

Graphene Synthesis via CVD on Palladium

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Chemical vapor deposition (CVD) has become an essential method for monolayer and multilayer graphene production because of its low cost and relatively easy implementation. Although this method has driven graphene studies on specific substrates such as Cu and Ni, the nature of large-area graphene on certain substrates such as Pd is still not completely studied. We present an investigation of graphene samples synthesized via CVD on Pd foil substrates according to Xiaohong An et al. (2012)(1). The CVD chamber was controlled over two different growth temperatures ($T = 950^\circ\text{C}$ and $T = 1000^\circ\text{C}$) and durations (15 min and 20s, respectively), and the graphene growth under these conditions was investigated using scanning electron microscopy and analysis of Raman spectra. At $T = 950^\circ\text{C}$, defect-free multilayer graphene was found to grow in some islands of the substrate, both Bernal and mixed species, which turned into macroscopic coverage of the substrate by regions. At the same sample, monolayer graphene with defects was found to grow in a different region. The evolution of different types of graphene as a function of temperatures and duration is presented. Optimal growth conditions can be improved in future research.

Graphene | CVD | Palladium | CVD | SEM | Raman Spectroscopy

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Introduction. Due to its properties and applications, carbon graphene synthesis has become an important object of study nowadays, since its explanations of Carbon interactions at atomic levels have led to fundamental understanding of phenomena in diverse fields. Both science and industry have focused their efforts on taking advantage of Graphene's electrical (2D circuits), optical (transparent) and mechanical (inherent strength) properties (2). Hence, there is an increasing demand on the development of this Carbon's allotrop with quality enough to optimize these properties, in particular large-area graphene with low defect density and large crystallographic domains.

Graphene's hexagonal lattices have $\sim 120^\circ$ edge angles. Scanning Electron Microscope (SEM) analysis can reveal this geometric flakes as we can see in the next figure.

CVD has become one of the most popular methods of graphene production since it has a lot of benefits, such as high-quality of the resulting graphene, imperviousness, high purity, low cost production (depending on the substrates), fine grained and hardness improvements over other coating methods. It also eases the transferability onto certain surfaces for industry applications (it is a common method for deposition of semiconductor films) (3).

CVD is a process where gaseous precursors react to form a solid coating on a heated substrate. It takes place in a vacuum reaction chamber where the component to be coated is located.

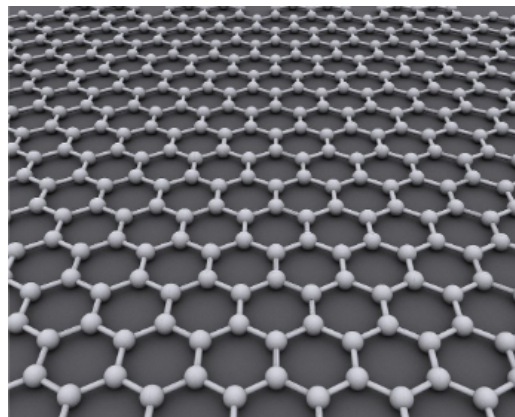


Fig. 1. Artistic representation of graphene[7].

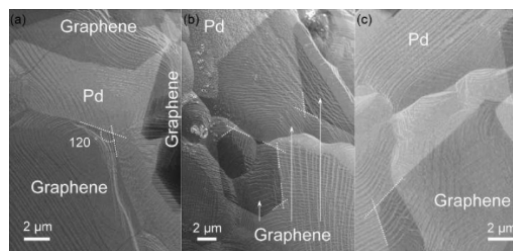


Fig. 2. SEM images of CVD-grown graphene on Pd substrates ($T = 1000^\circ\text{C}$, $t = 17\text{ s}$), taken from representative regions of the substrate. The hexagonal-shaped graphene flakes and flake edges are seen to grow continuously over Pd terraces, step edges, and grain boundaries. The dashed lines demarcate 120° angles(1).

The component, in this case Pd, is heated to the desired reaction temperature, which depends on the substrate (200° to 2000°). Once the component reaches the desired temperature, a controlled flow of mixed reactant gases is introduced into the reaction chamber. An example of those gases are Ar, H, and CH_4 . The process conditions are adjusted, so that the mixture does not react until it comes into contact with a solid surface, such as the substrate. In the case of Pd, as some of the gas molecules come into contact with the substrate, carbon atoms diffusion occur in the substrate, as it is shown in Figure 3 for a Ni substrate.

Some of the most common substrates in which successful growth of both, mono-layered and multilayered graphene, has been reported include Cu, Co, Ni, Ir, Ru, Rh, Pt, Pd, etc. The growth of graphene in Cu and Ni has received special attention among the others due to the low cost in its production and the interest of understanding the whole process of nucleation and growth on these substrates. Even though there has been a demonstration of graphene growth on these substrates, the nature of large-area graphene on some of them, such as Pd is still not completely studied.

The most common use for palladium is in catalytic converters

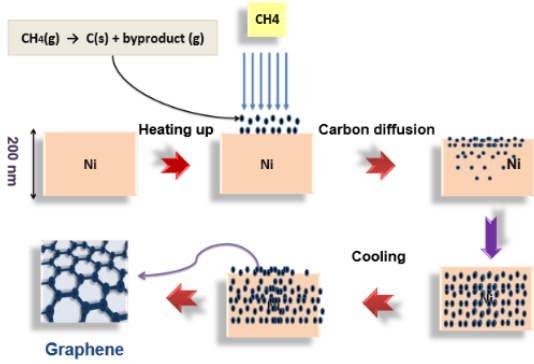


Fig. 3. CVD on Ni substrate[4]. Comparable to CVD on Pd since it occurs faster on the latter than on Ni.

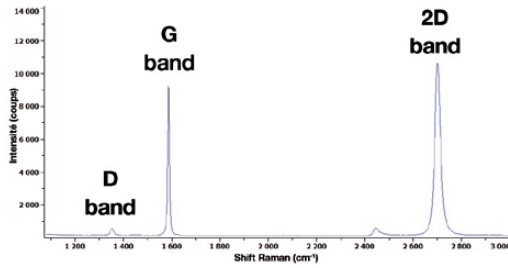


Fig. 4. Typical Raman spectra of graphene()

since it has excellent catalytic and chemical stability properties, also it is used in multilayer ceramic capacitors and as a connector plating for a number of electronics. Its applications in chemistry, electronics and other areas, increases as technology does, hence the importance of understanding its nature and the way it interacts with all the phenomena that involves it. As well, Pd has excellent carbon solubility and diffusivity.

In this work, we present a study of large-area growth of graphene on a Pd sheet as a substrate based on previous works carried out by Xiaohong An et al[1]. The process of CVD graphene synthesis will be exposed as well as the results from Raman spectroscopic analysis of the obtained sample. Further, results from Scanning Electron Microscope (SEM) observations will be exposed and compared to the studies of the variety of terrace of structures and it's influence on the growth-initiation conditions on this substrate.

Raman spectroscopy. Raman spectroscopy consists of a vibrational technique with sensitivity enough to reach geometric structure and bonding within molecules. This sensitivity is very useful for the study of different allotropes of carbon, since the differences exist only in the relative position of their carbon atoms and the bondings between them. (5)The Raman spectrum of graphene shows a structure characterized by two principle bands, G and 2D bands (band D may appear in graphene when defects are present in the carbon lattice). These bands differ not only in their positions, but also in their shapes and intensities. Nevertheless, Raman spectroscopy provides us the ability to identify single, double, and triple layer graphene. i.e., it can determine layers thickness at atomic resolutions.

.1. G band. It's a sharp band that appears around 1587cm^{-1} in the spectrum of graphene. It represents a vibrational mode involving the sp^2 hybridized carbon atoms that incorporates the graphene sheet. It is highly sensitive to the number of layers in the produced sample, one method for determining layer thickness is based upon the observed position of this band for a particular sample. The band position shifts to lower energy as the layer thickness increases, it means a softening in the bonds as another layer is added. The following relation relates the band position to the number of atomic layers present in a sample for SiO_2/Si .

$$\omega_G = 1581.6 + \frac{11}{1 + n^{1.6}} \quad (1)$$

Where ω_G is the band position in wave numbers and n is the number of layers.

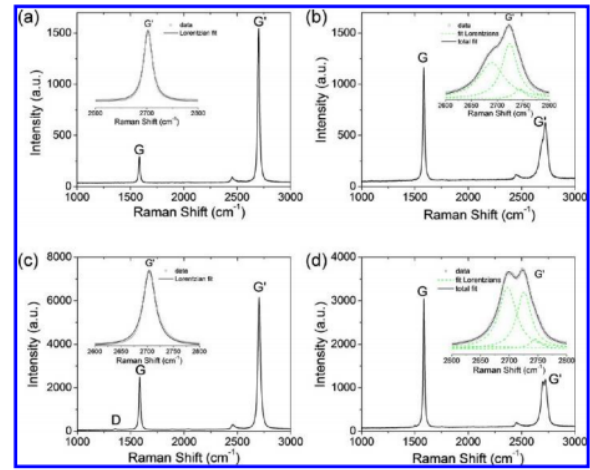


Fig. 5. Typical Raman spectra of the four different categories of graphene samples found to grow on Pd by Xiaohong An et al. (2012)[2]. (a) Monolayer graphene, (b)Bernal multilayer graphene, (c) turbostratic multilayer graphene, and (d) mixed species of graphene.

.2. D band. Also known as the disorder band or defect band. It appears because of a breathing mode from sp^2 carbon rings, although it must be next to a graphene edge or defect to be active. It is weaker as the quality of graphene improves. This band exhibits a dispersive behavior, which means that there are weak modes underlying this band and depending on the excitation of the laser used. Hence, the position and shape of the band vary with the frequencies.

.3. 2D band. This band is the result of a 2 phonon lattice vibrational process and does not need to be activated as D band. It is a strong band and is used to determine graphene layer thickness. For this method, both, the band positions and shape are needed. For a single layer graphene, the 2D band is a symmetric peak with a full width at half maximum of $\sim 30\text{cm}^{-1}$ for SiO_2/Si . As more layers are added, the 2D band splits into overlapping modes as we can see in Figure 5b) and d) for SiO_2/Si . As for the D band, the frequencies used imply a dispersive behavior.

A single layer graphene can also be identified by analyzing the peak intensity ratio of the 2D and G bands. The ratio

I_{2D}/I_G of these bands for high quality (defect free) single layer graphene will be ~ 2 . This ratio is often used as a confirmation for a high quality defect free graphene sample[(1)]. From the analysis of this bands, the characterization of graphene can be done as its shown in Figure 5.

Experimental section. Before introducing the Pd substrate to the vacuum chamber, it was cleaned with acetone and isopropanol for 15 min, respectively.

Graphene was synthesized by low-pressure CVD technique in a split tube furnace with a quartz tube (10 cm in diameter). Pd substrates (Alfa Aesar), in the form of a 25 μm thick foil, cut into small pieces (5x5mm).

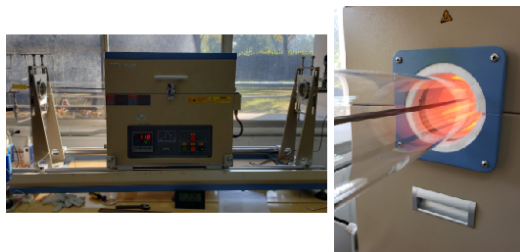


Fig. 6. Experimental setup Left: OTF 1200 oven quartz tube for CVD. Right: Heated oven.

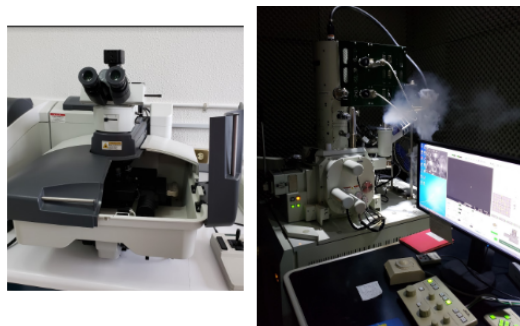


Fig. 7. Raman spectroscopy SEMLeft: Thermo Scientific DXR Raman Microscope at Advanced Materials Laboratory. IF-UNAM. Right: SEM JEOL JSM-7800F en el Central Laboratory of Microscopy, IF-UNAM.

The synthesis of graphene on Pd foils was carried out at different temperatures. The sample was placed in the center of the furnace with a flow of hydrogen (60 sccm) and argon (30 sccm). The whole system was kept under vacuum (1.5 Torr), heated to $T = 950^\circ\text{C}$, for the first batch and $T = 1000^\circ\text{C}$, for the second, and kept for 30 min in order to anneal the Pd and clean its surface before the growth of graphene. After annealing, methane gas (50 sccm) was introduced into the chamber for 15 minutes (20 seconds for the second batch). For the second batch another quartz tube with a smaller diameter(2.5cm) was introduced in the first one used. During the growth process, the vacuum of the whole system was kept at 2 Torr. Finally the furnace was let to naturally cool to room temperature under a pure argon flow by removing the oven off the quartz tube.

After CVD was completed the obtained graphene samples are characterized and analyzed by scanning electron microscopy (JEOL JSM 7800F) and Raman spectrometry (DXR 532nm FILTER).

Results Discussion. A first sample of graphene, grown at 950°C , was produced and the correct annealing can be observed in the obtained images via SEM at 10kV, see Figure 8. However, in the Raman spectroscopy analysis at 3mW, 532nm and a pinhole of 50 μm , there is no evidence of graphene growth, even though the presence of unknown carbon structures can be identified at approximately 1550cm^{-1} 9.

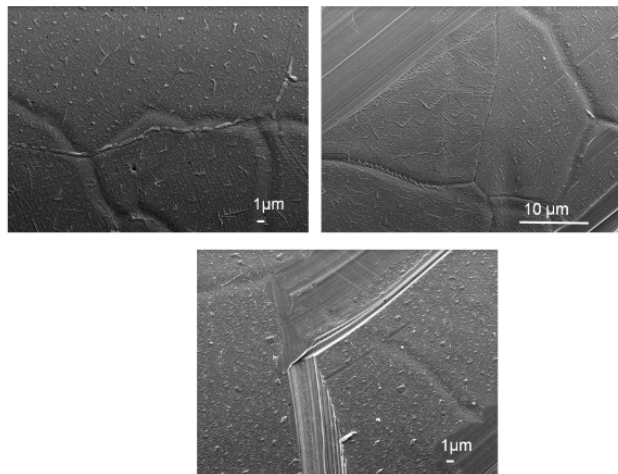


Fig. 8. SEM images For the first sample at $T = 950^\circ\text{C}$, no evidence of region concentrations are observed.

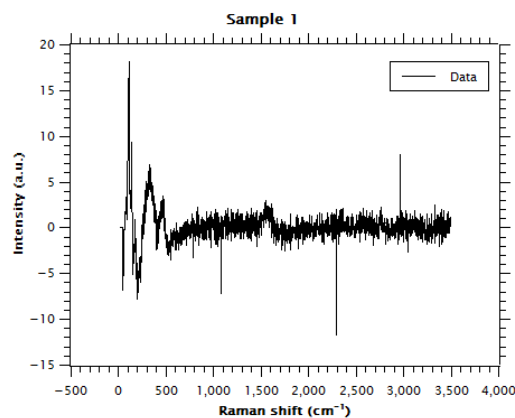


Fig. 9. Raman For the first sample at $T = 950^\circ\text{C}$, no evidence of graphene growth is observed, since the characteristic bands of graphene's Raman spectra are missing.

A second sample of graphene was produced repeating the process at the same growth temperature with the same fluxes. As for the previous sample, SEM technique was applied at representative regions of the coated Pd substrate, see Figure 10.

As we can see from Figure 10, the low-magnification images show the nucleation that took place on Pd, as it appears to occur close to the terrace edges, in a similar way as the behavior observed by Xiaohong An et al. [(1)].

A survey over large areas of the substrate revealed hexagonal-shaped flakes (see Figure 11).

For each sample, Raman spectra was obtained for different regions of interest. Each spectra was analyzed in order to

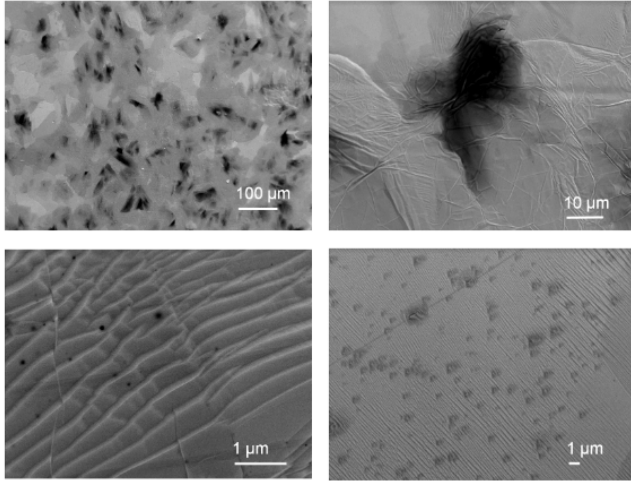


Fig. 10. SEM images For the second sample at $T = 950^\circ\text{C}$, different regions of the produced sample are shown at different approaches. Darker and patterned regions appear all over the surface of the sample. Images show the correct process of annealing on Pd.

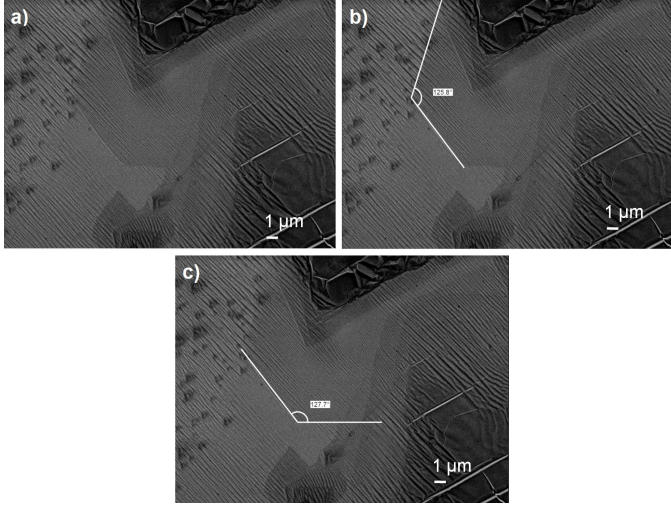


Fig. 11. SEM Images For the second sample at $T = 950^\circ\text{C}$, $t=30\text{min}$) Hexagonal-shaped flakes and flake edges observed in certain regions of the Pd surface seen to grow over Pd terraces and step edges. **b)** 125.8° Edge angle measured for the hexagonal region **c)** 127.7° Edge angle measured for the hexagonal region of the neighbor edge.

determine the position of the G band by a Lorentzian fitting. Moreover, using equation (1), the n values corresponding to the number of graphene layers present on the sample were calculated for each analyzed region by substituting the position of G band (ω_G). Thereafter, multi peak Lorentzian fits were applied at the 2D regions of the spectra in order to know if the region corresponded to a monolayer or multilayer graphene.

ω_G	δ
1587.32	0.03
ω_{2D}	δ
2560.37	19.00
2697.30	0.37
2718.28	0.41
2735.61	0.87

Table 1. Obtained peak positions for both, G and 2D bands

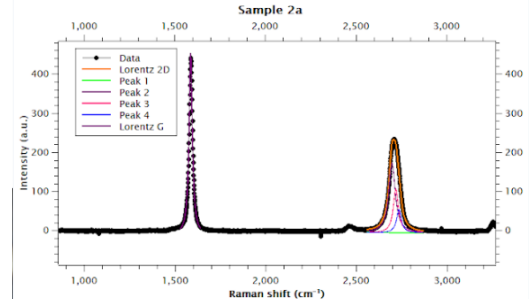


Fig. 12. Raman Second sample at $T = 950^\circ\text{C}$ growth temperature, region a. The G and 2D characteristic bands of graphene appear.

of Sample 2a

The n value calculated for this region using the G band position is $n_1 = 0.95$. As we can see from Raman spectrum in Figure 12, the graphene produced corresponds to the category of Bernal multilayer graphene (see Figure. 5b)). Also, we can see from the 4-peak Lorentzian fit that peak 1 also goes to zero, which means a 3-peak fit would have been enough to fit the 2D band.

I_G	I_{2D}	I_{2D}/I_G
441.92	233.89	0.52

Table 2. Obtained ratio I_{2D}/I_G for Sample 2a.

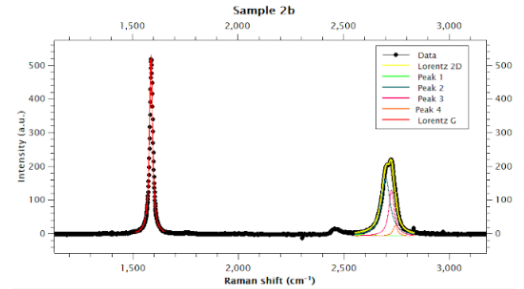


Fig. 13. Raman Second sample at $T = 950^\circ\text{C}$ growth temperature, region b. The G and 2D characteristic bands of graphene appear.

ω_G	δ
1587.40	0.02
ω_{2D}	δ
2581.79	9.57
2700.10	0.31
2727.12	0.24
2745.19	0.74

Table 3. Obtained peak positions for both, G and 2D bands of Sample 2b

The n value calculated for this region using the G band position is $n_1 = 0.94$. For this region, the Raman spectrum of Figure 13 corresponds to the category of mixed species of graphene (see Figure 5d)). As for region a, we can see from the 4-peak Lorentzian fit that peak 1 goes to zero, which means a 3-peak fit would have been enough to fit the 2D band.

I_G	I_{2D}	I_{2D}/I_G
517.71	21.48	0.04

Table 4. Obtained ratio I_{2D}/I_G for Sample 2b.

The ratio of intensities between 2D and G band confirms sample 2b corresponds to a multi layer graphene.

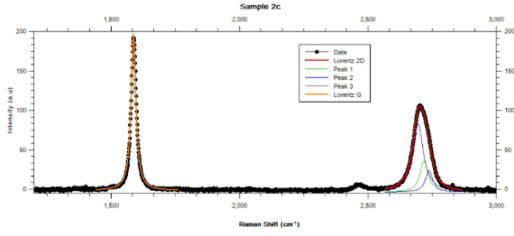


Fig. 14. Raman Second sample at $T = 950^\circ\text{C}$ growth temperature, region c. The G and 2D characteristic bands of graphene appear.

ω_G	δ
1588.28	0.03
ω_{2D}	δ
2719.12	0.83
2738.95	1.28
2696.09	0.61

Table 5. Obtained peak positions for both, G and 2D bands of Sample 2c.

The n value calculated for this region using the G band position is $n_1 = 0.76$. For this region, the Raman spectrum 14 corresponds to the category of Bernal multilayer graphene (see Figure 5b)). A 3-peak Lorentzian fit was enough to analyze 2D band in this region.

I_G	I_{2D}	I_{2D}/I_G
191.85	106.82	0.55

Table 6. Obtained ratio I_{2D}/I_G for Sample 2c.

The ratio of intensities between 2D and G band confirms sample 2c corresponds to a multi layer graphene.

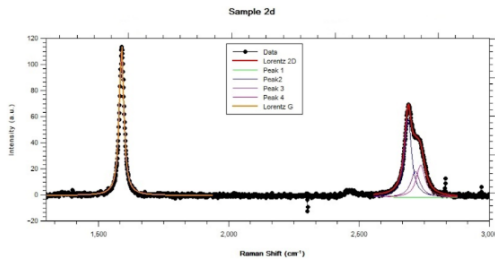


Fig. 15. Raman Second sample at $T = 950^\circ\text{C}$ growth temperature, region d. The G and 2D characteristic bands of graphene appear.

ω_G	δ
1589.89	0.03
ω_{2D}	δ
2568.92	35.95
22689.21	0.32
2717.18	3.12
2737.52	2.44

Table 5. Obtained peak positions for both, G and 2D bands of Sample 2d.

The n value calculated for this region using the G band position is $n_1 = 0.50$. For this region, the Raman spectrum 15 corresponds to the category of Bernal multilayer graphene (see Figure 5 b)). A 4-peak Lorentzian fit was used to analyze 2D band in this region. However a 3-peak would have been enough since peak 1 goes to zero.

I_G	I_{2D}	I_{2D}/I_G
113.41	69.00	0.50

Table 6. Obtained ratio I_{2D}/I_G for Sample 2d.

The ratio of intensities between 2D and G band confirms sample 2d corresponds to a multi layer graphene.

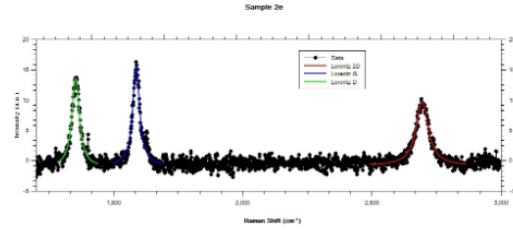


Fig. 16. Raman Second sample at $T = 950^\circ\text{C}$ growth temperature, region e. The G and 2D characteristic bands of graphene appear. Also the D band corresponding to defects appear.

ω_G	δ
1588.48	0.23
ω_{2D}	δ
2695.29	0.35
ω_D	δ
1354.27	1.03

Table 5. Obtained peak positions for G, D and 2D bands of Sample 2e.

The n value calculated for this region using the G band position is $n_1 = 0.73$. For this region, the Raman spectrum corresponds to the category of monolayer graphene (see Figure 5 a)). A 1-peak Lorentzian fit was used to analyze 2D band in this region, which corroborates there's a mix of multi and monolayer graphene present in the sample.

I_G	I_{2D}	I_{2D}/I_G
16.29	10.23	0.63

Table 6. Obtained ratio I_{2D}/I_G for Sample 2e.

The intensity of the D band is $I_D = 13.74$ and the intensity of the G peak are very similar. As the D peak denotes defects in the sample, the ratio value obtained between the intensities of G and 2D bands is reasonable. We have a mono layer graphene region with defects.

The Raman spectrum of the third sample produced at $T = 1000^\circ\text{C}$, an accelerated growth process, is shown below.

From Figure 17, there is no evidence of graphene growth, even though the presence of unknown carbon structures can be identified at approximately 1550cm^{-1} .

The ratio of intensities between 2D and G band confirms sample 2b corresponds to a multi layer graphene.

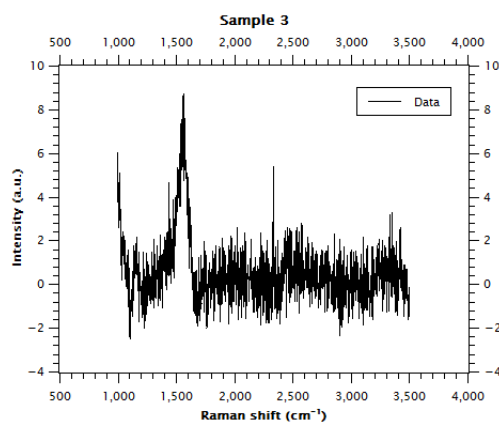


Fig. 17. Raman Second third at $T = 1000^{\circ}\text{C}$ growth temperature. The G and 2D characteristic bands of graphene appear. Also the D band corresponding to defects appear.

Conclusions. A successful method to perform CVD on Pd substrates was implemented. The temperatures and concentrations require to be optimized in order to improve the method. The method did not work the first time, this is attributed to the fact that the gas flow system had not been used for a while and its operation was not as optimal as for the second time. Very little monolayer graphene (mixed with multilayer) was found in sample 2, the majority was of the Bernal multilayer type. This can be explained by the long deposit time.

Although is reported (1) an accelerated growth at $T = 1000^{\circ}\text{C}$, we did not observe the same rate in sample 3, in which no graphene was formed.

An approach such as that of Xiaohong, An et al (1) to determine temperature and optimum methane flow in the device would be useful in future research.

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