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COMMUNICATION

Graphene growth by transfer-free chemical vapour deposition on a cobalt layer

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The contribution deals with the preparation of graphene films by a transfer-free chemical vapour deposition process utilizing a thin cobalt layer. This method allows growing graphene directly on a dielectric substrate. The process was carried out in a cold-wall reactor with methane as carbon precursor. We managed to prepare bilayer graphene. The best results were obtained for a structure with a cobalt layer with a thickness of 50 nm. The quality of prepared graphene films and of the number of graphene layers were estimated using Raman spectroscopy. with a minimal dots diameter of 180 nm and spacing of 1000 nm were successfully developed.

K e y w o r d s: graphene, cold wall reactor, CVD process, transfer-free process

1 Introduction

Graphene is a very interesting material with many applications in microelectronics due to its extraordinary parameters such as high electron mobility, very low resistivity, metallic and semiconductive behaviour, very low absorption of white light or high coefficient of thermal conductivity [1]. These parameters predestinate graphene as a possible candidate for substitution of silicon in future electronics. Utilization of graphene is prospective for fabrication of field effect transistors, ballistic transistors, transparent electrodes, sensors, batteries, memories, supercapacitors and other applications [2].

Graphene can be prepared by a number of various methods. One of the frequently used methods for graphene preparation is CVD (chemical vapour deposition),[3]. The said method is used for preparation of graphene layers onto thin metallic foils, mainly on copper. A disadvantage of this method is the necessity of transferring the prepared graphene onto a dielectric substrate. Such graphene films exhibit worse homogeneity and possible contamination by residues of the polymers that are used in the transfer process. This problem can be overcome using the so-called CVD transfer-free method [4,5] which makes possible to prepare graphene directly on a dielectric substrate (SiO_2/Si) without any transfer. In our experiments we applied a cobalt layer and a resistively heated stage cold-wall CVD reactor with high-efficiency heating. This setup reduced the processing time and energy consumption [6].

2 Sample preparation

Graphene preparation using the said method is carried out as follows. A silicon substrate with a 300 nm thick thermally grown SiO_2 layer is used as a substrate. The substrate plates were cleaned in acetone and in a mixture of NH_4OH:H_2O:H_2O_2 with ratio 1:1:1. Cobalt was employed as a metal catalyst layer, deposited by e-gun evaporation in a UNIVEX 450 apparatus, the layer thickness was in the range from 50 to 200 μm. Prior to deposition, the substrates were cleaned in oxygen plasma (time 30 min, pressure 10 Pa, power density 1.2 W/cm^2). The CVD process was carried out in the nanoCVD-8G apparatus by Moorfield Nanotechnology Ltd with a cold-wall reactor. The samples were first annealed at a temperature ranging from 800 to 1000 °C for 60 s in the atmosphere of Ar:H_2 5:1, pressure 1.33 kPa (10 Torr). The CVD process itself proceeded at the same temperature in an atmosphere of H_2:CH_4 with a ratio of 2:35 at a pressure of 1.33 kPa for 30 to 600 s. During the CVD process, methane dissociated on the metal surface and carbon atoms diffused into the metallic layer. During cooling of the structure in the chamber of the CVD apparatus (argon atmosphere, 2.67 kPa) to ambient temperature, the carbon atoms segregated both on the metal surface and at the metal-SiO_2 boundary, where they formed a graphitic layer. The upper carbon layer was removed by burning with oxygen plasma (the same process as for substrate cleaning). The last step of graphene preparation was etching-off of the metallic layer in the mixture of HNO_3:H_2O with ratio of 1:5. After this step, the lower graphitic layer; the graphene film; remains on the SiO2 surface.

Raman analysis was performed using the DXR Raman Microscope spectrometer of the company Thermo Scientific equipped with a confocal Olympus microscope. A solid-state Nd:YAG laser was used as an excitation source (wavelength 532 nm, maximum power 10 mW). Measurement conditions were as follows: 7 mW power, 10 accumulations of 10 s scans, grating with 900 lines/mm and slit aperture 50 μm. A multichannel thermoelectrically cooled CCD camera (magnification 50×) was used as a

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Table 1. Parameters of the prepared graphene films

CVD parameters			Basic parameters of graphene films		Estimated number of carbon layers
Thickness of Co layer (nm)	Temperature (°C)	Time (s)	I_{2D}/I_G	I_D/I_G	
50	900	480	1.19	0.11	2
100	900	600	1.07	0.03	2 to 3
150	900	600	0.77	0.32	3
200	900	600	–	–	aC

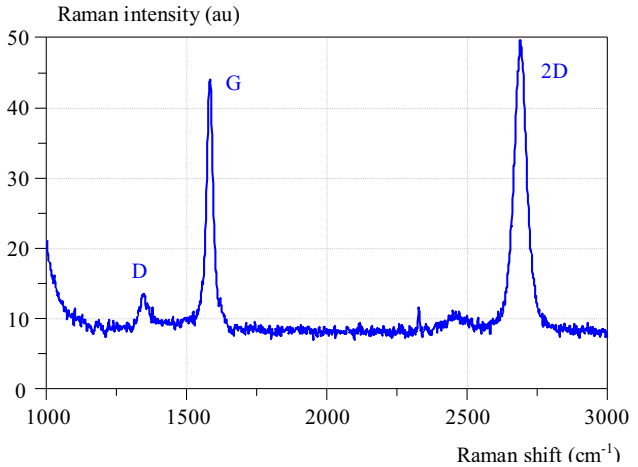

Fig. 1. Raman spectrum of the best graphene film

detector, providing measurement spot-size of approx. 1 μm^2.

Scanning electron microscopy (SEM) was used (LYRA3 GMU, Tescan, Czech Republic) for imaging the samples. The acceleration voltage was 10 kV. Atomic force microscopy (AFM) analysis was conducted in a Veeco CP II apparatus in the tapping mode. Photographs of the structures were made on a Laser Confocal Microscope CLS 3100 in the confocal mode.

3 Results

The quality of the prepared graphene films was evaluated by Raman spectroscopy. Figure 1 shows an example of the Raman spectrum of a graphene film prepared under these conditions: thickness of the Co layer 50 nm, temperature during the CVD process 900 °C, period 480 s. Analysing the spectrum peaks, the following intensity ratios were obtained: $I_D/I_G = 0.11$ and I_{2D}/I_G=1.19. These values are typical for bi-layer graphene [3].

In Tab. 1, parameters of the prepared graphene films of measured I2D/IG and I_D/I_G ratios are shown in dependence on the conditions of their preparation, mainly on the thickness of the Co layer. The table is completed with a column showing the estimated number of carbon monolayers within the graphene film [3]. The best graphene films exhibit the quality of bi-layer graphene (BLG). Graphene films prepared on cobalt layers with a thickness of 100 nm have a high homogeneity, as deduced from the low ID/IG ratio, but as for the thickness of the graphene film the structure with 50 nm of cobalt is better. The crystal size of the graphene film is within the range from 180 to 600 nm [4]. With a 200 nm thick Co layer we obtained only amorphous carbon (aC). The optimal CVD temperature for all structures was 900 °C. Structures prepared at other temperatures are not included in Tab. 1 because of their inferior parameters. The thinnest Co layer means the thinnest graphene film.

An important feature of graphene films is their morphology. In Figs. 2 to 5, parts of the surface of a graphene film prepared at 900 °C for 480 s on the structure with 50 nm of cobalt are visualized by various techniques. Figure 2 shows a photograph obtained by a confocal microscope. Blue areas represent the graphene film. One can see visible cracks and defects, which are caused by an imperfect preparation process and cleanliness of the surrounding environment during graphene preparation. Figure 3 shows a selected section without macroscopic defects, visualized by scanning electron microscopy. The area is 5×5 μm large. The surface consists of tiny flakes separated by narrow cracks. Figures 4 and 5 represent AFM pictures of about $2 \times \mu$m in size. Figure 4 shows the pristine SiO_2 surface. The roughness is $R_a = 2.2$ nm and the surface shows small spikes. On the other hands the graphene film surface, Fig. 5, shows a globular nature with $R_a = 2.6$ nm and seems to cover the spikes on the SiO_2 surface. Thus, we can conclude that the SiO_2 substrate is fully covered by the graphene film with macroscopic defects and cracks, but without any wrinkles.

The basic electronic parameters of the prepared graphene were measured by the van der Pauw method. Simple silver contacts were applied. The obtained results show a very low Hall mobility with approximate value of 500 cm^2/Vs for the graphene film prepared at 900 °CC for 480 s from the starting structure with 50 nm of cobalt (the sample the first row in Tab. 1). The value is probably influenced by defects and cracks in the graphene films, see Figs. 2 and 3. The accuracy of measurements was affected by the low quality of contacts.

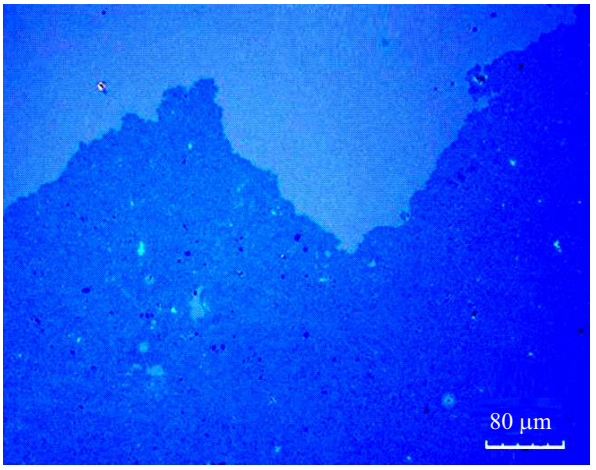

Fig. 2. Confocal microscope image of the graphene film

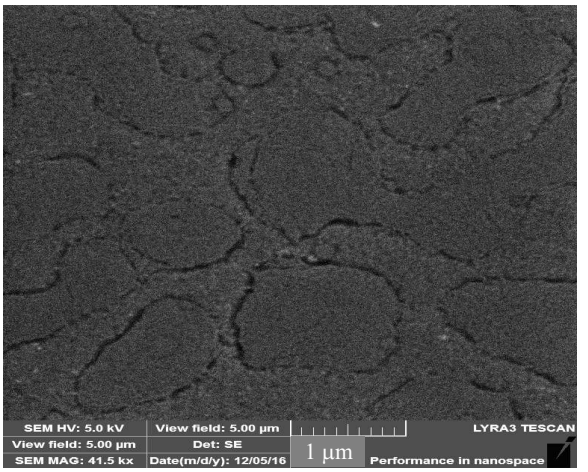

Fig. 3. SEM micrograph of the graphene film

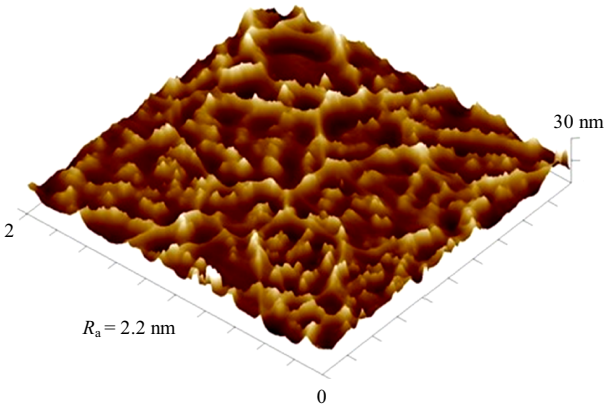

Fig. 4. AFM scan of the SiO2 surface

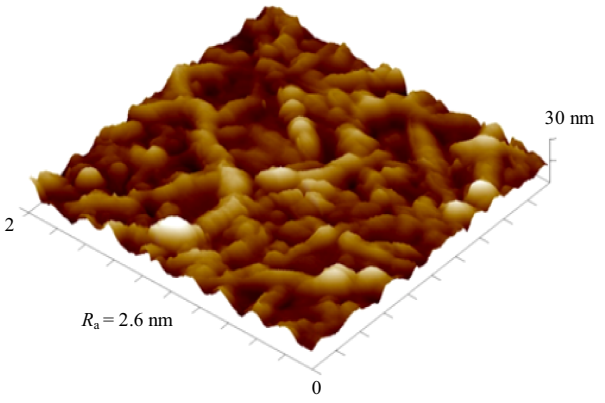

Fig. 5. AFM scan of the graphene surface

Finally, we try to compare the parameters of our graphene films with graphene layers prepared by a similar technique [4, 5]. In [4], few-layer graphene was prepared. The thickness of a Ni layer was 100 nm. In [5], the authors applied a Ni layer with a thickness of 55 nm and prepared a mono-layer graphene film. Electrical parameters were not measured in either of the two, cited works. A very interesting transfer-free method was used in [9]. The basic structure was Cu (300 nm)/$SiO2/Si$. The method was based on the phenomenon that carbon atoms diffused through Cu grain boundaries and directly formed a graphene layer at the Cu-dielectric interface. BLG was prepared with electron mobility 670 cm^2/Vs. We can state that our results are similar to the mentioned ones.

4 Conclusions

The paper describes graphene preparation using the CVD method directly onto a dielectric substrate. In this way, graphene films of BLG nature were prepared. The quality of films is influenced by defects and cracks. Confocal microscopy and SEM micrographs reveal cracks and defects in the structure but AFM measurements show that graphene has a very fine and homogeneous globular structure which covers the surface structure of SiO_2. Reliability of our experiments is good apart from electrical measurements for which samples of greater dimensions will be used in further studies.

Further research will be focused on optimizing the cobalt layer thickness and growth conditions with the aim to obtain a monolayer graphene of high homogeneity. Also, a nickel layer will be tested instead of cobalt. For electrical measurements, it is necessary to prepare high-quality contacts with better stability and reliability by evaporation.

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