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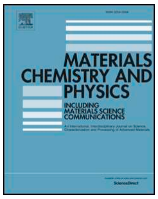

Role of inert gas in the Cvd-graphene synthesis over polycrystalline nickel foils

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HIGHLIGHTS

- Incorporation of inert gas in CVD synthesis improved graphene quality.
- A quality of 937 was obtained optimizing CVD-graphene synthesis parameters.
- Optimum conditions were obtained using a factorial design (Statgraphics).
- 947ºC and 13% of nitrogen were obtained as optimum reaction conditions.
- 93.4% of the sample was covered by monolayer graphene at optimum conditions.

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ABSTRACT

The role of the inert gas during CVD-graphene growth over polycrystalline nickel foils is reported. Nitrogen, hydrogen and methane were used as inert, reduction and carbonaceous gases, respectively. Graphene samples were characterized by using Optical Microscopy, Raman Spectroscopy and SEM equipped with EDX. Four different colors were distinguished over the optical microscope images. These colors were analyzed by Raman Spectroscopy and correlated to each type of graphene deposited over the foil (monolayer, bilayer, few-layers and multilayer). An Excel-VBA application was developed, which was used for computing the percentage of each type of graphene, resulting in an estimation of the graphene quality value. It was verified that the incorporation of the inert gas in the reaction step during CVD-graphene synthesis greatly influenced the quality of the obtained graphene. Different temperatures and percentages of nitrogen were studied in order to define the optimal reaction conditions. A factorial design study was performed to find the best experimental conditions leading to the highest quality graphene value, which resulted to be the following ones: 947 °C and 13 vol % of nitrogen in the feed stream, 1 min of reaction time, a relation between CH_4 and H_2 of 0.07 v/v, and a total flow of gases of 80 Nml/min.

1. Introduction

Graphene is a carbon allotrope that has attracted significant interest [1] due to its extraordinary properties which allows it to be used in several fields, including batteries, transistors and coatings [2]. This carbon nanomaterial can be defined as a single layer of sp^2-carbon atoms packed in a two-dimensional hexagonal lattice with a honeycomb shape [3]. Of all the graphene synthesis methods [4] Chemical Vapor Deposition (CVD) is the most widely used technique due to its ability to produce a continuous high-quality graphene film over different transition metals, which are used as catalysts [5]. During the CVD method, the hydrocarbon source is decomposed on the metal surface to form the graphene layers. Depending on the transition metals employed, two different graphene growth mechanisms can be distinguished: *surface* and *segregation ones* [6]. Metals with low carbon solubility favor the *surface growth mechanism*, in which graphene layers start to grow immediately after the decomposition of the hydrocarbon source. This process stops when the hydrocarbon source flow is set to zero. The *segregation growth mechanism* is observed for metals with high carbon solubility and starts when a threshold carbon atom concentration in the bulk metal is achieved prior to the nucleation process occurring during the cooling step. The excess diluted carbon atoms diffuse to the metal surface, leading to the segregation of carbon atoms that form graphene. Unlike the surface growth mechanism, the segregation

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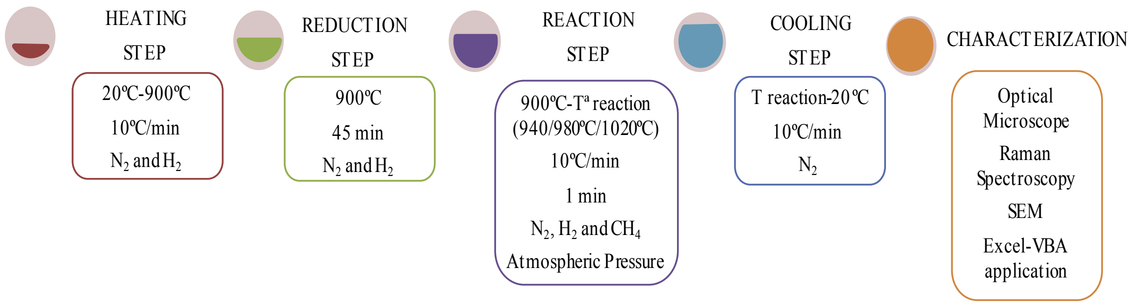

Fig. 1. CVD-graphene synthesis steps [24].

one does not stop until the concentration of carbon in the bulk metal has decreased to the equilibrium level, even though the hydrocarbon supply has been cut off [6,7]. Several authors have reported that the study of the operation parameters involved in the graphene synthesis can markedly influence the quality of the synthesized graphene [8]. In this sense, the reduction step [9], the influence of the reaction temperature [10–12], the reaction time [13–15] and the amount of the carbonaceous source [16] have been the most widely studied parameters with the aim of increasing the quality of synthesized CVD-graphene. The combined study of the reaction parameters and the carbon solubility of the metal is the most suitable way to improve the CVD graphene synthesis.

In previous studies, *Lavin-Lopez* et al. [13] demonstrated that the growth of the monolayer graphene was more favored for metals with high carbon solubility than for those with low carbon solubility due to, in the last case, carbon saturation of the metal at the optimal reaction conditions was not achieved and the remaining carbon atoms diffuse to form poorly layered graphene. Reaction step plays an important role in CVD-graphene synthesis. It has been demonstrated [9] that the presence of an active gas, such as hydrogen or oxygen, activated the catalytic metal allowing the removal of the ligand fragments from the surface through the metal reduction or oxidation, obtaining a clean surface. The reaction conditions (reaction temperature, CH_4/H_2 flow rate ratio, total flow of gases ($CH_4 + H_2$) during the reaction step and reaction time) may affect the graphene growth [17–19]. Regarding nickel, it was found that around 80% of the polycrystalline nickel metal sheet was covered by monolayer graphene. However, in the study reported by *Lavin-Lopez* et al. [13], the influence of the concentration of the inert gas during the graphene growth was not taken into account. It is well known that the incorporation of an inert gas in CVD-synthesis of other carbon allotropes, such as diamond, greatly influence the growth rates, improving the crystallinity and the quality of the carbon deposition [20]. Several authors studied the CVD-growth of graphene using an inert gas in the reaction step. For example, Park et al. [21] reporting the synthesis of few-layer graphene controlling the following synthesis conditions: reaction temperature = 960 °C, reaction time = 30s–7 min, CH_4:H_2:Ar = 250:4000:1000 sccm. In the case of Umair et al. [22] obtained bilayer graphene over nickel foils varying the synthesis conditions as reaction temperature = 1000 °C, reaction time = 50s–120 s, CH_4 = 6–23 sccm and argon was used as inert gas. However, an exhaustive study of the influence of the inert gas concentration was not considered and could significantly influence the quality of the synthesized graphene improving the growth of monolayer graphene.

In this work, considering the results obtained in the optimization of CVD-graphene synthesis over nickel [23], the influence of the concentration of the inert gas (nitrogen) in the CVD-graphene synthesis was investigated. The main aim was to decrease the number of layers and thus increase the quality of graphene formed by controlling the content of the inert gas in the feed.

2. Experimental

2.1. Graphene synthesis

Graphene synthesis was carried out using an atmospheric pressure CVD graphene system composed of a tubular quartz reactor placed in a furnace (LENTON, 1500 W and maximum temperature 1200 °C). Polycrystalline nickel foil (25 μm), supplied by Goodfellow, was used as the catalyst. Methane (99.5%), hydrogen (99.999%) and nitrogen (99.999%), purchased from Praxair, were used as the carbonaceous source, reduction gas and inert gas, respectively. During CVD-graphene synthesis the *heating step* was started by increasing the furnace temperature from room temperature (~20 °C) to 900 °C (reduction temperature), flowing the reduction and inert gases. At this temperature the *reduction step* began, and the furnace was maintained at this temperature for 45 min to complete the reduction. The temperature was then increased up to the reaction temperature (980 °C), at which point the carbonaceous source was switched on and was maintained for 1 min (reaction time) to complete the *reaction step*. The influence of the concentration of the inert gas in this feed during this step was studied.

During the "reaction step", the total flow rate ($N_2 + CH_4 + H_2$) is kept constant at Q_T = 80 Nml/min and that the proportion of N_2 in the gas phase is studied. Three different scenarios were considered: the absence of inert gas (1), flow the 15% (2) or 30% (3) of nitrogen during the reaction step. Once the reaction was completed, the flow of the carbonaceous source and the reduction gas was switched off and the system was cooled down to room temperature by flow the inert gas through the reactor.

Finally, graphene samples were exhaustively characterized using Optical Microscope, Raman Spectroscopy, SEM equipped by an EDX which allowed performing an elemental analysis of the sample. Optical Microscope images were analyzed using an Excel-VBA application programmed to know the percentage of each type of graphene and the quality value of the synthesized graphene (Fig. 1).

A factorial design was performed in order to know the optimal synthesis conditions leading to graphene of maximum quality. As independent variables, the reaction temperature and the percentage of the inert gas in the feed were considered. As the dependent variable, the graphene quality was established.

2.2. Characterization

A *SENTERRA Raman spectrometer* with a grating of 600 lines per mm and 532 nm laser wavelength, at a very low laser power level to prevent any heating effect, was used to characterize the CVD-graphene samples. Optical Microscopy images were collected using the *SENTERRA X50* microscope integrated into the Raman spectrometer and the system was equipped with the software OPUS. Four different colors can be distinguished in the graphene Optical Microscopy images. As reported in a previous paper [13], each color corresponds to one type of graphene. In this way, darker colors correspond to more layered graphene and lighter colors to less layered graphene. It was confirmed that dark orange corresponded to multilayer graphene, light orange colors to few-layer graphene, yellow to bilayer graphene, and, finally, white to monolayer graphene. A PhenomPro Scanning Electros Microscopy (SEM) system was used to study the morphology and, the Energy Dispersive X-Ray Spectroscopy (EDX) included in this SEM apparatus, was used to perform the elemental analysis of graphene samples.

2.3. Determination of the graphene quality

A homemade Excel Visual Basic Application (Excel-VBA) was programmed to obtain the percentage of each type of graphene and the quality of the graphene sample deposited on the nickel substrate. The software was used to analyze the different colors presented in the optical microscopy images and to calculate the percentage of each type of graphene present in the sample. According to these percentages, the software assigned a quality graphene value according to a logarithmic scale. Values of 1, 10, 100 and 1000 were assigned when 100% of the sample was covered by multilayer, bilayer, few-layer or monolayer graphene, respectively [11,12,23].

3. Results and discussion

In an effort to increase the CVD-graphene quality, the influence of the inert gas flow (concentration) during the reaction step was studied. Three different scenarios were considered: the absence of inert gas (1) and the presence of 15% (2) or 30% (3) of it in the feed composed in addition by CH_4 and H_2. In order to minimize the number of independent variables, the remaining reaction parameters were kept constant as in previous studies (1 min of reaction time, a total gas flow of 80 Nml/min and a volume ratio between carbonaceous source and reduction gas of 0.07 v/v). It is important to remark that the optimum conditions of graphene synthesis were obtained due to the combination of the entire factors which influence graphene synthesis in other words, it is important to find the equilibrium between all the parameters which influence CVD-graphene synthesis to obtain the optimum growth conditions.

The Optical Microscopy images of the samples prepared are shown in Fig. 2. In all cases, four different colors (dark orange, light orange, yellow and white) are observed. The Optical Microscopy images reveal that the presence of nitrogen in the reaction step at low (940 °C) and high temperatures (1020 °C) favored the formation of less layered graphene, as evidenced by the presence of lighter-colored areas. The opposite effect was observed at 980 °C, for which the presence of darker colors revealed the formation of more layered graphene when the inert gas was used. However, it is remarkable to note that the formation of high-quality graphene was not favored at higher temperatures (1020 °C), as was corroborated in previous studies [23].

The images obtained by the Optical Microscopy were analyzed by the Excel-VBA application, which provides the percentages of each type of graphene and, according to these ones, the graphene quality values (Table 1). It can be seen that in all samples there is a predominant occurrence of monolayer graphene over the metal foil respect to that of bilayer, few-layer and multilayer graphene. As revealed by the dark colors in the optical microscope image, just the sample synthesized at 1020 °C with a feed where nitrogen was absent presented the highest percentage of multilayer graphene. On the other hand, samples synthesized with 15% nitrogen in the feed at both 940 °C and 1020 °C and without nitrogen at 980 °C presented the highest percentage of monolayer graphene, thus expecting high graphene quality values.

According to the percentage of each graphene type, the Excel-VBA application assigned a graphene quality value which can vary between 0 and 1000. In this application, the higher the percentage of monolayer graphene, the higher the graphene quality value, having a value equal to 1000 when 100% of the sample was covered by monolayer graphene.

Fig. 3 shows the graphene quality value of the samples prepared at different reaction temperatures at different concentrations of the inert gas in the feed. The maximum observed at each reaction temperature corresponds to the samples presenting the highest percentages of monolayer graphene (15% nitrogen in the feed for the samples synthesized at 940 °C and 1020 °C and absence of nitrogen in the feed for the sample synthesized at 980 °C). Thus, the maximum quality graphene values obtained were 870, 803 and 587 at 940 °C (15% N_2), 980 °C (0% N_2) and 1020 °C (15% N_2), respectively.

It can be confirmed that CVD-graphene synthesis at high temperatures (1020 °C), with or without inert gas, does not favored the formation of high quality graphene. By comparing the results obtained at reaction temperatures of 940 °C and 980 °C, it can be corroborated that, at low temperatures (940 °C), the incorporation of low quantities of inert gas (15%) favored the formation of high quality graphene, while an increase of inert gas to 30% decreased the quality of the synthesized graphene, as occurred in CVD-process for other carbon allotropes [25]. The incorporation of low concentrations of inert gas favored the formation of well-ordered crystalline grains of graphene with high quality. However, an excess of inert gas greatly influences the morphology of the graphene obtaining poly-faceted graphene with low quality. At high concentration of inert gas, the formation of graphene clustered is favored, which are characterized for having more number of graphene layers [25]. Also, it has been demonstrated [20] that the incorporation of an inert gas in CVD-synthesis favored the amount of free carbon bonds which are not linked to the hydrogen atoms, provoking an increase of carbon concentration, which can favor the formation of more layered graphene over the nickel surface. The same tendency was observed for higher (1020 °C) and medium (980 °C) temperatures when inert gas is incorporated into the system. However, as was commented before, at high temperatures the quality of the obtained graphene is not too high compared with 940 °C, so the synthesis of graphene at high temperature incorporating inert gas was discarded. At medium temperatures (980 °C) the highest quality graphene was obtained in absence of nitrogen, because as was commented before, it is important to obtain the equilibrium between all parameters of CVD-graphene synthesis and, in this case, no nitrogen and medium temperatures are needed to synthesize high-quality graphene. However, again, the highest quality value was obtained for the lowest temperature (940 °C) which supposed the cheapest synthesis of CVD-graphene.

The morphologies of the samples analyzed by Scanning Electron Microscopy are shown in Fig. 4.

All SEM images showed the growth of graphene crystals on the polycrystalline nickel foils, which are delimited by the grain boundaries, which are characteristic of polycrystalline metals. It has been demonstrated that these grain boundaries favors the formation of more layered graphene on them [26] as revealed by the darker color observed in the SEM images. It can be observed that graphene crystals have growth heterogeneously over the metal sheet, presenting areas with more graphene that other due to the presence of impurities and grain boundaries. They presented two different areas, dark and light one. Darker and lighter areas are observed and correspond to more and less layered graphene, respectively. SEM results correspond to that obtained by Optical Microscopy and Excel-VBA analysis. For 940 °C and 1020 °C, it can be observer lighter areas, corresponding to less layered graphene, in samples synthesized with 15% of nitrogen, which show to the highest graphene quality value. Sample synthesized at 980 °C and without nitrogen presented the lighter SEM image, with less black regions.

In order to obtain the optimal operation variables in the CVD-graphene synthesis over polycrystalline nickel foil, a factorial design was performed by using the Statgraphics software. The estimated response area taking into account the reaction temperature and the concentration of nitrogen in the feed as the independent variables and the quality value as the dependent one is shown in Fig. 5). The optimal values of the reaction temperature and the concentration of nitrogen in the feed

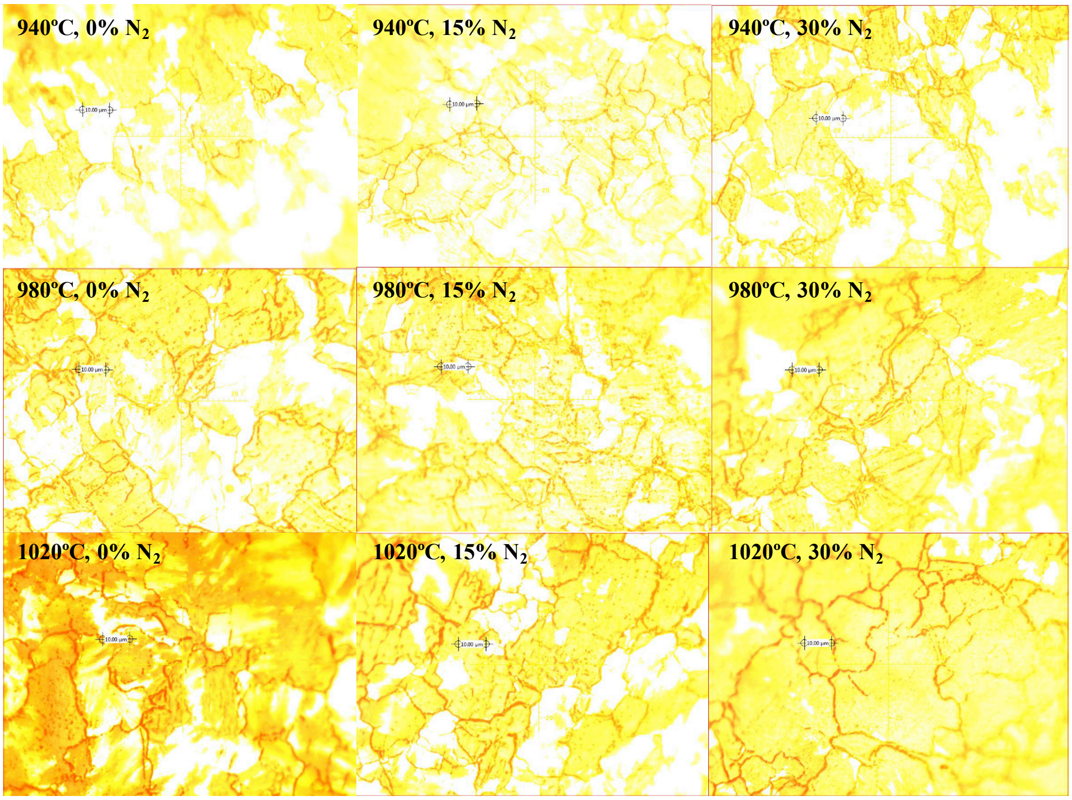

Fig. 2. Optical Microscopy images for samples obtained at different temperatures and percentages of nitrogen in the feed. *(Synthesis conditions:* 940 °C, 980 °C *and* 1020 °C*, 1 min, CH_4/H_2 = 0.07 v/v, Total flow of gases* = 80 Nml/min*, 0%, 15% and 30% of nitrogen).*

Table 1

Percentage of each type of graphene and graphene quality value (mean values) for samples obtained at different temperatures and percentages of nitrogen in the feed.*(Synthesis conditions:* 940 °C, 980 °C *and* 1020 °C*, 1 min, CH_4/H_2 = 0.07 v/v, Total flow of gases* = 80 Nml/min*, 0%, 15% and 30% of nitrogen).*

T^a	N_2	Monolayer Graphene	Bilayer Graphene	Few-Layer Graphene	Multilayer Graphene	Graphene Quality Value
940 ºC	0%	69.0%	14.9%	10.4%	5.7%	717
	15%	85.1%	9.2%	3.4%	2.3%	870
	30%	68.5%	13.4%	9.6%	8.4%	706
980 ºC	0%	78.3%	9.7%	5.8%	6.2%	803
	15%	69.3%	13.8%	9%	7.9%	718
	30%	55.6%	19%	15.3%	10.1%	589
1020 ºC	0%	42.6%	5.1%	5.6%	46.6%	438
	15%	56.5%	11.6%	15.1%	16.8%	587
	30%	34.4%	18.8%	24.9%	21.9%	378

are listed in Table 2.

The optimal synthesis parameters obtained by the factorial design are 947 °C and 13% nitrogen [23]. Six Optical Microscopy images, corresponding to different zones of the sample synthesized at the optimal conditions (947 °C, 1 min of reaction time, CH_4/H_2 = 0.07 v/v, Total gas flow = 80 Nml/min 13% nitrogen during the reaction step) are shown in Fig. 6. The corresponding quality value and the percentage of each type of graphene (monolayer, bilayer, few-layer and multilayer) obtained by the Excel-VBA application of each optical microscope image of Fig. 6 are listed in Table 3.

The Optical Microscopy images contain again four different colors (dark orange, light orange, yellow and white) with a considerable increase in the white areas, which is related to the presence of less layered graphene – as corroborated by the Excel-VBA results, which show that more than 90% of the sample was covered by monolayer graphene (note that the best sample, obtained at 940 °C and 15% nitrogen, was covered by 93.4% of monolayer graphene). Furthermore, the graphene quality value increased from 870 (value for the sample obtained at 940 °C) to 937 (value for the optimal sample obtained at 947 °C). That is the highest quality value obtained in this study.

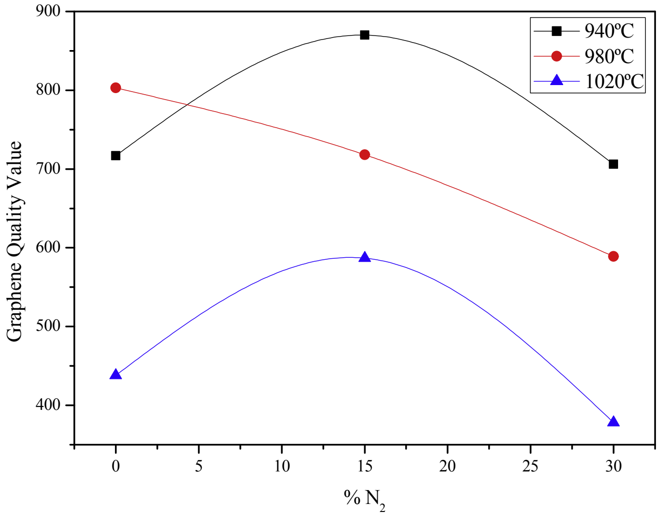

Fig. 3. Graphene quality values for samples obtained at different temperatures and different percentages of nitrogen in the feed.*(Synthesis conditions:* 940 °C 980 °C *and* 1020 °C*, 1 min, CH_4/H_2 = 0.07 v/v, Total flow of gases* = 80 Nml/min*, 0%, 15% and 30% of nitrogen).*

Fig. 7 represent SEM image of optimum sample and the percentage of Ni and C obtained from EDX software. Scanning Electron Microscopy corroborated that 13.8% of carbon covered the polycrystalline nickel foil and only dark areas were observed in the grain boundaries that delimit the nickel crystal. The rest of the sample was covered by small layered graphene, which is represented by lighter areas.

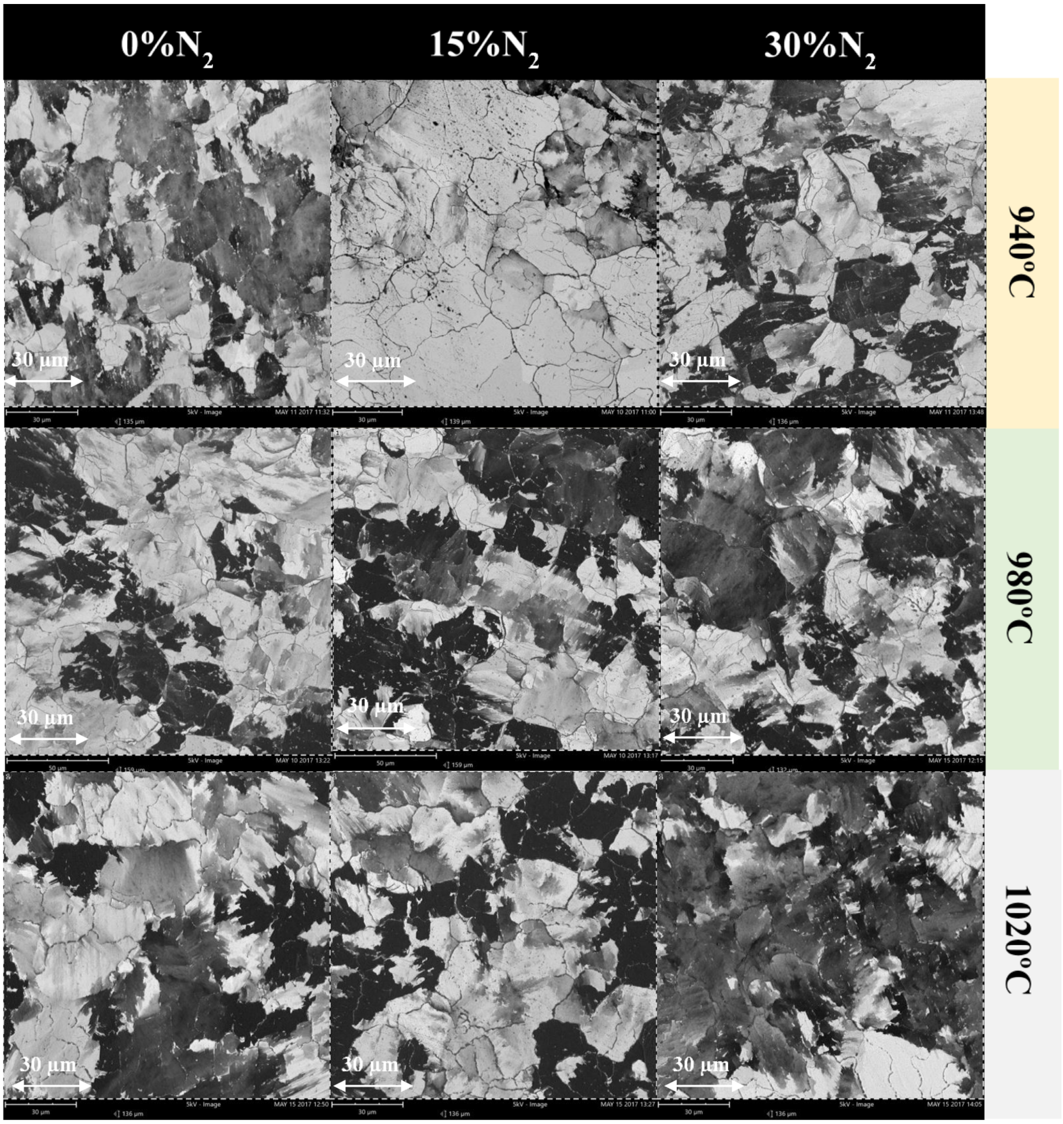

Fig. 4. SEM images of samples obtained at different temperatures and percentages of nitrogen.(Synthesis conditions: 940 °C, 980 °C and 1020 °C, 1 min, CH_4/H_2 = 0.07 v/v, Total flow of gases = 80 Nml/min, 0%, 15% and 30% of nitrogen).

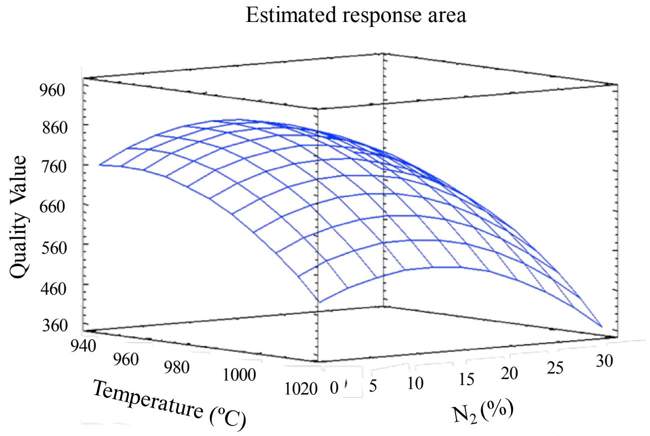

Fig. 5. Estimated response area obtained by factorial design (*Statgraphics*).

Table 2
Optimal reaction conditions obtained by factorial design (Statgraphics).(Other synthesis conditions: 1 min reaction time, a total gas flow of 80 Nml/min and a volume ratio between carbonaceous source and reduction gas of 0.07 v/v).

PARAMETER	OPTIMAL VALUES
TEMPERATURE (°C)	946.6
N_2 (%)	12.7

Raman spectroscopy was used to corroborate the presence of different types of graphene in the optimal sample synthesized at 947 °C and 13% N_2 (Fig. 8).

In general, a very low I_D/I_G ratio (related to the presence of defects in the sample) was observed for all of the graphene types deposited on the polycrystalline nickel foil.

As expected, I_{2D}/I_G ratios (related to the number of graphene layers) increased from the multilayer graphene to the monolayer one [27]. The

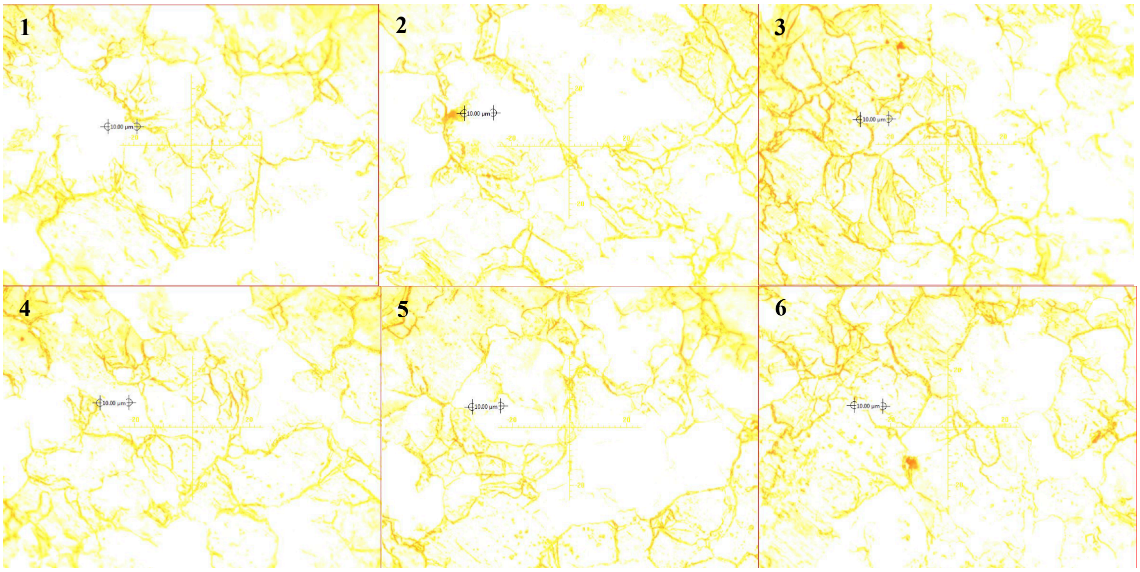

Fig. 6. Optical Microscopy images for the sample synthesized at the optimal conditions (947 °C and 13% of N_2). *(Synthesis conditions:* 947 °C*, 1 min reaction time, CH_4/H_2 = 0.07 v/v,* 80 Nml/min *13% nitrogen during the reaction step).*

Table 3
Percentage of each type of graphene and quality values for the sample synthesized at the optimal conditions at 947 °C and 13% N_2 by using the Excel-VBA software. *(Synthesis conditions:* 947 °C*, 1 min reaction time, CH_4/H_2 = 0.07 v/v,* 80 Nml/min *13% nitrogen during the reaction step).*

PICTURE	% MONOLAYER GRAPHENE	% BILAYER GRAPHENE	% FEW-LAYERS GRAPHENE	% MULTILAYER GRAPHENE	QUALITY VALUE
1	94.32	2.65	1.54	1.49	946
2	93.10	3.09	1.85	1.96	934
3	93.23	3.39	1.79	1.59	936
4	93.41	3.13	1.77	1.69	937
5	93.44	3.19	1.79	1.59	938
6	92.87	3.45	1.94	1.74	932
MEAN VALUE	**93.4**	**3.15**	**1.78**	**1.68**	**937**

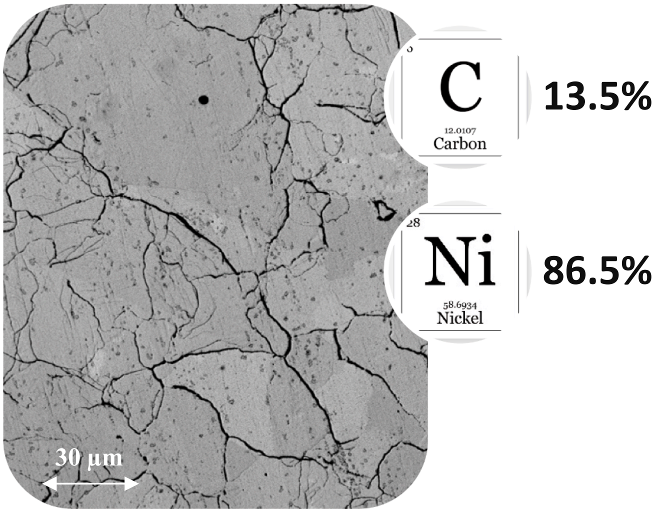

Fig. 7. SEM image and EDX result for the sample synthesized at 947 °C and 13% of N_2. (*Synthesis conditions:* 947 °C*, 1 min of reaction time, CH_4/H_2 = 0.07 v/v,* 80 Nml/min *13% nitrogen during the reaction step).*

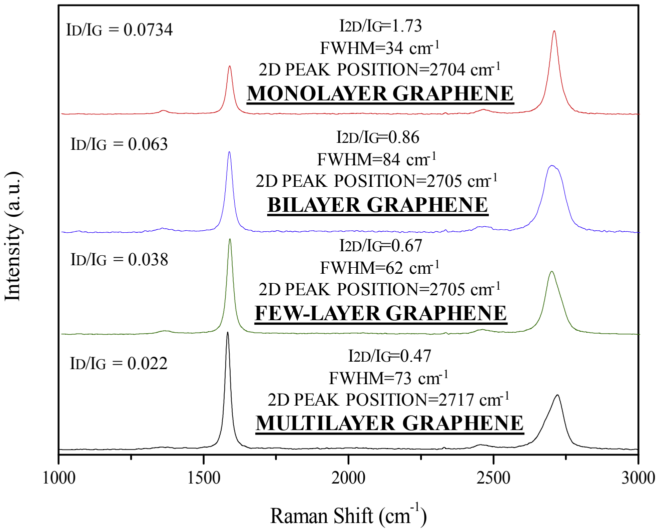

Fig. 8. Raman spectra of each type of graphene of the sample synthesized at 947 °C and 13% N_2. (Synthesis conditions: 947 °C, 1 min reaction time, CH_4/H_2 = 0.07 v/v, 80 Nml/min 13% nitrogen during the reaction step).

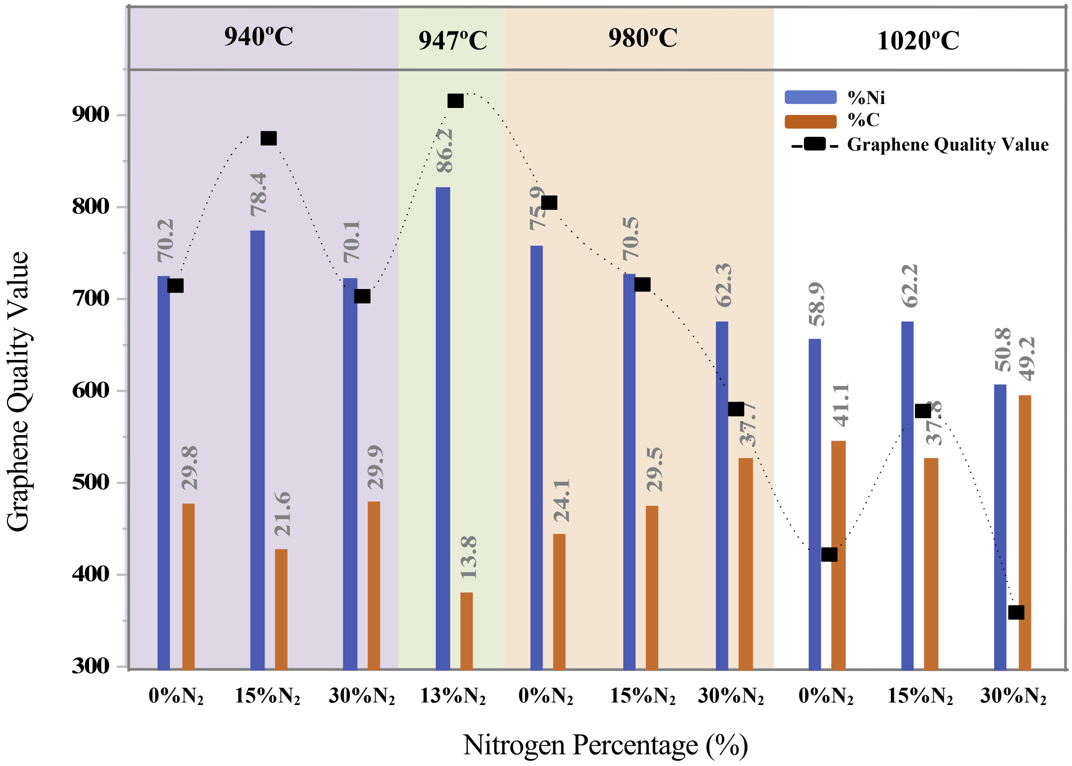

Fig. 9. Relation between the percentage of monolayer and bilayer graphene and the Graphene Quality Value.

opposite effect was observed for the FWHM parameters, which decreased from the multilayer to the monolayer graphene [27]. Finally, the 2D peak positions were located in the typical ranges for CVD-graphene [28]. All of the Raman parameters obtained are characteristic of the CVD-growth of graphene [29].

Finally, Fig. 9 shows the relation between the percentage of monolayer and bilayer graphene and the Graphene Quality Value for all the temperatures and percentage studied. As was observed, the higher the monolayer graphene, the higher the Graphene Quality Value, obtaining the highest values for the sample synthesized at 947 °C and 13% of nitrogen during reaction step.

4. Conclusions

The aim of this investigation was to study the influence of the concentration of inert gas in the reaction step during CVD-graphene growth over polycrystalline nickel foil. Methane and hydrogen were used as precursor gases while nitrogen was used as the inert gas. Different reaction temperatures and percentages of nitrogen were study with the aim of increasing the graphene quality value. A classical and a factorial design study were performed, demonstrating that the incorporation of an inert gas during the reaction step greatly influenced the graphene quality. Four different graphene types were obtained over the nickel sheet as evaluated by Raman Spectroscopy. At the optimal synthesis conditions (947 °C, 1 min of reaction time, $CH_4/H_2 = 0.07$ v/v, a total flow of gases of 80 Nml/min and 13% of nitrogen during reaction step), more than the 90% of the sample was covered by monolayer graphene, reaching a graphene quality value of 937.

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