

## EX-SITU AND IN-SITU STUDIES OF CVD GRAPHENE GROWTH WITH THE USE OF RAMAN AND REFLECTANCE SPECTROSCOPY

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### ABSTRACT

Graphene is used with exponential rate in many technological applications due to its unique properties. Lately, emphasis has been given to the mass production of graphene with epitaxial growth and more specific, Chemical Vapor Deposition (CVD). CVD is based on the decomposition of hydrocarbon molecules and their nucleation on a catalytic surface at high temperatures. The pressure, the temperature and the flow rates of precursors are major parameters, which must be regulated in order to produce continuous defect-free graphene sheets, so its outstanding properties can be exploited. The production of graphene sheets was performed in CVD reactor, with the use of a mixture of Methane (CH<sub>4</sub>) as carbon source, Hydrogen (H<sub>2</sub>) and Argon (Ar) onto copper (Cu) foils at high temperatures (~ 1270K). The goal is to obtain good quality graphene, so it is important to be found the conditions that CVD must take place. UV-Raman spectroscopy is carried out for a direct characterization/quality control of produced graphene (ex-situ). Additionally, a reflectometer was used for the in-situ monitoring of surface changes during graphene growth. The results shown that the reflectometer can be successfully adopted for in-situ characterization during CVD growth and its results can be used for estimation of the thickness of CVD graphene from the measured differential reflectance.

### INTRODUCTION

Two-dimensional (2D) materials are a family of materials with excellent physical and chemical properties<sup>[1]</sup>. The first material included was graphene<sup>[2]</sup>, which possesses a range of excellent properties. Graphene, one of the allotropic forms of carbon (C), is a flat layer of carbon atoms arranged in hexagonal mesh, with the C-C bond length is being 0.14 nm. Its remarkable properties such as enormous mechanical strength and high thermal and electrical conductivity are due to the crystalline structure of the graphene and the sp<sup>2</sup> hybridization of the electrons of the lattice. The main obstacle to the practical use of 2D materials is the difficulty of mass production due to the lack of control of the process, which is necessary to meet the qualitative and quantitative requirements that exist for both scientific and technological applications.

In 2009, Ruoff<sup>[3]</sup> was the first demonstration of the chemical vapor deposition (CVD) of graphene (CVD) and has since established itself as one of the most widespread methods of developing high quality and large-scale 2D materials<sup>[4,5]</sup>. The prospect of large-scale synthesis of 2D materials would lead to their incorporation into applications of high technological interest such as flexible electronics, gas sensors, energy storage and catalysis<sup>[6]</sup>. A typical CVD procedure for graphene synthesis comprises: i) adsorption and decomposition of a carbon source on the surface of a metal substrate, acting as a catalyst; ii) diffusion on the surface or dissolution in the bulk of the metal catalyst for the carbon products, (iii) the dissolved carbon atoms diffuse from the bulk to the surface, (iv) nucleation and spreading of the graphene. Initially, there are many studies to choose the carbon-containing precursor compound, which may be solid, liquid or gaseous<sup>[7,9]</sup>. All precursors (CH<sub>4</sub>, H<sub>2</sub> etc.) will undergo a decomposition process where its performance will determine the rate of growth

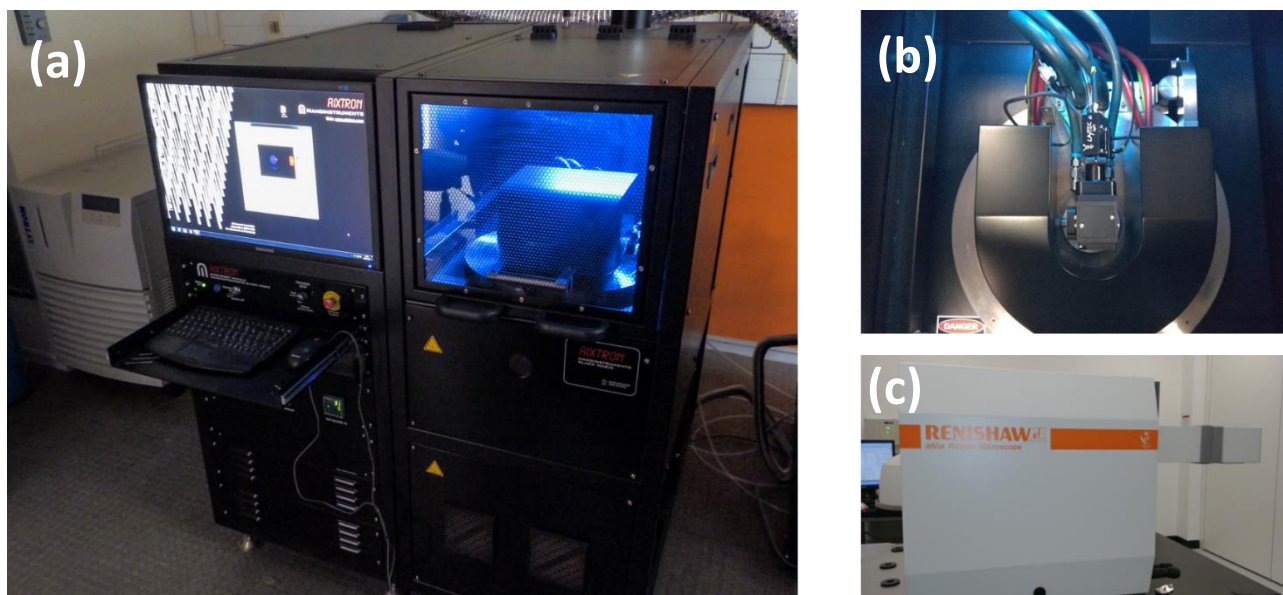
and the final quality of the graphene. Copper is used for metal substrate thus monolayer graphene is mainly produced, due to self-limiting behavior instead of other metals<sup>[3,9-10]</sup>.

Except for production a main topic that is vital to practical applications is the characterization of graphene in an efficient way. By varying the parameters of development, the size and quality of the graphene produced can be affected. In order to be able to monitor without effects of these changes in the quality of the produced material, it should have a way of observation at the time of in-situ development. Attempts have been made to observe and characterize graphene during CVD synthesis using optical microscopy<sup>[12]</sup>, electron microscopes (SEM, TEM)<sup>[13-14]</sup>, X-ray systems (XRD, XPS)<sup>[11]</sup> and Raman spectroscopy<sup>[15]</sup>. However, such monitoring systems, except for optical microscopy, are very expensive and require special conditions in order to be efficient. One of the simplest but at the same time rich in information ways to achieve this is through differences in the reflectivity of a surface<sup>[16]</sup>. The next important step after the synthesis and in-situ characterization of graphene is the characterization of their properties after production (ex-situ). For the quality control of graphene produced, the use of a chemically sensitive technique plays a key role. Among spectroscopic techniques, Raman spectroscopy is used to observe the vibrational and rotational states of a system and can provide us with important information about the chemical structure on the surface by analyzing several hundreds of nm<sup>[17]</sup>.

In this study, the production of Graphene sheets is taking place in a CVD reactor, with the use of a mixture of Methane (CH<sub>4</sub>) as carbon source, Hydrogen (H<sub>2</sub>) and Argon (Ar) onto copper (Cu) foils at high temperatures (~ 1270K). The goal was to study was good quality graphene, so it is important to be found the conditions that CVD must take place. Spectroscopic analysis is carried out with the use of Raman spectroscopy and reflectance spectroscopy in order to identify the presence and the quality of graphene films. More specific, UV-Raman spectroscopy has been adopted for a direct characterization/quality control of graphene grown on copper substrate without transferring it to a dielectric substrate. Moreover, in-situ reflectivity experiments will be used to study the kinetic growth kinetics. Initial results shown that the reflectometer can be successfully adopted for in-situ characterization during CVD growth and its results can be used for estimation of the thickness of CVD graphene from the measured differential reflectance.

## METHODOLOGY

Graphene sheets were produced with a cold wall CVD reactor (AIXTRON Black Magic) (Figure 1) that is able to produce high quality graphene of up to 100 cm<sup>2</sup>. Volumetric gas flow rates will be adjusted with digital flowmeters for the highest possible accuracy. In situ reflection spectra were acquired with an EpiTT 33-2178-2017 reflectometer purchased from Laytec and adapted to AIXTRON Black Magic CVD reactor. Raman spectra were acquired with an InVia Raman spectrometer purchased from Renishaw that allowed us to control the quality of the graphene grown on Cu substrate, as well as the effect of the growth conditions. A 355 nm laser beam were used for the direct characterization of graphene grown on Cu substrate. The ratio I<sub>2D</sub>/I<sub>G</sub> and the width at half of the maximum (FWHM) and the position of the peak 2D gave us information about the number of layers and the ratio I<sub>D</sub>/I<sub>G</sub> the percentage of imperfections. These studies will provide the opportunity to test a variety of conditions and lead to an optimal final recipe.



**Figure 1.** (a) AIXTRON Black Magic CVD for production of graphene, (b) EpiTT 33-2178-2017 reflectometer (Laytec) for in-situ characterization, (c) Raman spectrometer (Invia Renishaw) for ex-situ characterization.

## RESULTS AND DISCUSSION

In-situ reflectance measurements were acquired for different growing conditions and the results will be discussed at this point. First of all, a typical reflectance spectrum is presented in Figure 2b in which it is presented the changes of the reflectance during a growing cycle. The characteristic growth steps are visible and include the copper oxide reduction, copper surface smoothing, graphene deposition and cooling-down of the completed structure. The rapid increase in reflectance is caused by the reduction of hydrogen induced oxide from copper. At higher temperature and especially during the high temperature annealing, the Cu surface becomes smooth because of the high mobility on Cu atoms on the surface. The higher reflectance value at the end of annealing shows that an extended high temperature annealing produces a smoother Cu surface. Surface morphology changes are responsible for the reflectance rise. Then, an evident reduction in reflection due to graphene deposition under CH<sub>4</sub>.

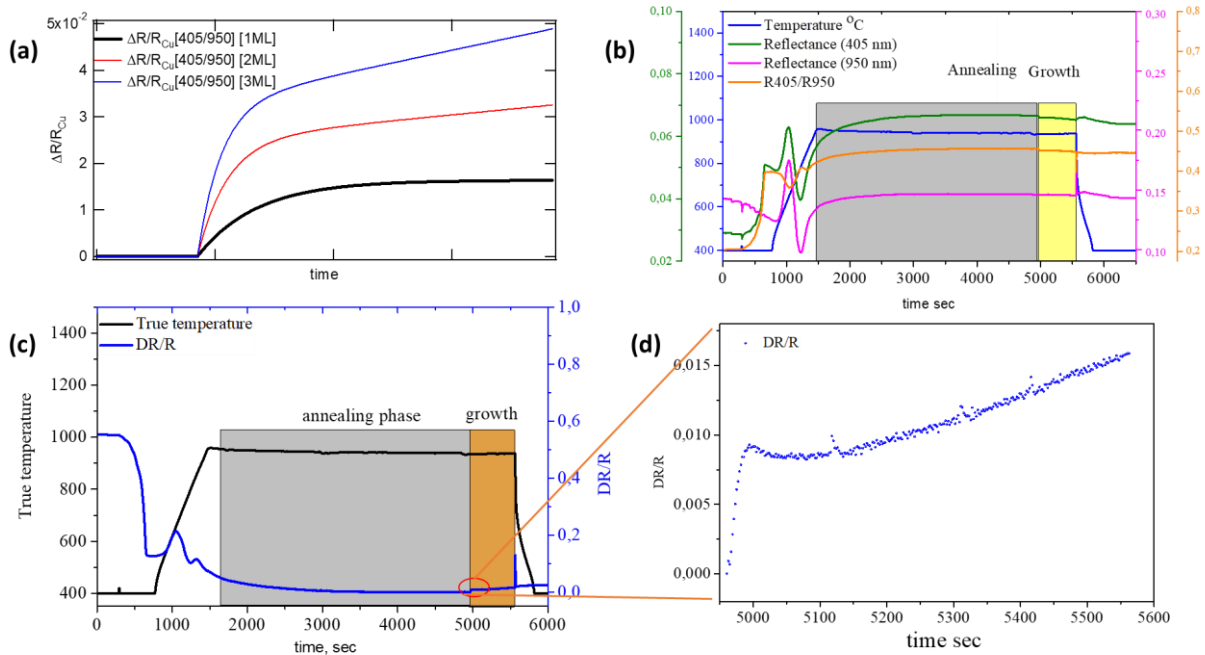
Continuing with the elaboration of reflectance spectra (Figure 2b), it must be underlined that the reflectance from 950 nm wavelength is more sensitive to morphological changes in contrast to the reflectance from the 405nm that depends mainly from the chemical changes. In order to eliminate the contribution of surface roughness to reflectance and observe only the chemical changes of the surface, which is object of study, it is used a normalized quantity, a ratio of reflectance 405 nm to reflectance 950 nm ( $R_{405}/R_{950}$ ). When the methane (CH<sub>4</sub>) precursor is fed to the chamber the slope of differential reflectance equation (1) changes:  $\Delta R/R_{Cu}$  is a measure of the graphene growth. The results indicate that  $R_{405}/R_{950}$  is an indicator for the surface state (prior to graphene deposition) and allows in-situ estimation of graphene growth.

$$\frac{\Delta R}{R} = \frac{R_{Cu} - R_{Gr/Cu}}{R_{Cu}} \quad \text{where } (R = R_{405} / R_{950}) \quad (1)$$

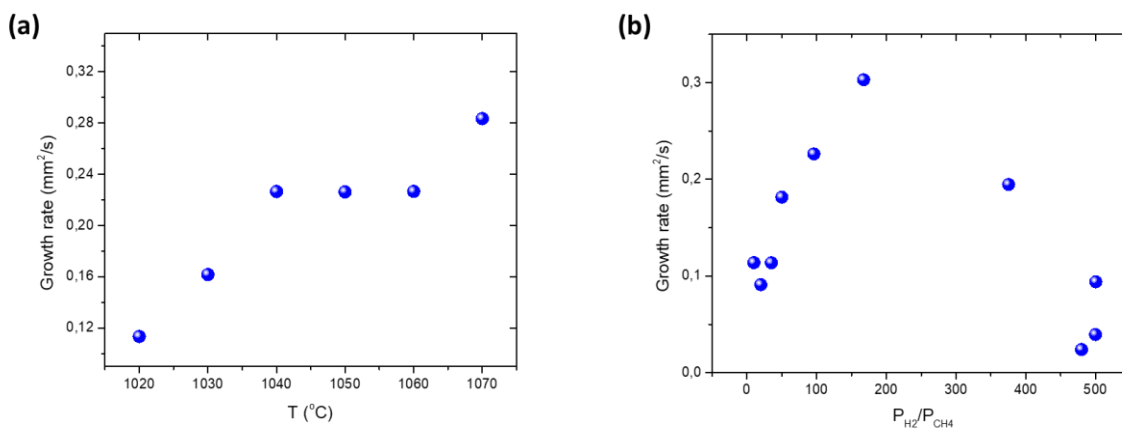
Comparing the theoretical (Figure 2a) with the experimental value (Figure 2d) of differential reflectance, we can validate the quality of the produced graphene. This method allows us to evaluate the grown film experimentally in real time.

Another interesting point with the use of reflectance measurements is that give the opportunity of understanding the growth kinetics in real time. This is a very important information which leads to a theory about how and when graphene starts developing. When the hydrocarbon source fed to the reactor, it is observed that reflectance presents a linear behavior with time and after a while,

depends on the experimental conditions, this behavior is changed. When the linear behavior is disappeared, it is assumed that with have full coverage of the surface with graphene. We use this information in order to calculate the growth rate of the formation of graphene from CH<sub>4</sub> and H<sub>2</sub>.



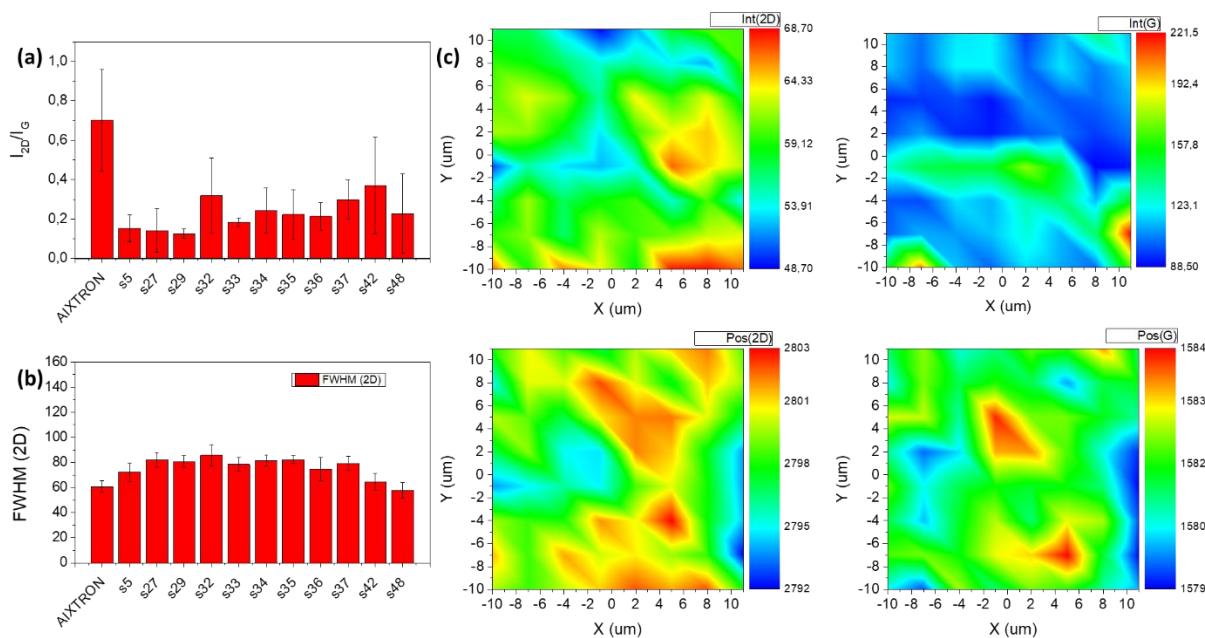
**Figure 2.** (a) The calculated differential reflectance spectra of the films comprising of 1 (black line), 2 (red line) and 3 (blue line) graphene layers<sup>[16]</sup>. (b) Reflectance spectra of CVD of Graphene on Cu in AIXTRON BM reactor, which include the process true temperature measured in-situ during the growth, 405 nm reflectance measured in-situ during the growth, 950 nm reflectance measured in-situ during the growth and  $R_{405}/R_{950}$  which is an indicator computed from 405 nm and 950 nm reflectance (c) The calculated differential reflectance spectra with the process true temperature measured in-situ during the growth. (d) Zoom area of differential reflectance spectra when the methane (CH<sub>4</sub>) precursor is fed to the chamber.



**Figure 3.** Experimental values of growth rates (mm<sup>2</sup>/s) for different major parameters that affect growth of Graphene on Copper. (a) growth temperature (b) total flow rates of precursors (c) partial pressure of CH<sub>4</sub> (d) ratio of partial pressures for H<sub>2</sub> to CH<sub>4</sub>.

In the Figure3 are presented the calculated growth rates in different growth conditions. Graphene was grown by CVD from mixtures of  $H_2:CH_4 = (50-1000 \text{ sccm}):(2-10 \text{ sccm})$  at a range of temperatures of  $1020^\circ\text{C} - 1070^\circ\text{C}$  and a total pressure of 25 mbar. It is clearly demonstrated that by varying the growth parameters such as temperature and gases partial pressure the growth rate changes. More detailed, it is observed that increasing temperature the growth rate increases. This correlation exists generally between growth rate and temperature in almost all cases. So, we can observe that graphene growth on copper appears Arrhenius like behavior. Figure3b presented the correlation of growth rate with the ratio of partial pressure of hydrogen to partial pressure of methane. It seems that growth rate increased as it reached a specific point for value of 200 for  $P_{H_2}/P_{CH_4}$  and then it decreased. In the range of 0-200 for  $P_{H_2}/P_{CH_4}$  the increment of growth rate with the increase of  $H_2$  is due to the better activation of the Cu substrate on the other hand, at higher amount of  $H_2$  the growth rate decreases since the excess of  $H_2$  might affect the decomposition of  $CH_4$  but also to etch graphene grown on Cu substrate. .

Furthermore, ex-situ spectroscopic characterization was performed using Raman spectroscopy. The samples(s(N) where  $N=5-48$ ) refer to same conditions that those we used in order to receive reflectance spectra and values of growth rates (Figure 3). The quality of graphene was determined by the spectral characteristics 2D and G bands such as Number of graphene layers ( $I_{2D}/I_G$ , FWHM2D), defects ( $I_D/I_G$ ), nanometric strain distribution of the graphene (Pos2D, PosG). Different growth conditions are studied, and analysis of Raman data indicates the conditions which produce better quality of Graphene. Parametric analysis took place and examined how annealing temperature and growth temperature affects the quality of the produced graphene. Figure4 (a,b) presents two bar charts for different conditions in which the first number refers to annealing temperature and the second to growth temperature. The best graphene was sample s42 with  $P_{H_2}=2,26$  mbar,  $P_{CH_4}=0,09$  mbar at a temperature of  $1065^\circ\text{C}$  and at total pressure 25 mbar in our CVD reactor.



**Figure 4.** Histograms of FWHM (2D) and  $I_{2D}/I_G$  for different growth conditions of Graphene on Copper (a,b) and topographic analysis of Graphene on Copper (c) by Raman (Invia Renishaw) spectroscopy with 355nm excitation wavelength.

Topographic analysis is useful in order to derive these information's that refer previously. In Figure 4c presented the topographic analysis for sample s42, which was the best quality graphene we produced. It should underline that in all cases, which are examined, 1L graphene was grown and confirmed with Raman spectroscopy.

## CONCLUSIONS

In conclusion, we have demonstrated that graphene growth can be monitored with reflectance measurements. Reflectometer is a very useful tool and provide us information about the growth kinetics of graphene on copper. The results indicate that  $R_{405}/R_{950}$  is an indicator for the surface state and  $\Delta R/R = (R_{Cu} - R_{Gr/Cu})/R_{Cu}$  allows in-situ estimation of graphene growth and number of layers of the produced graphene. The existence of 1L graphene was confirmed by Raman spectroscopy with a 355 nm laser beam, which allows us to collect information directly on the growth substrate without transfer to a dielectric substrate.

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## REFERENCES

- [1] K. S. Novoselov et al., (2005) Proc. Natl. Acad. Sci., vol. 102, no. 30, pp. 10451–10453.
- [2] K. S. Novoselov et al., (2004) Science (80-.), vol. 306, no. 5696, pp. 666–669, 2004.
- [3] X. Li et al., (2009) Science (80-.), vol. 324, no. 5932, pp. 1312–1314.
- [4] S. Bae et al., (2010) Nat. Nanotechnol., vol. 5, no. 8, pp. 574–578.
- [5] L. Banszerus et al., (2015) Sci. Adv., vol. 1, no. 6, pp. 1–7.
- [6] D. Deng, K. S. Novoselov, Q. Fu, N. Zheng, Z. Tian, and X. Bao, (2016) Nat. Nanotechnol., vol. 11, no. 3, pp. 218–230, 2016.
- [7] L. Growth, (2011) “62-ACSNano-2011-5-3385.pdf,” no. 4, pp. 3385–3390.
- [8] J. Giesl, R. Thiemann, and P. Schneider-Kamp (2006) Deduc. Appl. 23.-28. Oct. 2005, vol. 05431, no. 9, pp. 7601–7607.
- [9] Z. Sun, Z. Yan, J. Yao, E. Beitler, Y. Zhu, and J. M. Tour, (2011) Nature, vol. 471, no. 7336, p. 124.
- [10] R. S. Edwards and K. S. Coleman, (2013) Acc. Chem. Res., vol. 46, no. 1, pp. 23–30, 2013.
- [11] R. S. Weatherup et al., (2011) Nano Lett., vol. 11, no. 10, pp. 4154–4160.
- [12] A. J. Hart, L. Van Laake, and A. H. Slocum, (2007) Small, vol. 3, no. 5, pp. 772–777.
- [13] L. Zhang et al., (2014) J. Phys. Chem. Lett., vol. 5, no. 8, pp. 1427–1432.
- [14] M. Kurnatowska et al., (2015) ACS Nano, vol. 9, no. 2, pp. 1506–1519.
- [15] J. Binder, J. M. Urban, R. Stepniowski, W. Strupinski, and A. Wyszomolek, (2015) Nanotechnology, vol. 27, no. 4, p. 45704.
- [16] T. Kaplas, A. Zolotukhin, and Y. Svirko, (2011) Opt. Express, vol. 19, no. 18, p. 17226, 2011.
- [17] L. M. Malard, M. A. Pimenta, G. Dresselhaus, and M. S. Dresselhaus, (2009) Phys. Rep., vol. 473, no. 5–6, pp. 51–87.