Direct Growth of Graphene on SiO_2/Si Substrate

P. Macháč, T. Valentová, V. Bláhová
Department of Solid State Engineering
University of Chemistry and Technology, Prague, Technicka 5,
166 28 Prague 6, Czech Republic
E-mail: petr.machac@vscht.cz

Anotace:
This work is focused on graphene preparation using the transfer-free method from a metal/C/SiO_2/Si structure. We used nickel and cobalt as the metal layer. The technological process of graphene preparation is based on an optimization of metal thickness and annealing parameters (temperature and duration). We successfully prepared bi-layer graphene.
Práce je zaměřena na přípravu grafenu s využitím tzv. bezpřenosové metody, která vychází ze struktury kov/C/SiO_2/Si. Tenké vrstvy niklu či kobaltu byly použity jako kov. Článek se zabývá optimalizací tloušťky kovů a žíhacího procesu (teploty a doby žíhání) s cílem připravit grafen s co nejlepšími parametry. Úspěšně se nám podařilo připravit dvouvrstvý grafen.

INTRODUCTION

Graphene is a promising material with excellent electrical and thermal properties [1]. Many methods of graphene preparation are developed, but so-called transfer-free graphene is very promising [2]. The method comes from metal/C/SiO_2/Si structure. The synthesis of graphene is based on a metal-catalyzed crystallization of amorphous carbon (a-C) by thermal annealing. Polymer layer [3] or thin SiC layer [4] are used very frequently as the carbon source instead of a-C. Carbon atoms diffuse into a metal layer at elevated temperatures followed by their precipitation as graphene during the cool-down step as the solid.

SAMPLE PREPARATION

SiO_2(300nm)/Si substrate was taken as a starting material for graphene growth. After careful cleaning in the Piranha solution (H_2SO_4 : H_2O_2 4:1), washing in H_2O and drying by N_2, a layer of amorphous C (a-C) was deposited by flesh evaporation in the SCD050 apparatus. Thin nickel or cobalt films were deposited by e-gun evaporation in the UNIVEX 450 evaporator. The samples were then thermally annealed (650 – 1000 °C) in a small vacuum chamber equipped with a resistively heated ceramics Boraelectric Heating Element HTR-1001. Temperature was measured with an optical pyrometer. The etching of metallization together with top carbon layer was the final step of graphene preparation. Diluted HNO_3 acid was used (HNO_3 : H_2O 1:5 by volume) for 5 min. Samples were analyzed by means of Raman Spectroscopy using a LabRaman apparatus, Dilor system, with a 532.2 nm laser and spot diameter of 1 μm.

RESULTS

Typical Raman spectrum of the graphene film prepared from the Ni(200 nm)/C(20 nm)/SiO2/Si structure, which was annealed at 1000 °C for 60 s, is in Fig. 1. The spectrum contains 3 key carbon bands: D (1350 cm-1), G (1580 cm-1 and 2D (2700 cm-1). The integrated intensity ratio I_D/I_G for the D and G bands is widely used for the defect quantity characterizing in graphitic materials [5]. Similarly, the integrated intensity ratio I_{2D}/I_G for the 2D and G bands is used for the determination of carbon layer number [6]. As we can see from the spectrum in Fig. 1, the prepared graphene has bi-layer character.

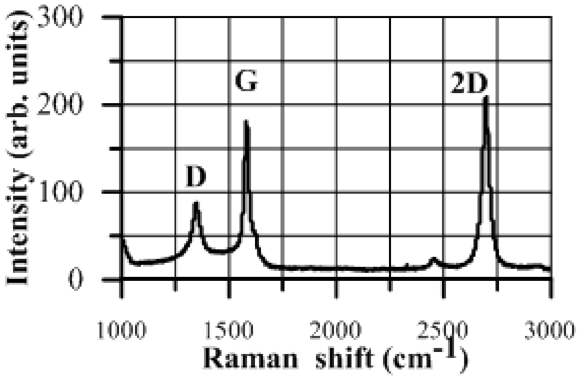

Fig. 1: Raman spectrum of the graphene film prepared from the Ni(200 nm)/C(20 nm)/SiO_2/Si structure.

A set of the structures was prepared with the aim to optimize graphene parameters. Tab. 1 shows a short list of prepared samples together with the best values of the intensity ratio I_{2D}/I_G and with optimal annealing conditions (temperature and period). The best results were obtained in the case of the mentioned structure Ni(200 nm)/C(20 nm)/SiO_2/Si. The structure C/Ni/SiO_2/Si did not produce graphene, but only amorphous carbon at any annealing conditions. The table contains further details concerning of the Co/C/SiO_2/Si structure. The

Tab. 1: List of structures prepared by the annealing

Structure	Thickness (nm)		Annealing conditions		Graphene	
	Ni(Co)	C	Temperature (°C)	Period (s)	Character	2D/G
$Ni/C/SiO_2/Si$	200	10	1000	0	FLG	0.65
	200	20	1000	60	BLG	1.24
	200	46	1000	300	BLG-TLG	0.95
	100	20	900	60	FLG	0.56
	50	10	700	300	FLG	0.47
$C/Ni/SiO_2/Si$	50	10	-		a-C	-
$Co/C/SiO_2/Si$	300	20	900	300	TLG	0.81
	300	10	900	60	BLG	1.20
	200	20	950	0	BLG	1.42
	100	10	1000	60	BLG	1.22

Tab. 2: Electrical parameters of graphene prepared from the $Co(200)/C(10)/SiO_2/Si$.

Annealing conditions		ρ_s	μ_H	c_s
Temperature (°C)	Period (s)	(Ω)	($cm^2V^{-1}s^{-1}$)	(cm^{-2})
950	0	90	150	$4.7x10^{14}$

structure shows similar parameters as previous one. The $Co(200)/C(20)/SiO_2/Si$ structure was the best, after the annealing at 950 ºC for 0 s BLG was obtained. Abbreviations BLG, TLG, and FLG mean bi-layer graphene, tri-layer graphene, and few-layer graphene respectively.

Basic electronic parameters are very important as we mentioned in the introduction. So surface resistivity ρ_s, Hall mobility μ_H and carrier concentration c_s were measured by the van der Pauw method on the graphene layer prepared from the $Co(200)/C(10)/SiO_2/Si$ structure. Tab. 2 shows obtained parameters. The surface resistivity is very low together with the mobility probably due to large concentration of defects in the graphene layer. The ratio of I_D/I_G was approximately 1 which means the crystalline size L_a = 20 nm [5].

Homogeneity of the prepared graphene films is very important. Fig. 2 shows example of the optical microscope image of the synthesized graphene on the SiO_2/Si substrate (the initial structure was $Co(300)/C(20)/SiO_2/Si$, 900 ºC, 0 s). Cluster-like structure of the graphene domains can be observed. Blue areas represent graphene and the violet parts represent net SiO_2 surface without graphene.

Surface of the chosen graphene layer was studied by the AFM method. The investigated sample of graphene showed the ratio of bands I_D/I_G = 0.28, which means L_a = 64 nm. Morphology of the graphene layer is in Fig. 3. The surface roughness was 8.9 nm. Clusters at the structure reach 200-500 nm with height resolution up to 50 nm. The size of the formed graphene crystallites well matches to the observed surface morphology and roughness determinate by AFM.

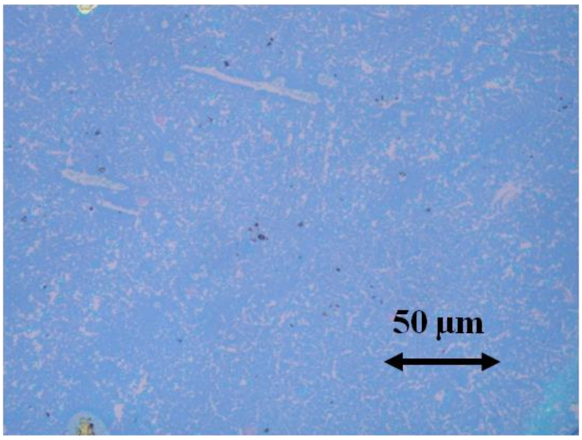

Fig. 2: Optical microscope image of directly synthesized graphene on the SiO_2/Si substrate.

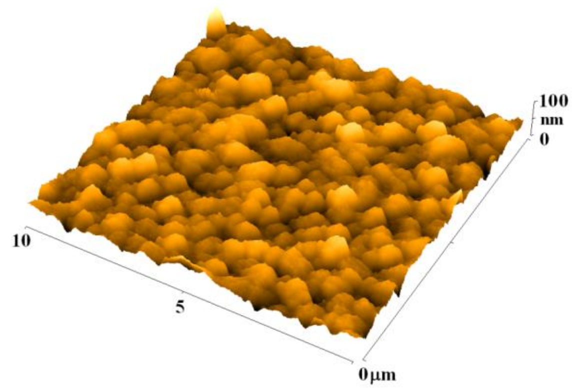

Fig. 3: Morphology of the graphene film.

CONCLUSION

We prepared the graphene layers directly on the SiO_2/Si substrate without the transfer necessity by the metal-catalyzed crystallization from a-C by thermal annealing. Through the optimization of technological process we prepared bi-layer graphene. The best results were obtained from following structures: Ni(200)/C(20)/SiO_2/Si annealed at 1000 ºC for 60 s and Co(200)/C(20)/SiO_2/Si annealed at 950 ºC for 0 s. The next aim of our research will be concentrated on the preparation of graphene films with better homogeneity and lower defectivity.

ACKNOWLEDGMENTS

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