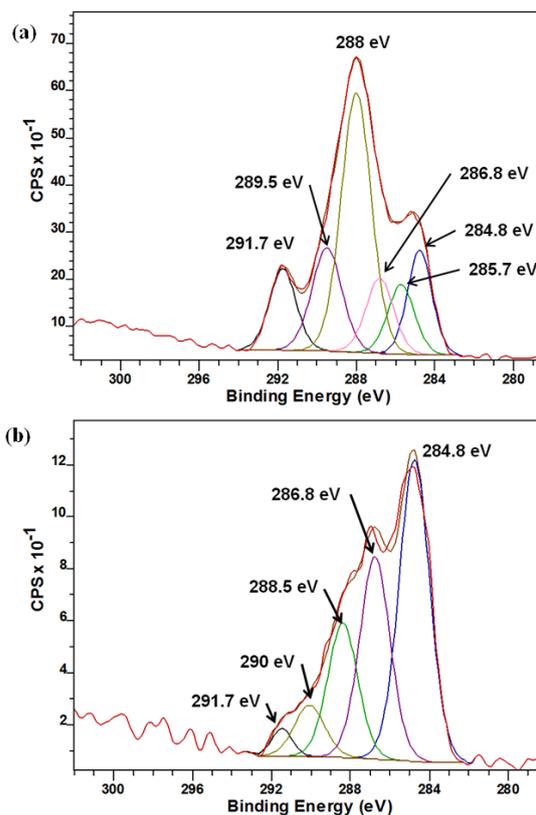


Fig. 3: Details of C 1s peaks from XPS spectra: (a) – measurement angle 90° , (b) – measurement angle 9° .

CONCLUSION

The paper describes preparation of graphene by the CVD method with cold-walled reactor, where copper was used as the basic material. Graphene films on the SiO_2/Si substrate were obtained by means of transfer. The prepared films have character of mono- or two-layered graphene. The optimal growth conditions are as follows: $1000 - 1025^\circ\text{C}$, growth time 300s, flow of gasses through the reactor H_2 0.4 sccm, CH_4 7 sccm. The surface of the prepared graphene films is not of a good quality due to defects, which occur at the transfer onto the dielectric substrate. The character of the surface is of tiny flakes, which are formed from crystals of various number of carbon monolayers. Existence of graphene on the surface of the samples was verified by the XPS analysis.

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