Graphene deposit in direct current abnormal glow discharge

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Abstract. With the advent of nanotechnology, graphene has gained relevance in the last two decades, due to its exceptional mechanical, electrical and thermal properties. This material being one of the thinnest existing, has at the same time great mechanical strength, flexibility, is transparent, in addition to very good conductor of electricity, much better than copper or any other known material. These properties are due to its structure constituted by a flat monoatomic sheet of carbon atoms arranged cyclically with the same structure of benzene. Several layers (>10) of superimposed graphene constitute the well-known graphite structure. To obtain it, among other methods, plasma enhanced chemical vapor deposition has been used, which uses electric discharges in the radiofrequency regime. In this work, the formation of graphene in the plasma of the abnormal glow discharge of direct current is reported. For this purpose, a mixture of 60% Ar, 5% C₂H₂ and 35% H₂ is used as gas atmosphere, at a pressure of 2.0 torr. Electrolytic copper sheets were used as substrate. Temperature of the process was 600 °C and the formation time was 5 s. Deposits characterization was made by infrared spectroscopy and Raman spectroscopy.

1. Introduction
The atomic-scale study of the different allotropic forms of carbon has made it possible to observe and investigate structures as important for the development of nanotechnology as graphene [1,2]. One of the methods used for the study of the molecular structure of graphene is infrared (IR) spectroscopy. This characterization method allows to identify the signals in wave numbers 3400.18 cm⁻¹ and 1563.80 cm⁻¹ [3], characteristics in the IR spectrum of graphene. However, IR spectroscopy presents the difficulty of identifying the defects presented by the graphene layers, while the Raman spectroscopy technique, due to its high sensitivity, makes it easier to identify the presence of defects in the crystal lattice. The D bands, corresponding to defects, in the wave numbers 1350 cm⁻¹, 1500 cm⁻¹ and 1620 cm⁻¹ have their origin related to a loss of structural symmetry due to the finite size of the graphene crystals. These bands are assigned to "defects" in the graphene structure that are directly related to the degree of structural disorder. On the other hand, the G band or graphite band appears at the wave number 1580 cm⁻¹. The 2D band appears around the 3250 cm⁻¹ wave number as a very weak narrow band. The 2D band has its origin directly related to the formation of graphene [2-6]. The crystalline structure of graphite can be considered as the formation of several layers of superimposed graphene [2-7]. Graphene is a flat monoatomic sheet of carbon atoms, linked together by strong covalent bonds based on the interaction of sp² atomic orbitals, allowing them to be densely packed in a benzene ring structure [2,8,9]. Graphene as a structural element of graphite, has such amazing properties that it has become a potential substitute for silicon [10]. On the other hand, graphene can be produced in large
quantities on copper substrates by chemical vapor deposition (CVD), at temperatures of the order of 1000 °C [11]. Another alternative method for the formation of graphene can be through the plasma of the abnormal luminescent discharge (AGD) in direct current, which is reported in this work. For this purpose, a gaseous mixture of argon, hydrogen and acetylene at low pressure is used. The difference in potential delivered to the stable AGD promotes the production of secondary electrons at the cathode of the discharge. These secondary electrons transfer their kinetic energy to the neutral atoms or molecules, creating an intense excitation and ionization of the mixture of these three gases, resulting in a great characteristic luminosity [12,13,14]. Thus, the active species generated in the plasma of the AGD react with each other and with the copper substrate forming the graphene deposits on its surface. After obtained, these deposits were analyzed by IR spectroscopy and Raman spectroscopy and the morphology of the surface of the deposits, was observed by scanning electron microscope (SEM).

2. Experimental setup
To perform the synthesis of graphene, the AGD was used in pulsating direct current (DC) in an atmosphere of 60% argon, 35% hydrogen and 5% acetylene at a pressure of 2 torr and a total flow of 100 mL/min. The deposits were made on an electrolytic copper substrate with a square geometry of 10 mm on each side placed in the cathode of the discharge. The anode, with a cylindrical geometry, housed the cathode and the copper substrate inside. The temperature of the process was adjusted to 600 °C, with the discharge voltage, and the deposition time was 5 s. These parameters were adjusted experimentally after testing with various percentages of acetylene, temperatures and deposition times. The deposited material was analyzed by IR spectroscopy and Raman spectroscopy.

3. Results and analysis
The infrared spectrum is used to determine the functional groups present in the molecular structure of the deposited carbon. The IR spectrum of the carbon deposit is shown in Figure 1. The signals correspond together to absorbance and transmittance signals since the Kubelka-Munk method was used, which facilitates transforming the IR spectra from diffuse reflection to linear absorbance [15], since the deposits present a rough surface. In Figure 1 the characteristic signals of the aromatic structure C-C and C= C are identified in wave numbers 1547 cm⁻¹ and 1711.96 cm⁻¹, respectively, which are characteristic of the graphene structure [3]. The signals are also presented at 2856.77 cm⁻¹ and 2941.59 cm⁻¹, corresponding to the symmetric and asymmetric elongation, respectively, of C-H in CH₃. The signal present at 2354.72 cm⁻¹, corresponds to the CO₂ of the environment.

Thus, the molecular structure of graphene with a high concentration of defects, associated with the intensity of the D (~1380 cm⁻¹) signal, was identified. This prevents the formation of the 2D signal of graphene associated with the two-dimensional structure. The amount of these defects could be reduced.

![Figure 1. Infrared spectrum of graphene on copper, obtained by the AGD method.](image)
by pretreating the surface of the substrate. In the micrographs of Figure 2 it can be seen that the graphene deposit covering the entire substrate is also transparent.

It is noteworthy that through the AGD it may be possible to obtain graphene deposits on copper substrates in a small time and with a lower energy cost, compared to the CVD process, given that the temperature used here was 600 °C, lower than the used in CVD that is of the order of the 1000 °C.

Figure 2. Raman spectroscopy in two different regions of the sample (signaled by de colored dot) of the graphene formed in the AGD in a time of 5 s.

4. Conclusions
Graphene deposits were formed on copper substrates by the AGD in a stable atmosphere with acetylene contents. Graphene layers with large concentrations of defects were obtained in atmospheres with 5% acetylene at 600 °C, for 5 s of treatment. These defects prevent the generation of the 2D signal characteristic of graphene. It may be possible to obtain graphene deposits on copper substrates in a small time and with a lower energy cost, compared to CVD process.

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