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COMMUNICATIONS

SYNTHESIS OF GRAPHENE ON Ni/SiC STRUCTURE

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Abstract — graphene is a promising material with excellent electrical, thermal, optical and mechanical properties. Therefore, it is a material of high relevance for various applications in many branches of technique. Graphene has received much attention recently in scientific community. The contribution reports formation and characterization of few-layer graphene (FLG) films on a SiC substrate from nickel silicide supersaturated with carbon by annealing at a favourable low temperature.

Keywords: graphene, Ni/SiC structure, carbon segregation, Raman spectroscopy

1 INTRODUCTION

Graphene, a mono-layer or few-layer of sp^2 hybridized carbon atoms, has significant perspective of use in microelectronics, due to its highly interesting features [1] — high carrier mobility, excellent electrical conductivity and superior thermal conductivity. These favourable properties predestinate graphene as a possible candidate for post-silicon electronics.

Currently, graphene can be prepared by different methods such as mechanical cleavage or exfoliation [2], chemical reduction of graphite oxide [3], epitaxial growth by SiC thermal graphitization in vacuum [4] or in an Ar atmosphere [5] and chemical vapour deposition (CVD) on transition metals [6]. Very promising is the synthesis of graphene on SiC substrates at a relatively low temperature [7] based on the carbon segregation from a metal layer saturated by carbon. This technique utilizes a Ni/SiC structure. The method is very promising for stripping of graphene layers from the substrate and their transfer to other substrates. Annealing of the structure results in a chemical reaction that forming silicides and carbon rich products at the Ni-SiC interface and in accumulation of graphite at the top of the Ni layer.

2 SAMPLE PREPARATION

N-type 4H-SiC substrate wafers, 4° off-axis, Si-face polished, doping level $4 \times 10^{18}\mathrm{cm}^{-3}$ (supplied by SiCrystal A.G.) were used in our experiments. Deposition of Ni metallization was performed using an e-beam evaporator at 135 °C in vacuum of 2×10^{-4} Pa. The purity of Ni was 4N or 5N. Alternatively the metallization was prepared by magnetron sputtering in an Ar atmosphere (the purity of the deposition target was 4N). Standard thickness of Ni layer was 300 nm. Immediately before metal deposition, SiC wafers were chemically cleaned using the previously mentioned process [8].

Graphene layers were prepared by thermal treatment of Ni/SiC structures in a small vacuum chamber equipped with a resistively heated table (temperature ranging from 850 to 1050 °C, the annealing duration ranging from 0 to 120 s). First of all, the Ni/SiC samples were degassed at 350 °C for 5 min and then annealed at a pressure bellow 3×10^{-4} Pa. Temperature was measured with an optical pyrometer. The heating rate was approximately 17.5 °C/s and the cooling rate was 15 °C/s.

The samples were analysed by means of Raman spectroscopy using a LabRaman apparatus, Dilor system, with a 532.2 nm laser and spot diameter 1 μm. XPS measurements were performed in ultra high vacuum (10^{-8} Pa) using an ESCAProbe P apparatus (Omicron Nanotechnology Ltd.) equipped with an Al anode as an X-ray source with energy 1486.7 eV. The X-ray source was monochromatic. The size of the analysed area was approximately 1 mm^2. Ar ions of 5 keV energy were used for ion sputtering during depth profiling. AFM analysis was conducted in a Veeco CP II apparatus in the tapping mode.

3 RESULTS

In Fig. 1, an example of Raman spectra of the structure after annealing at 950 °C (annealing period 30 s, Ni was deposited by the sputtering) is shown. The solid line represents the spectrum after annealing, the dashed line represents the spectrum of the graphene layer exfoliated onto a SiO_2/Si substrate. Exfoliation was done by etching the silicide layer by a mixture of HF and HNO3 acids with the help of polymethyl methalcrylate (PMMA). PMMA was burned after transferring onto SiO_2 in H_2 atmosphere at 400 °C. The integrated intensity ratio $I_\mathrm{D}/I_\mathrm{G}$ for the D and G bands is widely used for the defect quantity characterizing in graphitic materials [9], the main parameter is the crystallite size L_a

$$L_a(nm) = \frac{560}{E^4_{\mathrm{laser}}(\mathrm{eV})}\left(\frac{I_\mathrm{D}}{I_\mathrm{G}}\right)^{-1}, \qquad (1)$$

where E_{laser} is the laser excitation energy utilized in Raman analysis. Similarly, the integrated intensity ratio

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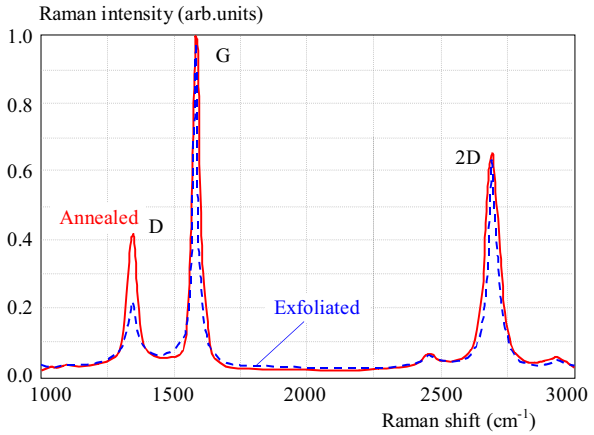

Fig. 1. Raman spectra of Ni/SiC sample after the annealing and after the exfoliation

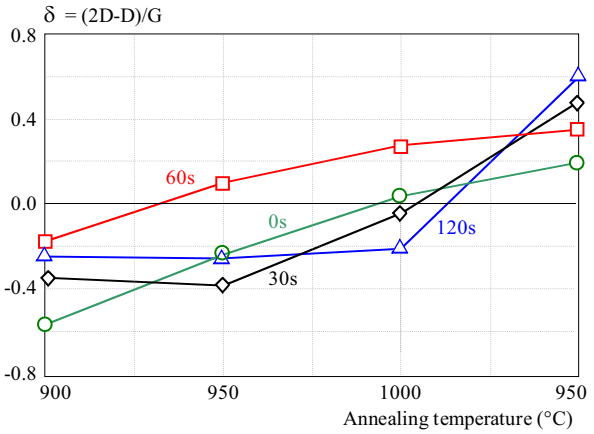

Fig. 2. Parameter δ as a function of the annealing temperature and time for Ni metallization with 5 N purity

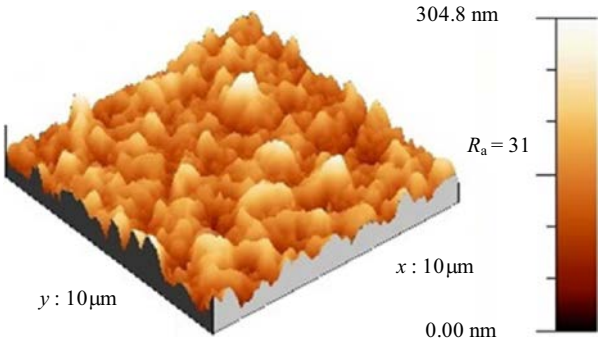

Fig. 3. AFM picture of the graphene film surface prepared on the Ni(300)/SiC structure annealed at 1000 °C for 120 s

I_{2D}/I_G for the 2D and G bands is used for determination of the number of carbon layer [10]. It is possible to estimate that graphene in Fig. 1 contains 4 carbon layers, its crystallite size is 43 nm and exfoliation increases its value to 82 nm. The difference is probably due to a smoother surface of SiO_2.

Graphene preparation was aimed at studying the influence of Ni deposition conditions, annealing temperature and annealing time on graphene parameters. The quality of the 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 La increases). This motivated us to introduce a criterion for evaluation of graphene layers quality in the form of the parameter [8]

$$\delta = (I_{2D} - I_D)/I_G\,, \tag{2}$$

which should be as high as possible.

Some results are presented in Fig. 2, where Ni with purity 5 N was deposited by evaporation. The figure shows the dependence of δ on the annealing time and temperature. Parameter δ increases with increasing temperature for all annealing periods and reaches a maximal value 0.6 for 1050 °C and 120 s. Metallizations prepared by sputtering and by evaporation with less pure nickel show similar behaviours. The results of optimization are summarized in Tab. 1. The table shows the values of δ, 2D/G and D/G ratios, and L_a for graphene prepared from all metallizations at the annealing temperature 1050 °C. The data are the average values of all annealing periods. In the case of nickel with purity 5 N we obtained a graphene film with the highest value of $\delta = 0.42$. The prepared graphene has a nature of three-layer graphene but its crystallinity is low. The first two metallizations produce four-layer graphene with a better crystallite structure.

For verification of the results provided by Raman spectroscopy, the Ni/SiC structure annealed at 1000 °C for 120 s (evaporation, Ni of 4 N purity) was subjected to XPS analysis (spectrum not shown here). Carbon is a dominant element on the structure surface. The dominant C1s peak at 284.5 eV corresponds to the C-C bond [11] and confirms the presence of graphene.

The morphology of the structure surfaces was studied by AFM. Figure 3 shows the surface morphology of the Ni(300)/SiC structure (evaporation, Ni of 4 N purity) annealed at 1000 °C for 120 s. Extensive reaction of the nickel film with the SiC substrate occurred during the annealing process. The reaction was not homogeneous, which is confirmed by large roughness $R_a = 31nm$. The prepared graphene film lies on the metallization surface and consequently it exhibits a large number of defects, thus it has low crystallinity.

Finally the basic electronic parameters of prepared graphene were measured. Experiments were done with the metallization prepared by evaporation of 5 N nickel. For the measurements it is necessary to have a dielectric substrate, therefore a semiinsulating SiC plate (SI-SiC) was used and the graphene film on the interface between SiC and the metallization were tested (after annealing the silicide layer was etched-off by HNO_3 acid hereby obtaining the graphene/SI-SiC structure). Au(30)/Cr(10) contacts prepared by evaporation were applied to measure the electrical parameters by van der Pauw method. The obtained results are shown in Tab. 2 (p_s is surface resistivity, μ_H is Hall mobility and c_s is the concentration of charge carriers). Hall mobility of the prepared graphene

Table 1. Results of the graphene film optimization

Deposition	δ	2D/G	D/G	L_a(nm)
Sputtering, Ni – 4N	0.39 ± 0.075	0.58 ± 0.05	0.185 ± 0.10	97
Evaporation, Ni – 4N	0.39 ± 0.05	0.59 ± 0.05	0.20 ± 0.08	90
Evaporation, Ni – 5N	0.42 ± 0.15	0.86 ± 0.07	0.44 ± 0.21	41

Table 2. Electrical parameters of graphene on SI SiC

Annealing conditions		$\rho_s(\Omega)$	$\mu_H\,(\mathrm{cm}^2/\mathrm{Vs})$	$c_s\,(\mathrm{m}^{-2})$
$T(^\circ\mathrm{C})$	t(s)			
1000	120	1130 ± 24	$7.6 \pm 5.5 \times 10^{-2}$	$7.21 \times 10^{18} \pm 5.2 \times 10^{16}$
1050	60	527 ± 2.5	300 ± 7.3	$3.85 \times 10^{17} \pm 7.3 \times 10^{15}$

films is very low probably due to a large concentration of defects in graphene layers.

4 CONCLUSIONS

Graphene films were prepared by synthesis on a SiC substrate via Ni-silicidation reaction. Through optimization of the technological process, three-layer graphene was prepared. The best results were provided by evaporation of nickel with 5 N purity, the optimal annealing temperature was 1050 °C and the best annealing time was 120 s. The graphene film was successfully exfoliated onto the SiO_2/Si substrate and its crystallinity was better (the I_D/I_G ratio is much smaller). XPS analysis confirmed the presence of graphene on the Ni/SiC surface. Basic electrical parameters were measured, from the results it is evident that the graphene films have relatively low quality. The AFM measurement showed that the surface of metallizations is very rough. This fact confirms the poor quality of graphene. The next aim of our research will be concentrated on the preparation of graphene films with lower defectivity.

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