Applied Surface Science 320 (2014) 544–551

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Graphene preparation by annealing of Co/SiC structure

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ARTICLE INFO

Article history:
Received 11 February 2014
Received in revised form 5 September 2014
Accepted 18 September 2014
Available online 28 September 2014

Keywords:
Graphene
Silicon carbide
Cobalt
XPS analysis
Raman spectroscopy

ABSTRACT

This work is focused on graphene preparation using the segregation method with Co/SiC structure, the method being a viable low temperature synthesis approach. The graphene preparation was carried out with the cobalt layer of 300 nm thickness; the technological process is based on an optimization of parameters (temperature and duration) of annealing which is a crucial step of the synthesis. 850 °C as an annealing temperature and 10 s as an annealing duration have been found to be the most optimal. The prepared graphene is close to the bi-layer graphene structure with its parameters. Structural parameters of the prepared graphene were determined from spectra obtained by Raman spectroscopy.

1. Introduction

Graphene, a mono or few layers of sp^2 hybridized carbon atoms, has significant perspective of use in microelectronics, thanks to its highly interesting properties [1–3]: high electron mobility at room temperature, very low resistivity, very high thermal conductivity, very low absorption of white light, very low electrical noise, existence of quantum Hall effect and other. These favorable properties predestine graphene as a possible candidate for post-silicon electronics.

Currently, graphene can be prepared by different methods such as mechanical cleavage or exfoliation [4,5], chemical reduction of graphite oxide [6,7], epitaxial growth by SiC thermal graphitization in vacuum [8,9] or in an Ar atmosphere [1,10] and chemical vapor deposition (CVD) on transition metals [11–13].

Very promising is the synthesis of graphene on SiC substrates at a relatively low temperature [14] based on the carbon segregation from a metal layer saturated by carbon. This technique utilizes Ni/SiC structure. The method is very perspective for the stripping of graphene layers from the substrate and their transfer to other substrates. An annealing of the structure results in a chemical reaction forming silicides and carbon rich products at the Ni–SiC interface and in the accumulation of graphite at the top of the Ni layer. This approach has been developed in a great deal of ways [15–20]. Cobalt can be used instead of nickel [21,22]. In this work, we reported our results concerning of graphene preparation by the annealing of the Co/SiC system. The annealing was produced in the temperature range from 750 to 1050 °C. We studied an influence of cooling rate after the annealing on the parameters of formed layers and a detailed chemical composition and morphology characterization of the structure surface during the structure preparation. Further, we presented measurements of basic electrical parameters of the prepared graphene layers.

2. Sample preparation

N-type 4H–SiC substrate wafers, 4° off-axis, Si-face polished, doping level 4×10^{18} cm^{-3} (supplied by SiCrystal A.G.), doping element nitrogen were used in our experiments. Co deposition was performed using electron-gun evaporation. Directly before the metal deposition, SiC wafers were chemically cleaned using the previously mentioned process [22] and they have also been treated in-situ by a DC Ar plasma (10 min, 10 W). Prepared thickness of the Co layer was 300 nm.

Graphene layers were prepared by a thermal treatment of Co/SiC structures in a small vacuum chamber equipped with a resistively heated ceramics Boralectric Heating Element HTR-1001. The first step is sample degassing at 350 °C for 5 min and then the sample is annealed in the range of temperatures from 750 to 1050 °C at a pressure below 3×10^{-4} Pa. Temperature was measured with an optical pyrometer. Heating rate was approximately 17.5 °C/s and cooling rate was 15 °C/s.

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http://dx.doi.org/10.1016/j.apsusc.2014.09.104
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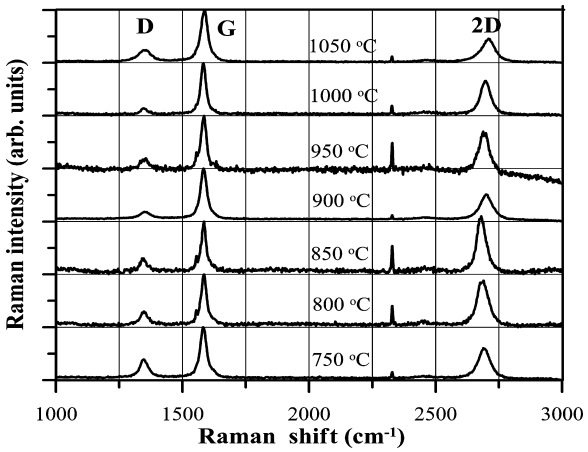

Fig. 1. Raman spectra of several Co/SiC samples differing in annealing temperature. Annealing duration was 10 s for all samples.

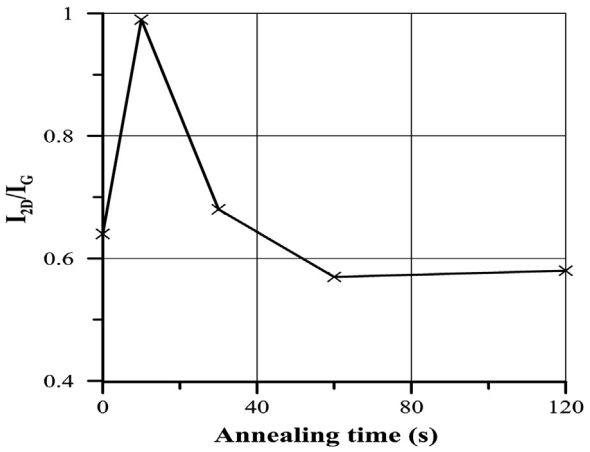

Fig. 2. Ratio of 2D and G band intensities in Raman spectra of graphene prepared by annealing at 850 °C and at various times.

Exfoliated graphene layers were transferred onto a SiO_2 (300 nm)/Si plate. A PMMA (polymethylmetacrylate) layer about 5 μm thick was deposited on the structures with graphene. PMMA was hardened at 180 °C for 30 min. The silicide layer, the Co plus SiC reaction product, was etched-off in a 1 HF:3 HCl acids mixture for approximately 30 min. The resulting PMMA/graphene membrane was washed in water, transferred onto the surface of the SiO_2/Si plate and finally dried with a nitrogen stream. The PMMA layer is removed by evaporation at 450 °C in a hydrogen atmosphere for 2 h. Electrical parameters were measured by van der Pauw method at $B = 0.4$ T. Au (30 nm)/Cr (10 nm) metallization was used as contacts to the graphene layer.

Samples were analyzed with Raman Spectroscopy using a Jobin Yvon apparatus Labram HR (spectral range 100–4000 cm^{-1}), with a 532.2 nm laser and spot diameter of 1 μm. X-ray Photoelectron Spectroscopy (XPS) measurements were performed in an ultra high vacuum chamber (10^{-8} Pa or less) using a NanoESCA apparatus (Omicron Nanotechnology Ltd.) equipped with a PEEM navigation technique, radiation sources: Hg-lamp (5.2 eV), HeI (21.2 eV) and a monochromatic X-ray source Al K-alpha (1486.7 eV). 100 μm X-ray spot size was used. This area roughly corresponds with the area on the sample from which the XPS signal was collected. CasaXPS software was used for spectra processing and evaluation. Peak components fitting was performed using symmetric Gaussian(70%)–Lorentzian(30%) peaks and Shirley background. No additional spectra shifting were carried out. Atomic Force Microscopy (AFM) morphology analysis was done by Veeco CP II.

3. Results

3.1. Raman spectroscopy

Graphene layers were prepared by the thermal processing of the Co/SiC structure at temperatures ranging from 750 to 1050 °C. The annealing duration was varied from 0 s (the power of the Heating Element was switched off immediately after the desired temperature had been reached) to 120 s. Basic parameters of the prepared graphene were obtained employing Raman spectroscopy. This method is a non-destructive, fast and simple one. Graphene's Raman spectra contain 3 key carbon bands: D (1350 cm^{-1}), G (1580 cm^{-1}) and 2D (2700 cm^{-1}).

On Fig. 1, there are shown Raman spectra of the samples in dependence on the annealing temperature. Annealing time was set to 10 s for all the samples. We can easily identify the number of layers the graphene is formed from using the integrated intensity ratio of the 2D and G bands [23]. Generally, the greater the ratio I_{2D}/I_G, the fewer carbon layers constitute the graphene. It is evident from the above mentioned picture that the least number of layers is present at the sample annealed at 850 °C. Fig. 2 shows dependence of the I_{2D}/I_G ratio on annealing time of the mentioned sample. Results confirm that the sample annealed at 850 °C for 10 s is nearly bi-layer graphene.

Authors of a number of studies, which describe preparation of graphene by segregation on metal/SiC structures [14,16,21,24], point out that graphene parameters depend on the samples cooling rate after the annealing is finished. We performed similar experiments. Samples annealed at 1050 °C for 120 s were selected for the test. For these experiments, samples were annealed mounted on a special molybdenum tray resistively heated by passing current. This setup enables controlled cooling within the rate from 2 to 70 °C/s. The highest cooling rate is simply given by the situation when power supply is switched off and the sample cools down freely. We adjust the rate by controlled attenuation of the passing current. The results are shown on Fig. 3, where the cooling rate is plotted to show its influence on the resulting I_{2D}/I_G and I_D/I_G ratios of prepared samples. As evident from the picture, the cooling rate has shown to have almost no influence onto the 2D band size (onto the number of carbon layers within graphene). However, there has appeared a significant influence on the D band form, i.e. onto the number of defects within the prepared graphene layer, with the results being such that faster cooling creates more defects.

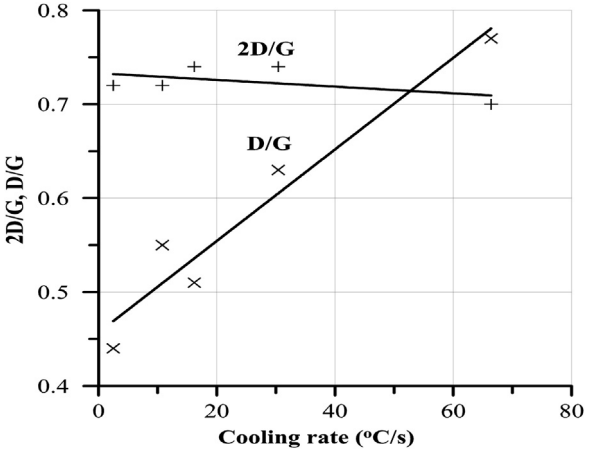

Fig. 3. I_{2D}/I_G and I_D/I_G ratios for different cooling rates.