Graphene synthesis on copper from ethylene by Catalytic Chemical Vapor Deposition

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Graphene is a promising material thanks to its physical properties and presents many potential applications for example as transparent electrodes in the field of OLED, solar cells or sensitive flat displays. However its production at low cost and large scale with controlled characteristics remains elusive. This is the reason why its synthesis has still to be improved in order to control its crystallinity and its number of layers over large areas.

Catalytic CVD (Chemical Vapor Deposition) appears to be the most promising commercially viable process, since it allows forming cm^2 scale areas of good quality graphene. However, most high quality CVD graphene is at present grown at temperatures close to 1,035°C on copper catalytic substrates from methane. This temperature is very close to the melting point of Cu (~1,085°C), and then creates intense Cu evaporation and then condensation fluxes upon cooling, which can affect the reproducibility of graphene synthesis and also decrease the samples quality and the reactor lifetime [1].

Some attempts have been made to decrease the synthesis temperature of graphene using alternative precursors like toluene, benzene, ethylene or acetylene [1-3]. Ethylene seems to be a good candidate to replace methane since it is cheap and easy to handle, and presents a higher reactivity than methane [1-2]. High quality graphene has already been obtained using ethylene on Cu foils at 850°C [1-2], but only at low total pressure (max. 100 Pa) and without a complete analysis of the key synthesis parameters influence.

In the present study, the influence of the main deposition conditions on the graphene crystalline quality and number of layers has been analyzed using ethylene diluted into hydrogen and argon on copper foils (25 μm thick, 99,999% Alfa Aesar) of 2x2 cm^2. The operating temperature was varied between 700 and 850°C, the hydrogen on ethylene inlet molar ratio between 1.5 and 14 and the total pressure between 3 and 700 Torr, as detailed in Table 1. The ethylene partial pressure was maintained at 30 mTorr for all experiments conducted at the total pressure of 3 Torr and was equal to 7 Torr at 700 Torr of total pressure.

Optical microscopy and Raman spectroscopy measurements (confocal Raman microscope Labram – Horiba Yvon Jobin) with a laser excitation wavelength of 532 nm were carried out to investigate the quality and extend of graphene sheets. For each sample, at least three Raman analyses were performed at various points of the surface. The number of graphene layers was estimated from the 2D (~2,670 cm^{-1})/G (~1,582 cm^{-1}) Raman peaks average ratios. The graphene crystalline quality was deduced from the average ratio between the disorder-induced D-peak (~1,350 cm^{-1}) and the G peak. Table 1 details the ratios obtained for the various conditions tested.

Table 1: 2D/G and D/G ratios measured for the various conditions tested

	700°C H_2/C_2H_4=1.5 3 Torr	**750°C H_2/C_2H_4=1.5 3 Torr**	**800°C H_2/C_2H_4=1.5 3 Torr**	**850°C H_2/C_2H_4=1.5 3 Torr**	**H_2/C_2H_4=7 750°C 3 Torr**	**H_2/C_2H_4=14 750°C 3 Torr**	**700 Torr 750°C H_2/C_2H_4=7**
2D/G ratio	0.23	0.47	0.84	1.1	1.4	1.1	0.19
D/G ratio	1.76	1.87	1.1	0.45	1.3	2.3	2.75

First, for all the conditions tested, graphene is continuous and uniform on the whole substrates surface.

Figure 1a presents the Raman spectra obtained at 3 Torr for the various temperatures studied. It appears that the best graphene quality is obtained at 850°C and corresponds to bi-layer graphene. So, these results confirm that the use of ethylene allows decreasing the synthesis temperature of 250°C in comparison with methane. These results are close to those obtained by other authors [1,2].

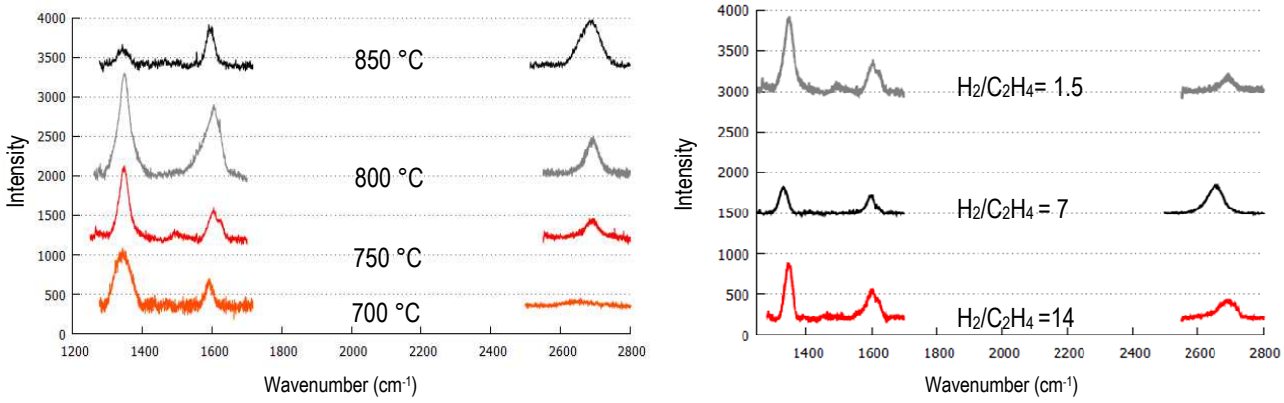
At 700°C, the 2D peak has very low intensity and is quite large, which could indicate the presence of amorphous carbon. Between 750 and 850°C, the 2D/G peak ratio increases with the temperature, meaning that the number of graphene layers decreases, whereas an opposite trend is observed for the D/G peak ratio. So, at 750 and 800°C, the amount of defects is much higher than at 850°C and graphene is multi-layers. These results could be explained by the fact that at low temperature, the etching activity of hydrogen and its catalytic role for ethylene dehydrogenation are reduced. Knowing that ethylene is highly reactive, this could lead to a higher number of graphene layers presenting more crystalline defects.

Then, the influence of the hydrogen on ethylene ratio has been studied at 750°C and 3 Torr of total pressure, as detailed in Figure 1b. The best results in terms of defects and of number of layers have been obtained for the intermediate H_2/C_2H_4 ratio of 7. When the hydrogen partial pressure is lower or is higher than that of this ratio, the amount of defects increases. This could be explained by the fact that if the H_2 concentration is too high, graphene can be damaged by the etching activity of H_2 [4]. At the opposite, if the H_2 concentration is too low, an effect similar to that observed when the temperature is too low could appear.

Lastly, the influence of the total pressure (or ethylene partial pressure) has been investigated at 750°C, as detailed in Table 1. The number of layers and the amount of crystalline defects notably increase with the total pressure. It is likely that at high ethylene pressure, the high ethylene reactivity generates a high concentration of carbon ad-atoms on the copper surface. The temperature tested here being not high enough to compensate this high carbon flux by the hydrogen etching activity, graphene is multi-layers with numerous defects.

In conclusion, ethylene allows decreasing of 250°C the temperature of graphene synthesis on copper in comparison with methane, but the operating conditions must be selected with great attention to form good quality graphene, due to the high reactivity of this precursor.

Figure 1: Raman spectra - a) influence of the temperature - b) influence of the H_2/C_2H_4 ratio



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References

[1] Wirtz C., Lee K., Hallam T., Duesberg G.S., Chem. Phys. Lett., **595-596** (2014) 192.
[2] Celebi K., Cole M.T., Teo K.B.K., Park H.G., Electrochem. Solid State Lett., **15(1)** (2012) K1.
[3] Gao L., Guest J.R., Guisinger N.P., Nano Lett., **10** (2010) 3512.
[4] Losurdo M., Giangregorio M.M., Capezzuto P., Bruno G., J. Phys. Chem., **13** (2011) 20836.