Synthesis and characterization of CVD-grown graphene on copper: influence of the synthesis conditions

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Abstract
Graphene, an extraordinary two dimensional carbon material with a honeycomb structure, has been the focus of many researches due to its characteristics and its extraordinary mechanical, electronic and optical properties. It can be synthesized by a variety of methods such as discharge, epitaxial growth on SiC, unzipping carbon nanotubes, reduction of CO, chemical conversion, self assembly of surfactant and Chemical Vapor Deposition (CVD)[1]. Among them, CVD method has been shown to produce large-area and high quality graphene [2]. In CVD, Ni and Cu are normally used as substrates although other transition metals are also used, but less frequently[3].
Raman spectroscopy has been shown to be the most potential method for non-destructive and quick structural and electronic characterization of graphene and graphite materials[4].
In the present work, different studies have been performed with the goal of optimizing CVD synthesis of graphene on copper. In order to achieve that objective, the influence of different synthesis conditions such as temperature (900-1050 ºC), reaction time (5-45 min), CH_4/H_2 ratio (3%-45%) and total flow rate of gases involved in the reaction (40-140 ml/min) have been studied. Raman spectroscopy was used to characterize the obtained products.

Influence of the reaction time at different synthesis temperatures.

Table 1 shows the most important characterization parameters obtained with RAMAN spectroscopy for the best reaction temperature (1050ºC) and the influence of different temperatures at the same reaction time. In general, I_D/I_G ratio (related with the amount of defects in the sample) tended to increase and, I_{2D}/I_G ratio (related to the number of graphene layers) tended to decrease with the reaction time at 1050ºC and with the increase of temperature at the same reaction time. By its part, FWHM (Full Width at Half Maximum) parameter varied between 62 and 76 for 1050ºC and varied between 56 and 67 for the synthesis performed at different temperatures for 25 minutes reaction time. 2D position in the RAMAN spectra is considered an important parameter in graphene characterization because, in the case of graphene, this peak should be displaced to values around 2700 cm^{-1} if compared with graphite, which is around 2740 cm^{-1}[5]. In Figure 1 it could be observed the optimum sample of the study, obtained at 1050ºC and 10 minutes reaction time, observing that the defects in the sample are very low. 2D peak deconvulation of sample synthesized at 1050 ºC during 10 minutes originated four different peaks which is a common feature of bilayer graphene [6]. According to the obtained results, a synthesis temperature of 1050 ºC and a reaction time of 10 minutes were selected as the optimum values to carry out the following experiments.

Influence of the CH_4/H_2 ratio.

Figure 2 shows RAMAN spectrum and, Table 2 shows the most important RAMAN parameters obtained in the study carried out varying the CH_4/H_2 ratio in the range 3-45%. As observed, D peak increased and 2D peak even disappeared with the increase of CH_4/H_2 value. According to the obtained results, the I_D/I_G and I_{2D}/I_G ratio values were the lowest and the highest respectively for a CH_4/H_2 ratio value of 7%, indicating that the obtained graphene had the lowest amount of both, defects and layers. FWHM value was for this sample of 61 cm^{-1} and, the 2D peak appeared at 2706 $cm\text{-}^{1}$ which was in the range generally accepted for graphene. Again, the 2D peak deconvolution showed the presence of the 4 different peaks characteristics in bilayer graphene [6].

Influence of the total gas flow rate.

Figure 3 shows RAMAN spectrum and, Table 3 shows the most important RAMAN parameters obtained in the study carried out varying the total gas flow rate in the range 40-140 ml/min. As observed, D peak was practically non-existing for a total flow rate of 60 ml/min and, 2D peak position was displaced to better positions (2706 cm-1)

As observed, the lowest I_D/I_G ratio value was obtained using a total flow rate of 60 ml/min although the I_{2D}/I_G ratio was not the higher one. The values obtained for the parameters FWHM and 2D position were not determinant in this study due to they were maintained practically constant.

References:

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Figures:

Table 1: Influence of the reaction time at different synthesis temperatures: RAMAN spectroscopy parameter (only the best product at each temperatures are showed)

Relation conditions: 900-1050ºC; 5-45 min; CH_4/H_2 ratio=30%; total flow rate=130 ml/min

Tª reaction (ºC)	t reaction (min)	I_D/I_G	I_{2D}/I_G	FWHM (cm^{-1})	2D Position (cm^{-1})
1050	5	0,08	0,38	67	2709
1050	10	0,12	0,36	67	2709
1050	15	0,14	0,32	73	2709
1050	20	0,16	0,30	73	2709
1050	25	0,17	0,34	62	2704
1050	30	0,22	0,33	76	2714
1050	40	0,22	0,33	73	2709
1050	45	0,28	0,35	73	2693
900	25	0,29	0,32	56	2704
950	25	0,28	0,26	67	2708
1000	25	0,17	0,41	65	2704

Table 2: Influence of the CH_4/H_2 ratio: RAMAN spectroscopy parameters

Relation conditions: 1050ºC; 10 min; CH_4/H_2 ratio=3-45%; total flow rate=130 ml/min

CH_4/H_2 (%)	I_D/I_G	I_{2D}/I_G	FWHM (cm^{-1})	2D Position (cm^{-1})
3	0,18	0,36	62	2714
5	0,16	0,38	70	2711
7	0,15	0,46	61	2706
10	0,21	0,35	62	2714
20	0,17	0,37	67	2714
30	0,17	0,43	67	2709
40	0,22	0,29	67	2714
45	0,54	0,04	612	2730

Table 3: Influence of the total flow rate: RAMAN spectroscopy parameters

Relation conditions: 1050ºC: 10 min: CH_4/H_2 ratio=7%: total flow rate=40-140 ml/min

Q_{total} (ml/min)	I_D/I_G	I_{2D}/I_G	FWHM (cm^{-1})	2D Position (cm^{-1})
40	0,09	0,45	61	2713
60	0,09	0,44	61	2706
100	0,10	0,39	61	2706
130	0,15	0,46	61	2706
140	0,14	0,40	61	2711

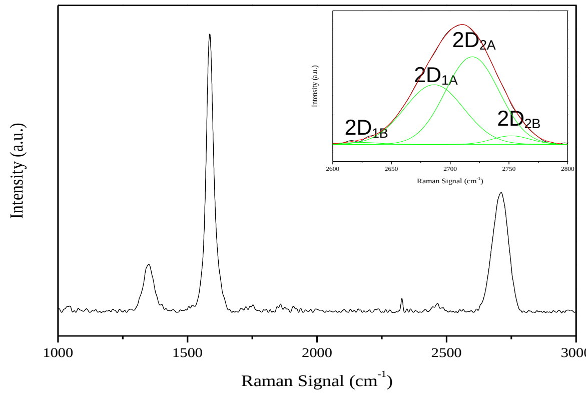

Figure 1: Raman spectrum for the optimum sample. Relation conditions: 900-1050ºC; 10 min; CH_4/H_2 ratio=30%; total flow rate=130 ml/min

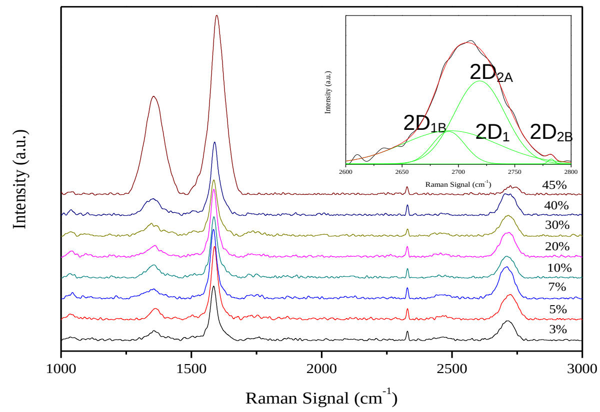

Figure 2: Raman spectrum for the CH_4/H_2 ratio. Relation conditions: 1050ºC; 10 min; CH_4/H_2 ratio=3-45%; total flow rate=130 ml/min

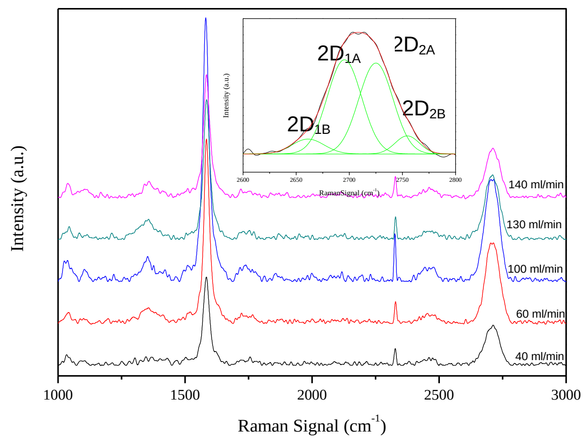

Figure 3: Raman spectrum for the total flow rate. Relation conditions: 1050ºC; 10 min; CH_4/H_2 ratio=7%; total flow rate=40-140 ml/min