U.P.B. Sci. Bull., Series B, Vol. 82, Iss. 3, 2020 ISSN 1454-2331

# PREPARATION, RAMAN SPECTROSCOPY AND MORPHOLOGYCAL ANALYSIS OF VERTICALLY ALIGNED GRAPHENE NANOSHEETS

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*This paper presents an interesting material, vertical graphene (VG), also known as graphene nanowalls (GNW), one of the newest forms of carbon materials. We obtained vertical graphene films using Plasma Enhanced Chemical Vapor Deposition (PECVD) and we investigated its morphology. Raman spectroscopy was performed to assess the quality of the deposited films and to identify the characteristic vibrational modes. Scanning Electron Microscopy (SEM) has been used to investigate the morphology of vertical graphene layers deposited at several substrate temperatures. Vertical graphene is intensively studied for applications in biomedical field, and we hereby present a study on the morphological differences between PECVD growth processes at different temperatures.*

**Keywords:** vertical graphene (VG), Plasma Enhanced Chemical Vapor Deposition (PECVD), carbon thin films

## 1. Introduction

Vertical graphene (VG) was first obtained in 2002 accidentally by Wu and his group when attempting to grow carbon nanotubes. Vertical graphene can be described as a nano-graphite material, consisting of carbon nanocrystalline hexagonal structure with $sp^2$ hybridization having a vertical component (perpendicular to the substrate), resulting in the growth conditions specific to this development [1]. It can be represented as graphitic nanostructures with sharp edges consisting of small layers of graphene sheets, oriented almost perpendicular to the substrate [2]. These sheets interact with each other and form a network with nanometric thickness and lengths of up to several micrometers.
Since 2002, several groups of researchers have been able to obtain vertical graphene using different techniques such as microwave-assisted chemical vapor

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deposition (MPECVD) [3], radio frequency inductively coupled plasma (RF ICP-CVD) [3], radio frequency capacitive plasma (RF CCP-CVD) [4], remote plasma ICP-CVD [5] and DC-PECVD [6]. Considering that it is part of the nano-graphenic material group, the vertical graphene exhibits properties similar to those of other graphene-like materials [7], such as elastic strength, high electron mobility, hydrophobicity, electrical and thermal conductivity, optical transparency [8]. Vertical graphene has shown potential in many applications because of its unique properties. Vertical orientation on the substrate is one of the most important features, which improves the property of mechanical stability. It is considered that each vertically grown nanosheet represents a self-supported structure with rigid integrity by itself [9] and the interlayer spacing of the nanosheets is usually in the range between 0.34 and 0.39 nm [10]. Another feature is its specific surface area with non-agglomerated morphology, vertical graphene networks having a value of 1100 $m^2g^{-1}$ in order to the specific surface area [11]. Furthermore, the vertical graphene morphology presents exposed, ultra-thin and reactive edges. According to Zhang et al. [12], VG has surface area 1100-1800 $m^2g^{-1}$, pore size less than 1 µm and electrical conductivity in range of $10^2$-$10^3$ $Sm^{-1}$. In a study from 2017 [13], Yamada et al. found the reflectance of VG less than 0.067%. This group of researchers has grown vertical graphene nanosheets by MPECVD on Cu foil and transferred it to quartz substrates to evaluate optical reflectance and transmittances. Due to its unique structure, excellent physical and chemical properties (high specific surface area, high electrical conductivity), vertical graphene films are considered promising for manufacturing biosensors with enhanced figures of merit [14]. For example, the large graphene surface may increase the surface load of the desired biomolecules, and excellent electrical conductivity is favorable to conducting electrons between biomolecules and the surface of the electrode [14]. According to the experiments conducted by Al-Jumaili et al. in 2017, graphene nanowalls (GNW) have shown antimicrobial effect on certain microorganisms through interactions that occur in cell membranes [15]. In 2018, Borghi et al. conducted a study using vertical graphene as a substrate for bone growth and cell differentiation [16]. In a study from 2018, Mao et al. developed a sensitive and selective field-effect transistor biosensor using vertical graphene as sensitive area grown between the source and drain electrodes [17]. In 2017, Chen et al. have developed a flexible electrochemical biosensor based on VG to determine real-time lactic acid levels in various probes [18]. In the study from 2018, Tzouvadaki et al. achieved an ultrasensitive detection method for etoposide, being one of the main drugs used in cancer chemotherapy, reaching a detection limit (LOD) of up to 4.36 nM by using vertical graphene as a work electrode [19].

In this study, we prepared VG films on silicon (Si) substrate at different temperatures and we evaluated the morphological structure of the samples by

Scanning Electron Microscopy (SEM). We performed Raman Spectroscopy to identify the vibrational modes of the deposited vertical graphene films and evaluated modifications in the chemical structure induced by different growth temperatures. The purpose of this comparative study is to determine the temperature dependent morphology and to identify suitable growth recipes for use in sensor fabrication for biomedical applications.

## 2. Materials and methods

In our laboratory, we synthesized VG using PlasmaPro100, model Nanofab 1000 (Oxford Instruments, UK). This equipment is dedicated to carbon materials growth and it can work both in thermal (CVD) and plasma assisted (PECVD) modes. In the PECVD mode, the equipment uses capacitively coupled plasma generated between two planar electrodes, with temperatures ranging from 200 °C to 900 °C applied on the lower electrode.

Si wafers, <111> crystallographic orientation were used as substrate, without any additional catalyst layers or nanoparticles. Prior to vertical graphene growth, the Si wafers were cleaned in piranha solution ($H_2SO_4$:$H_2O_2$, volume ratio 10:1) at 120 °C for 30 minutes, followed by 10 minutes rinse in isopropyl alcohol and deionized water.

VG was grown directly on the Si substrate using the recipe presented in Table 1.

*Table 1*

**Vertical Graphene growth process parameters**

| **Parameter** | Time (min) | RF power (W) | Pressure (mTorr) | Ar flow (sccm) | $CH_4$ flow (sccm) |
|---|---|---|---|---|---|
| **Value** | 60 | 300 | 300 | 190 | 10 |

The substrate temperature was varied for each wafer, starting from 600 $^oC$ up to 850 $^oC$ with an increment of 50 $^oC$ from run to run.

Raman Spectroscopy was performed using a high-resolution Scanning Near-Field Optical Microscope fitted with a Raman Module (Witec Alpha 300S) at 532 nm wavelength.

Morphological investigations were performed using the FEI Nova™ NanoSEM 630 microscope (FEI Company). The height of graphenic structure and its growth rate were determined from SEM images about film cross-section.

## 3. Results and discussion

In this chapter we discuss the modifications of the vertical graphene morphology (determined by SEM) induced by the substrate temperature during the growth process. We are comparing 6 samples grown using the same general parameters, at 600 $^{o}$C, 650 $^{o}$C, 700 $^{o}$C, 750 $^{o}$C, 800 $^{o}$C and 850 $^{o}$C. Results of Raman analysis (including full width half maximum (FWHM) of peaks) for VG films grown at various temperatures are summarized in Table 2.

Sample grown at 600 $^{o}$C is presented in Fig. 1. Raman spectrum (Fig. 1A) shows the specific bands D, G and 2D centered at D ~ 1347 $cm^{-1}$, G ~ 1571 $cm^{-1}$, 2D ~ 2683 $cm^{-1}$. The G and 2D band appear shifted from their normal positions at 1580 $cm^{-1}$ and 2690 $cm^{-1}$. Additionally, the D’ band can be seen as a shoulder to the main G band, centred around 1620 $cm^{-1}$, while the D+G can be clearly seen at ~2918 $cm^{-1}$ blue shifted from its usual position at 2940 $cm^{-1}$. The $I_D/I_G$ ratio of about 1.4, correlated with the appearance of the D’ and D+G bands indicates a low defect density. The $I_{2D}/I_G$ ratio of about 0.76 suggests the nanosheets are formed of few layers of graphene. The full spectral data for this sample are presented in Table 2.

The typical morphology of the vertical graphene, with the "ridge" profiles of the raised walls can be observed in the top view SEM image (Fig. 1B), while the height of the graphenic structures was measured at ~430 nm from the cross section presented in Fig. 1C.

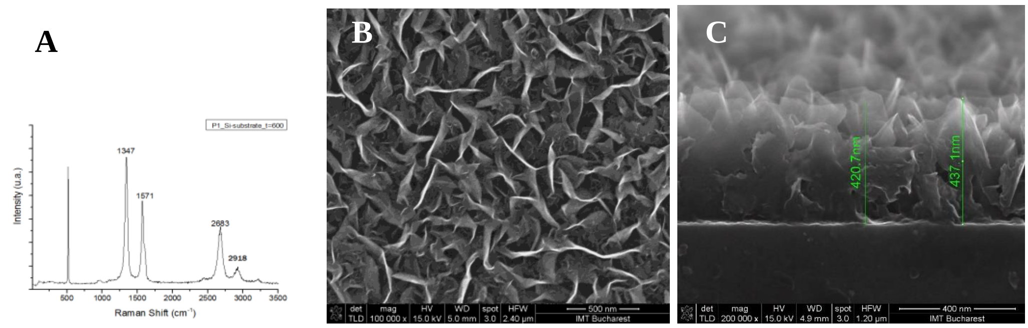


Fig.1 A – Raman spectroscopy of VG grown at 600 °C on Si substrate; B (top view), C (cross-section) – SEM images of VG grown at 600 °C on Si substrate

Sample grown at 650 $^{o}$C is presented in Fig. 2. Raman spectrum (Fig. 2A) shows the D band centered at ~1348 $cm^{-1}$, while the G band slightly shifts towards the normal position, being found at ~1576 $cm^{-1}$, and the 2D band is blue shifted at ~2674 $cm^{-1}$. Just like in the previous case, the D’ band can be seen as a shoulder to the main G band, centred around 1620 $cm^{-1}$, while the D+G can be clearly seen at ~2924 $cm^{-1}$. The $I_D/I_G$ ratio slightly increases to about 1.57, consistent with a low defect density state. The $I_{2D}/I_G$ ratio of about 0.8, suggesting the nanosheets are still few layers of graphene, just like in the previous case. The full spectral data for this sample are presented in Table 2.

As previously reported at 600 °C, the "ridge" profiles can be observed in Fig. 2B but a slight spacing decrease between neighbouring nanosheets is noticeable, resulting in a more compact arrangement of the vertical graphene nanosheets. From the cross section presented in Fig. 2C we can measure the height of the graphenic structures at ~440 nm.

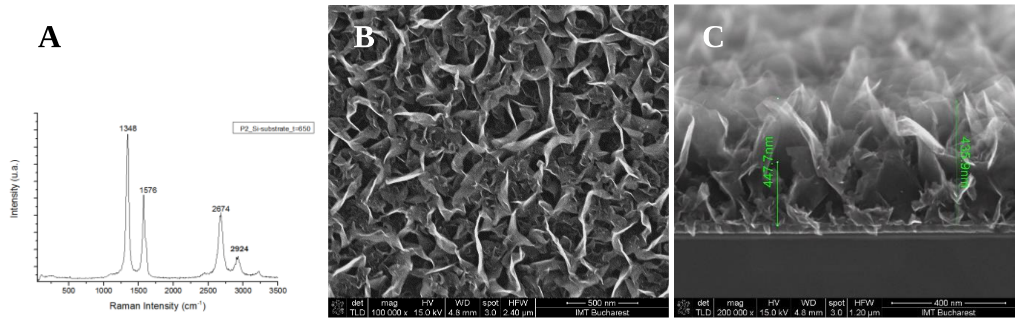


Fig.2 A – Raman spectroscopy of VG grown at grown at 650 °C on Si substrate; B (top view), C (cross- section) – SEM images of VG grown at 650 °C on Si substrate

In the case of the sample grown at 700 °C (Fig. 3), the Raman spectrum is presented in Fig. 3A. The D and G bands are centered at ~ 1348 $cm^{-1}$ and ~1575 $cm^{-1}$, while the 2D band continues to blue shift towards ~2668 $cm^{-1}$. The D' band can be seen as a shoulder to the main G band, centred around 1620 $cm^{-1}$, while the D+G can be clearly seen at ~2923 $cm^{-1}$. The $I_D/I_G$ ratio increases to ~1.79 but is still in the low defect density range, while the $I_{2D}/I_G$ suggests formation of few layers. The full spectral data for this sample are presented in Table 2.
The characteristic "ridge" profiles can be observed in Fig. 3B where a continuous crowding tendency of the nanosheets can be observed. Fig. 3C shows the cross section of the sample, the measured height of the graphenic structures increasing to ~460 nm.

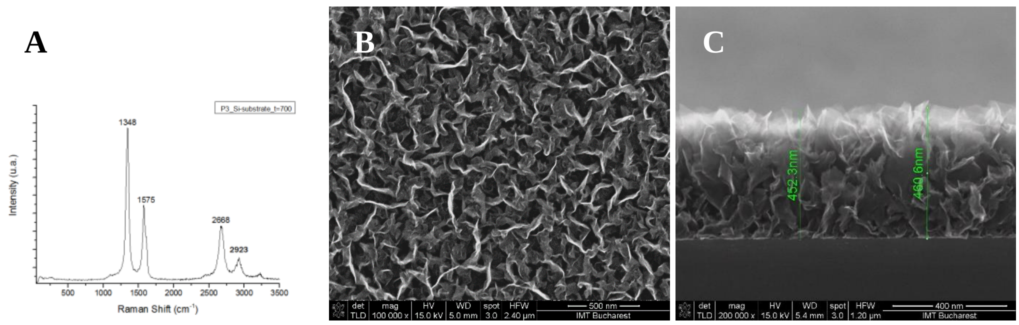


Fig.3 A – Raman spectroscopy of VG grown at 700 °C on Si substrate; B (top view), C (cross- section) – SEM images of VG grown at 700 °C on Si substrate

In Fig. 4 we present the results for the sample grown at 750 $^oC$. The Raman spectrum, in Fig. 4A, shows the D and G bands centered at ~ 1336 $cm^{-1}$ and ~1575 $cm^{-1}$, while the 2D band continues to blue shift towards ~2662 $cm^{-1}$. The D' band appearing at ~1620 $cm^{-1}$, the D+G at ~2911 $cm^{-1}$ combined with the $I_D/I_G$ ratio of ~1.41 indicates a low defect density range. The $I_{2D}/I_G$ ratio of about 0.73. The full spectral data for this sample are presented in Table 2.
The top view, presented in Fig. 4B, and the cross section view, presented in Fig. 4C, clearly indicate a more random growth of the vertical graphene nanosheets leading to a more denser film. The measured height of the film grown at 750 $^oC$ is ~600 nm.

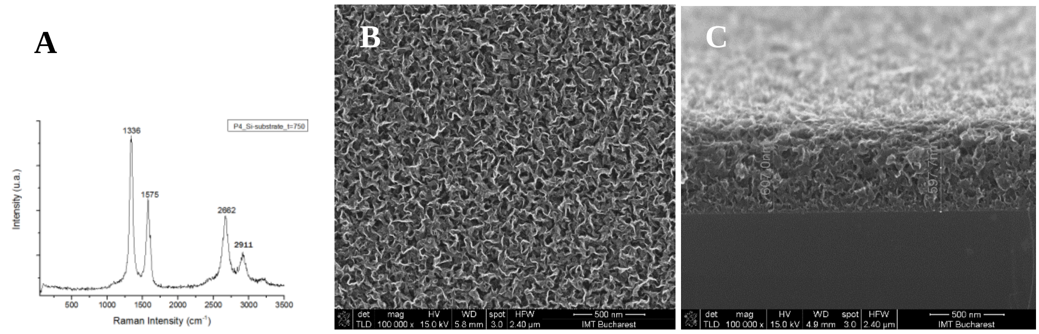


Fig.4 A – Raman spectroscopy of VG grown at 750 °C on Si substrate; B (top view), C (cross-section) – SEM images of VG grown at 750 °C on Si substrate

The sample grown at 800 $^oC$ is presented in Fig. 5, while the sample grown at 850 $^oC$ is presented in Fig. 6. In both cases, the Raman spectra (Fig. 5A for 800 $^oC$ and 6A for 850 $^oC$) show the characteristic D, G and 2D bands in their expected positions at 1330 $cm^{-1}$ – 1340 $cm^{-1}$, 1580 $cm^{-1}$ and, respectively, 2668 $cm^{-1}$. The D' band is no longer visible, most likely due to the increase of the FWHM of the G band, while the D+G band is clearly visible at 2923 $cm^{-1}$ and 2911 $cm^{-1}$. The $I_D/I_G$ ratio is constant at ~1.5 indicating low defect density. The $I_{2D}/I_G$ ratio of sample grown at 800 $^oC$ is 0.67 and for sample grown at 850 $^oC$, the $I_{2D}/I_G$ is 0.59. The full spectral data for these samples are presented in Table 2.

The characteristic "ridge" profiles can still be observed in Fig. 5B and Fig. 6B, but an evident random growth of the nanosheets concurrent with a densification of the film can be observed. The cross section images show a height increase to ~690 nm at 800 $^oC$ and ~940 nm at 850 $^oC$.

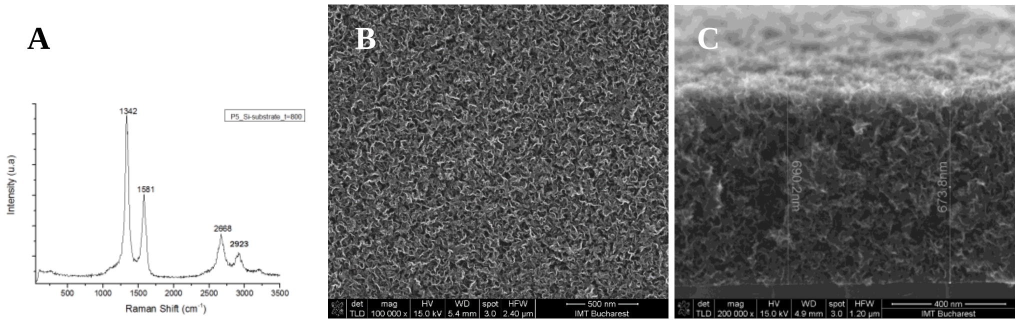


Fig.5 A – Raman spectroscopy of VG grown at 800 °C on Si substrate; B (top view), C (cross-section) – SEM images of VG grown at 800 °C on Si substrate

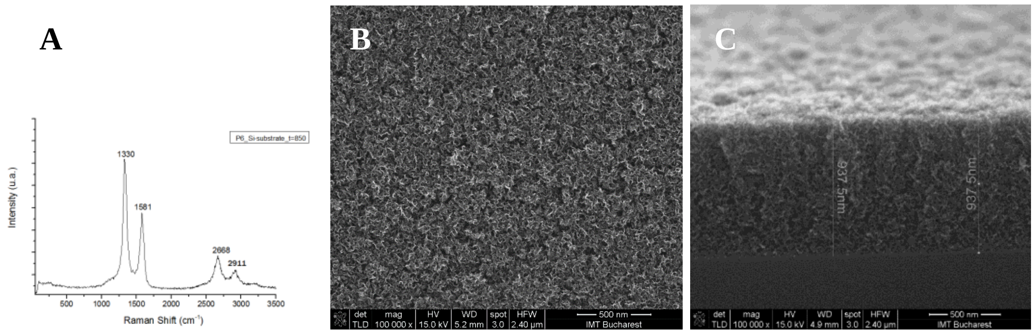


Fig.6 A – Raman spectroscopy of VG grown at 850 °C on Si substrate; B (top view), C (cross-section) – SEM images of VG grown at 850 °C on Si substrate

For all samples, Raman spectroscopy shows the characteristic D, G and 2D bands slightly shifted from their normal positions, an indication of possible strain present in the crystalline lattice induced by the vertical orientation of the graphene nanosheets. The $I_D/I_G$ ratio can be observed to slightly vary between 1.4 and 1.8, but it’s value much lower than 3, corroborated with the presence of the D’ and D+G bands indicate low defects density. The FWHM of the G band continuously increases from 53 $cm^{-1}$ to 78 $cm^{-1}$ with the increase of substrate temperature, indicating a higher crystalline disorder at higher growth temperatures. Also, the $I_{2D}/I_G$ ratio is consistent with few layers of graphene up to 700 $^oC$, at higher temperatures there is a clear tendency of multi-layer growth. This may be explained by additional nucleation centers which are allowed to form at higher temperatures leading to the branching of additional nanosheets growing outwards from the main vertical sheet. This statement is also supported by the SEM images, which in cross section show a highly disordered growth at higher temperatures, while the top views present more compact films. Cross section views of the films indicate an increased growth rate at higher temperatures, at 850 $^oC$ the growth rate of ~16 nm/min being more than double that at 600 $^oC$. This is to be expected as the higher the temperature the faster the chemical reactions between the carbon-based precursor and nucleation areas. Also, the high growth rates may lead to the inclusion a higher number of impurities, which can further explain the lower crystallinity degree and overall quality of vertical graphene grown at 750 $^oC$ and above. For easier comparison between the samples, the values of film thickness and growth rate are presented in Table 3.

*Tabel 2*

**Results of Raman analysis for VG grown on Si substrate**

| Temp. (°C) | D ($cm^{-1)}$) | G ($cm^{-1)}$) | 2D ($cm^{-1)}$) | D+G ($cm^{-1)}$) | $I_D/I_G$ | $I_{2D}/I_G$ | FWHM D ($cm^{-1)}$) | FWHM G ($cm^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| 600 °C | 1347 | 1571 | 2683 | 2918 | 1.41 | 0.76 | 47 | 53 |
| 650 °C | 1348 | 1576 | 2674 | 2924 | 1.57 | 0.8 | 49 | 56 |
| 700 °C | 1348 | 1575 | 2668 | 2923 | 1.79 | 0.78 | 53 | 64 |
| 750 *°C* | 1336 | 1575 | 2662 | 2911 | 1.41 | 0.73 | 59 | 68 |
| *800 °C* | 1342 | 1581 | 2668 | 2923 | 1.66 | 0.67 | 69 | 74 |
| 850 °C | 1330 | 1581 | 2668 | 2911 | 1.5 | 0.59 | 77 | 78 |

*Tabel 3*

**Results of SEM analysis for VG grown on Si substrate**

| Temperature (°C) | Height (nm) | Growth rate (nm/min) |
|---|---|---|
| 600°C | 430 | 7.2 |
| 650°C | 450 | 7.5 |
| 700°C | 460 | 7.7 |
| 750°C | 600 | 10.0 |
| 800°C | 690 | 11.5 |
| 850°C | 940 | 15.7 |

The growth processes performed at temperatures below 600 °C have resulted in irregular growth of vertical graphene on the Si substrate. We consider that it is possible to grow vertical graphene at process temperatures lower than 600 °C, by varying the parameters, which will be studied in the future.

## 4. Conclusions

From the characterizations performed in this study, we can conclude that vertical graphene films grown at temperatures ranging from 600 $^oC$ to 700 °C present low defect density, lower crystallinity disorder and are mostly made up of few layers of graphene. SEM images show that increased temperature leads to more compact and thicker films. Depending on the application in which the vertical graphene films are used, the most suitable parameters (temperature) of deposition must be chosen to provide the appropriate structure and properties according to the potential application.

In future studies we will focus our attention towards the change in specific surface area, electrical properties and cytotoxicity of the vertical graphene depending on growth temperature and conditions.


### Acknowledgements

This work was supported by a grant of the Ministry of National Education and Scientific Research, PN-III-P1-1.2-PCCDI-2017- 0619, Project Nr. 42PCCDI/ 2018.


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