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Graphene Post-Processing

B Tincu^{1, 2, *}, A Avram¹, V Tucureanu^{1, 3}, A Matei¹, C Marculescu¹, T Burinaru^{1, 4}, F Comanescu¹, M Popescu¹ and M Avram¹

¹National Institute for Research and Development in Microtechnologies (IMT-Bucharest), Bucharest, Romania

²University Politehnica of Bucharest, Faculty of Applied Chemistry and Materials Science, Bucharest, Romania

³Transilvania University of Brasov, Department of Materials Science, Brasov, Romania

⁴University Of Agronomic Sciences and Veterinary Medicine of Bucharest, Faculty of Veterinary Medicine, Anatomic Pathology Department, Bucharest, Romania

*bianca.tincu@imt.ro

Abstract. Graphene is a two-dimensional wonder material, used for electronic and medical applications. To date, various synthesis method of graphene layers is proposed, such as: SiC epitaxial growth, Chemical Vapor Deposition (CVD) and mechanical exfoliation. Graphene single layer can be rapidly produced by CVD. Although the transfer process on different substrates has been researched, a post-processing step after graphene growth for understanding influence of radical of carbon unreacted in graphene properties has not been studied. Deposition of graphene on metal transition substrate involves many reactions, and is not clear what happens with the unreacted methane. The scanning electron microscopy is the best method to visualize this unreacted species as a thin film which covers the graphene layer. The post-processing of graphene after CVD is a crucial step for the performance of graphene-based devices. The graphene film is characterized morphologically and structurally before and after the post-processing step, with the scope of removing the unreacted film and investigating the influence of this step on the graphene properties. To identify the specific vibration of graphene layer before and after post-processing step, Raman spectroscopy has been used. Here, we investigate the quality of CVD graphene before and after removing unreacted hydrocarbon, to better understand the importance of post-processing process for device applications, before the graphene transfer.

1. Introduction

Graphene, two-dimensional alternative of graphite, is one atom layer of carbon atoms [1–3] arranged in a hexagonal lattice. Graphene is the best conductor of electricity and a great material with remarkable properties (mechanical [4–6], electrical [7, 8]) and one of the most studied area in the recent years [9], [10]. Andre Geim and Konstantin Novoselov discovered graphene in 2004 and they won the Nobel Prize for Physics in 2010 [11].

The history of graphene dates back from 1840, since Schafhaeuti report an experiment about the oxidation and exfoliation of graphite with a variety of interpolating [12–15]. The next step, in 1859 was marked by graphene used in attempts to a British chemist, Brodie to characterize the molecular weight



of the graphite. In 1962, Boehm et al. has studied the characterization by transmission electron spectroscopy of some thin lamellas obtained by oxidation of graphite and reducing the graphene layers of graphite and for this proposed term of graphene, but in 1997 the term of graphene will be formalized by IUPAC. Graphene has been obtained by the method of chemical vapor deposition (CVD) [16–21] since 2006. Currently, graphene growth by CVD is the most studied method that can produce graphene in significant quantities, and on a high quality. The process is based on the carbon saturation of a transition material regarding the exposure to a carbon-hydrogen gas mixture at high temperature. The various hydrocarbons such as methane, ethylene, acetylene or benzene are decomposed on the surfaces of some transition metal substrates as: Co [23], Ni [24–26], Cu [27]. Copper is an excellent candidate for the preparation of large area of single layer graphene with a uniform thickness (95%) due to the solubility of carbon in copper [28]. Most of the studies directed the post-processing step for the graphene transfer on a different substrate. After a structural analysis of the samples obtained in our laboratory by Nanofab 1000, we observed a film formed on the graphene layer grown on Cu substrate, and as we want to remove it this study aims on the aspect of the post-processing step as cleaning samples after CVD growth of graphene. Graphene has particularly properties and the edges of the graphene are more reactive atoms that have a unique energy that is not present in the bulk. Similar to the carbon nanotubes, this can be either zigzag or armchair. The introduction of the defects is an important step for many applications. The structure of the surface on which graphene deposition occurs is also a field of study for understanding the connection between Cu substrate and CVD graphene growth [29]. The literature does not report a study on this issue and it is not clear what happens with the unreacted methane, after the graphene CVD process.

The introduction of this post-processing step brings many advantages in the next uses of this product. Through this study we have seen getting defects after post-processing, which leads to increased chemical reactivity. Most of the studies bring into discussion obtaining graphene free defects, useful aspect and well defined in electronic applications, but exactly these defects [30] give the remarkable properties of graphene, well illustrating in chemical applications [31]. These defects are the results of post-processing step due to rearrangements of the graphene structure and the possibility of forming at the edge to zigzag and armchair arrangement. But, it is important to note that this experiment is not focused on the analysis of defects, it is aimed at the removal of the unreacted hydrocarbon.

2. Experimental

2.1 Materials

For the experiments of the graphene growth at high temperature, as a catalyst was used the copper foil with a thickness of 35 μm (Graphene Platform Corporation, Japan: Cooper Foil Special for CVD Single Layer Graphene, specification of Copper Foil, Copper purity: over 99.95%, thickness: 0.035 mm). Methane (CH_4 -99.9%) and Hydrogen (H_2 -99.9%) were used as precursor gases for graphene growth, connected to the Nanofab system. Acetic acid, deionized water and isopropyl alcohol (Sigma Aldrich) were used for the pre-cleaning step of copper foil. Acetone and isopropyl alcohol were used for post-cleaning step for samples with the graphene single layer on copper foil.

2.2 Pre-processing step

For the processes of graphene growth, the copper foil was used as a substrate with a thickness of 35 μm (Graphene Platform Corporation, Japan), delivered in the form of sheets with the size of 210 mm x 300 mm. For the CVD experiments the copper sheets have been cut using a catheter for pieces of 20 mm x 20 mm. Before processing, each substrate has been cleaned up in acetic acid for 10 minutes, for pickling surface. This step was followed by a rise in deionized water for 10 minutes, then maintained in isopropyl alcohol until use. The substrate has dried with nitrogen before placing in equipment by flushing.

2.3 Graphene synthesis by thermal chemical vapor deposition

For the graphene growth has been used PlasmaPro100 equipment, design Nanofab 1000 (Oxford

Instruments, UK) dedicated for growth processes of carbon materials. In order to obtain graphene are used hydrocarbon-based reactants. In this experimental paper we used the methane. Due to the strong C-H bond of methane molecule (440 kJ / mol), its thermal decomposition occurs at temperatures from more than 1200 degrees Celsius. The graphene growth process by CVD method has been of one hour in presence of methane and hydrogen followed by cooling the reactor and then the sample is transferred in Load Lock. The graphene growth by CVD method includes five steps: vacuum, heating, thermal treatment, growth and cooling down.

2.4 Post-processing step

Due to the presence of pellicular film on graphene growth on copper, observed by scanning electron microscopy, we tried different cleaning processes, with various steps. In this experiment, the samples are exposed to a post-cleaning step: in acetone and isopropyl acid. For the removal of any residue it was used the heat treatment at 400°C degrees in an inert atmosphere.

The best results have been observed in samples where the post-processing involves bringing to the boiling point of acetone and maintaining the samples for 5 minutes, rinsed in isopropyl acid and dried on the plate. Samples have been exposed to the thermal analysis.

3. Results

Raman spectroscopy has been used to identify the specific vibrational modes of the graphene layer. We used a high-resolution spectrometer LabRam HR 800. The LabRAM HR 800 Raman spectrometer in a setup with the HeNe Laser at 633 nm were used for spectra acquisition. Scanning electron microscopy (SEM) was used to investigate layers of graphene from the early stages to continuous films. For the SEM investigation was used a Line Raith microscope.

3.1 Raman Spectroscopy

We have investigated CVD graphene on copper samples before and after post-processing by taking into account the main characteristic Raman bands of graphene which are [32–34]: D band- defects band, its intensity is proportional with the density of defects in the investigated area, its position being around 1322 cm⁻¹, G band- the first optical phonon corresponding to graphene, its position being around 1582 cm⁻¹, 2D band- the overtone of D band. This band appears even in the absence of D band.

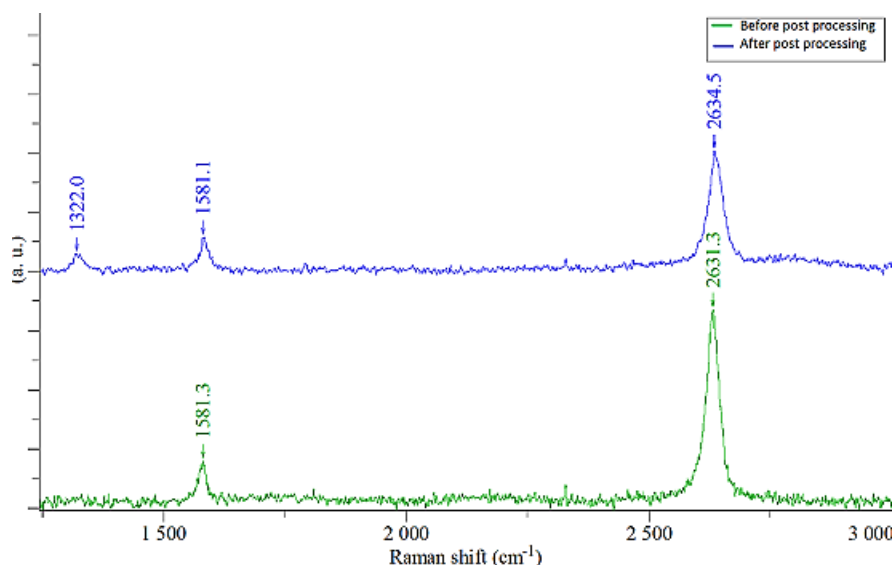


Figure 1. Raman spectra of graphene before and after post-processing

In Figure 1 are comparatively presented Raman spectra acquisitioned on CVD graphene grown on copper substrate before and after post-processing. Both spectra are revealing the characteristic Raman

bands of single layer Graphene: D, G and 2D bands.

In Figure 2 are comparatively presented the defect and quality ratios extracted from CVD graphene Raman spectra before (figure 2a) and after (figure 2b) post-processing. After post-processing, the density of defects has increased which is confirmed by the defect's ratio. In the investigated areas the quality ratio (I2D/IG) has values larger than 2 being more uniform after post-processing.

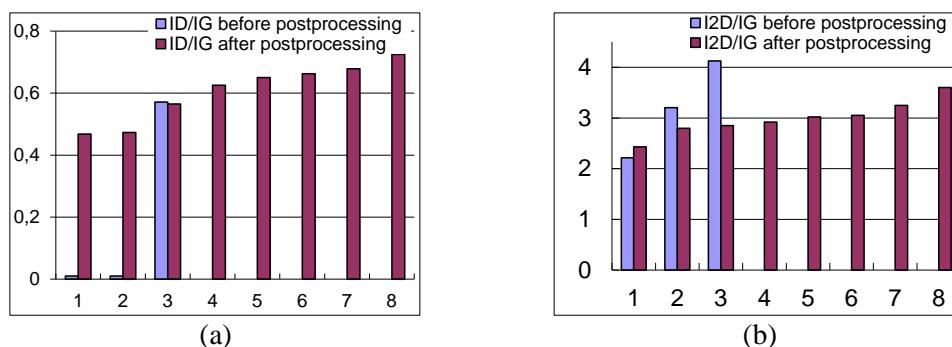


Figure 2. Defect (a) ID/IG and quality ratio (b) I2D/IG) extracted from the Raman spectra of single layer CVD graphene samples before and after post-processing

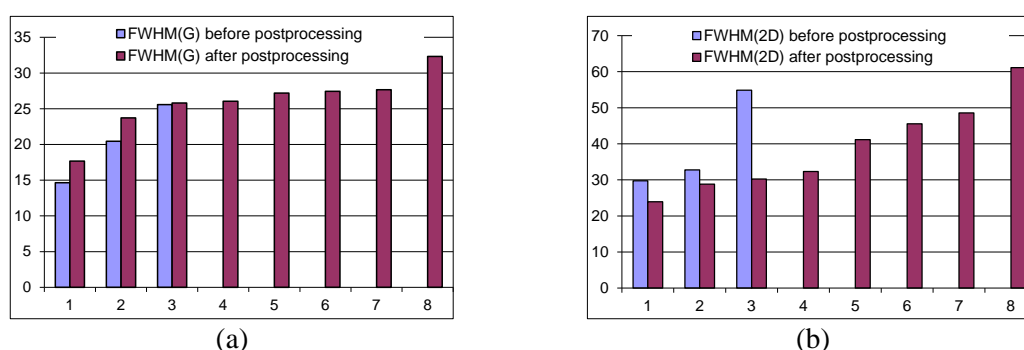


Figure 3. Parameters extracted from the Raman spectra of single layer CVD graphene samples before and after post-processing: FWHM corresponding to: a) G; b) 2D Raman bands

In Figure 3 are comparatively presented FWHM values corresponding to G and 2D bands before and after post-processing. G band FWHM values are higher than 17 cm^{-1} which indicates a large strain in graphene especially after post-processing. 2D band FWHM is higher than 25 cm^{-1} before and after post-processing which suggests a high degree of crystalline disorder. After post-processing graphene D and 2D bands position are blue shifted, D band position being in range $1313 - 1333 \text{ cm}^{-1}$, 2D band position being in range $2613 - 2648 \text{ cm}^{-1}$.

3.2 Surface morphology of graphene on cooper foil

The morphology of single layer graphene grown on Cu foil can be observed using SEM techniques, due to the different energy levels of electrons back-scattered from the materials, which results in images with different shades of grey, depending on the number of graphene layers present. SEM images show the graphene layer to be non-uniform, but graphene domains are clearly visible on copper substrate. The importance of the post-processing step is clearly observed during SEM investigations, as can be seen in Figure 4a and figure 4c where the surface morphology of the graphene is obscured by unreacted hydrocarbon by-products. This post-processing step, not only removes deposition by-products, but also introduces defects in the graphene layers, which are very important for the reactivity of graphene structure. During the graphene growth, CH_4 concentration is stable, thermally decomposed on the surface of the copper where the hydrogen sites are previously formed. Controlling the debit of precursor gases is an advantage for graphene CVD synthesis, but the reaction of methane and hydrogen is not

controlled and secondary products can appear on the surface.

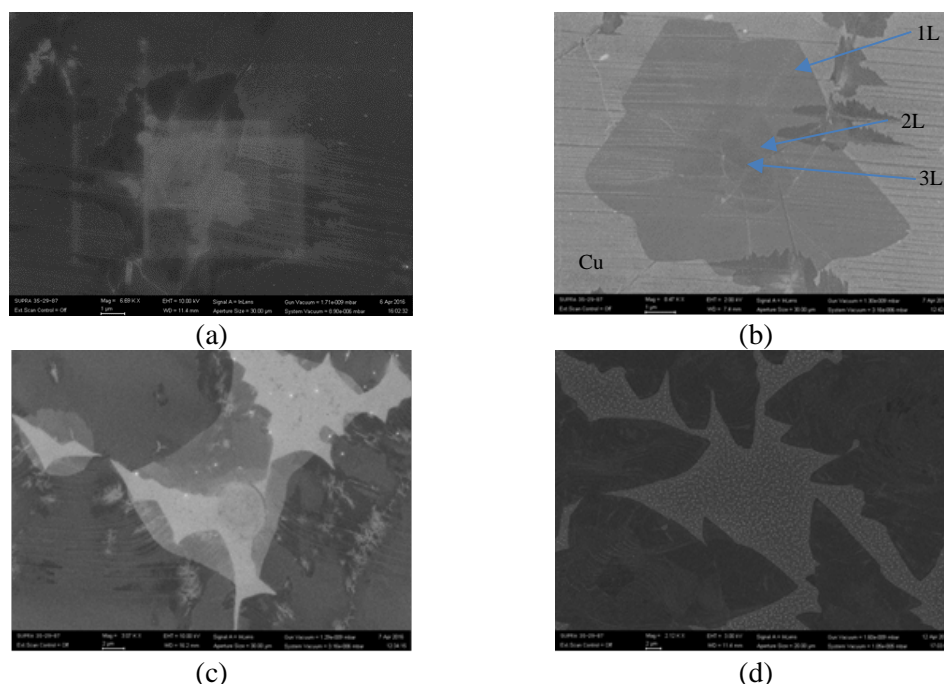


Figure 4. SEM images of graphene on copper foil: (a), (c) before post-processing, (b), (d) after post-processing

After the growth step, an additional thermal annealing at 400°C helps remove these unreacted groups and causes stress induces the defects in graphene structure. In Figure 4b and figure 4d, we can observe the graphene morphology after the post processing step, revealing the shape of the domains, as well as additional multi-layered features. In figure 4b multiple layers of graphene: single-, double- and tri-layer (1L, 2L and 3L) grown around the nucleation center can be observed.

4. Conclusions

We investigated the importance of post-processing step for CVD graphene layer with Raman and SEM methods. It has been found that the post-processing step adds to the graphene structure defects. The defects are very useful for chemical applications. The step of introducing defects in the graphene structure is very important when in the applications the structure is needed as such.

The post-processing step has been optimized as a result of the characterizations accomplished during the experiments of CVD graphene synthesis. Our results are beneficial for the uses of graphene in different applications, by the control of defects.

Acknowledgments

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