Carbon structures obtained from acetylene in a continuous current abnormal glow

B Alvarez¹, A Sarmiento-Santos¹, and Y Hernández²
¹ Grupo de Superficies Electroquímica y Corrosión, Universidad Pedagógica y Tecnológica de Colombia, Tunja, Colombia
² Grupos de Nanomateriales, Universidad de los Andes, Bogotá, Colombia

E-mail: brenda.alvarez@uptc.edu.co

Abstract. Carbon is the great constituent of all organic matter and a key element of the compounds that make up the enormous and very complex discipline of organic chemistry. It was already known in antiquity to be obtained as a by-product of the incomplete combustion of organic materials. At present the properties of this atom constitutes a potential source for research due to its promising application in nanotechnology and new materials because of its unique mechanical, electrical and optical properties. Carbon has several structural configurations that are known as allotropes, these allotropes have the same basic component, but its molecular conformation is different. Other elements of the fourth column of the periodic table such as silicon, germanium and tin have characteristics similar to those of carbon, however, this is unique in the variety of its allotropes. The different allotropes of carbon can be produced, among other methods, by the chemical vapor deposition method, however, the energy cost of this type of growth is relatively high. Another technique that would allow to obtain deposits of carbon in the laboratory is the plasma of the glow discharge of direct current in abnormal regime, which also offers a wide range of applications in plasmo-chemistry and in the thermochemical treatment of materials. The application of the abnormal glow discharge in the deposition of synthetic materials is a recent technique that represents a decrease in the time and in the energy consumption of the process, because the heating is carried out directly by the bombardment of the ions and neutral atoms on the surface of the cathode where the sample is usually located. The technique of abnormal glow discharge was used in this work with the objective of studying the possibility of formation of carbon deposits, in a copper substrate, from an atmosphere of argon, hydrogen and acetylene. Thus, in the temperature of 600 °C, deposits of graphite, graphene and an acetylene polymer compound were obtained. These were identified by infra-red spectrometry and Raman spectrometry.

1. Introduction
Carbon was already known in antiquity to be obtained as a byproduct of the incomplete combustion of organic materials. At present the unique properties of this atom constitute a potential source of new materials, becoming a great constituent of all organic matter and a key element of the compounds that form the enormous and very complex discipline of organic chemistry [1]. Carbon integrates several structural forms that are known as carbon allotropes. These allotropes have the same basic component, but their molecular structure is different [1,2]. Other elements of the fourth column of the periodic table such as silicon, germanium and tin also have the same characteristic, however, carbon is unique in the number and variety of its allotropes [3,4]. Graphite is an allotropic form of carbon that is constituted by
flat sheets of carbon atoms that constitute a system of condensed rings, this crystalline structure can be considered as the formation of several layers of superimposed grapheme [5-7]. Graphene is a flat monoatomic sheet of carbon atoms, linked together by strong covalent bonds based on the interaction of SP2 atomic orbitals, allowing to be densely packed in a benzene ring structure [4-7], other carbon compounds such as the acetylene polymer or poly-acetylene consists of a long chain of carbon atoms with alternating single and double bonds [8,9]. The carbon can be deposited on a substrate using the plasma of the abnormal glow discharge (AGD) through an atmosphere containing gaseous hydrocarbons. The secondary electrons generated in the cathode of the discharge transfer their kinetic energy to the neutral molecules of the gaseous hydrocarbon, creating an intense excitation and ionization of the atmosphere, resulting in a characteristic intense luminosity [10-13]. Most of the dissociated ions and molecules promote the reaction with the substrate, generating deposits whose structure depends on the concentration of hydrocarbon in the atmosphere of the discharge, the time of the process and the substrate condition [12]. This is verified by the present work in which a AGD is used in pulsating DC, in an atmosphere of argon, hydrogen and acetylene through which carbon characteristic structures such as graphite, a polymeric compound and graphene are deposited [14-20].

2. Experimental setup
Copper was selected as a substrate due to its catalytic properties and its low carbon solubility [21,22]. On this substrate, carbon deposits were made by the AGD in pulsating direct current. For this purpose, a confined anode geometry was used, consisting of a cylindrical anode inside which the cathode of the discharge, on which the substrate is placed, is housed. All these elements were manufactured in 1020 steel. As discharge atmosphere, a mixture of argon, hydrogen and acetylene was used, varying the acetylene ratio for a total flow of 100 ml/min at a pressure of 2 torr. The substrates were sheets of electrolytic copper with square geometry of 10 mm side and 0.5 mm thick. The temperature of the cathode and, consequently, that of the substrate was adjusted, with the discharge voltage, to 600 °C. The carbon deposits were made during a period of time from 5 to 900 s. To study the incidence of substrate conditions in the formation of the carbon deposit, two substrate conditions were used, one only cleaned with a cloth and isopropyl alcohol and another where, in addition to cleaning with cloth and isopropyl alcohol, it was subjected to a treatment of sputtering in AGD of 75% argon and 25% hydrogen at 2 torr of pressure for a time of 6 min., during which the temperature was increased at a rate of 100 °C/min until the 600 °C. The samples were analyzed by infrared spectroscopy (IR) and Raman spectroscopy.

3. Results and analysis
With the help of the analysis by IR spectroscopy three well differentiated structural characteristics were established, depending on the parameters as the carbon deposits were made, which are shown in Figure 1. The IR spectra show signals of absorbance and transmittance since the Kubelka-Munk method was used, which allows to pass the IR spectra from diffuse reflection to linear absorbance [23], since the carbon deposits present a rough surface.

For substrates cleaned with cloth and alcohol, subjected to the discharge in an atmosphere of 60% Argon, 20% hydrogen and 20% acetylene, with a total flow of 100 mL/min, at a pressure of 2 torr and a time of 900 s, the IR spectrum is shown in Figure 1(a). In this spectrum, the signals corresponding to the C-C, C=C, and C-H bonds attributed to the aromatics and carbon and hydrogen compounds are observed. This deposit corresponds to the structure of the graphite as it will be verified by the Raman spectroscopy analysis.

On substrates cleaned with cloth and alcohol, varying the hydrocarbon content, establishing an atmosphere of 60% Argon, 35% hydrogen and 5% acetylene with flow of 100 mL / min and pressure of 2 torr, and considerably decreasing the deposition time to 5 s in the AGD at 600 °C carbon deposits were obtained with the IR spectrum shown in Figure 1(b). This spectrum presents signals corresponding to the C-C, C=C and C-H bonds with great intensity at 1547 cm⁻¹, 1711.96 cm⁻¹, 2354.72 cm⁻¹ and
respectively. The structure of this deposit corresponds to the graphene structure as it will be verified by Raman spectroscopy analysis.

The spectrum of Figure 1(c) corresponds to carbon deposits made on copper substrates previously subjected to sputtering treatment as described in the experimental design. In this case, the discharge atmosphere of 60% Argon, 35% hydrogen and 5% acetylene is used, with a total flow of 100 mL / min at a pressure of 2 torr and a time of 120 s. The IR spectrum of this deposit contains the signals associated with the C-C, C=C, C-H, C=O, and O-H bonds. This spectrum corresponds to a polymer deposit as reported in the literature [24] for deposits obtained in the radio-frequency AGD. The presence of oxygen in these deposits may be due to the presence of free radicals in the carbon deposit, which could react with the oxygen in the environment when they are removed from the reactor chamber. Thus, by modifying the surface of the substrate, the structure of the carbon deposit can be modified. It is noteworthy that in the generality of reported plasma polymerization works, radio frequency power sources are used. However, in this work the possibility of carrying out the process of polymerization of gaseous hydrocarbons in AGD of direct current is shown. Another fact to highlight is that the polymer deposit has been made at a relatively high temperature when those obtained in radiofrequency discharges are performed at much lower temperatures [25-27].

In the different types of deposits made, the presence of the C≡C bond of the initial hydrocarbon is not observed, which must have been broken by the action of the energetic particles present in the AGD.

![Figure 1. IR spectra of carbon deposits on copper substrates at T = 600 °C, in atmospheres with a flow of 100 mL / min and a pressure of 2 torr: (a) 60% Ar+20% H₂+20% C₂H₂ and t = 900 s; (b) 60% Ar+35% H₂+5% C₂H₂ and t = 5 s; (c) 60% Ar+35% H₂+5% C₂H₂; and t= 120 s, on substrate subjected to sputtering.](image-url)
The verification of the chemical structure of the molecules formed in the deposits was made by Raman spectroscopy. The Raman spectrum of Figure 2(a) shows signals characteristic of the graphite configuration given by the G signal, showing defects in its structure that are accused by the D signal [7,18]. Figure 2(b) shows a lower defects-graphite structure intensities ratio (I_D/I_G), while in the spectrum of 2(b), corresponding to the molecular structure of graphene, there is a higher concentration of defects, related to the intensity of signal D, which prevents the formation of the 2D signal characteristic of flat graphene [7,22]. This high concentration of defects may be due to the irregular surface of the substrate, since this was not subjected to previous polishing treatment to reduce possible irregularities.

![Figure 2. Raman spectroscopy of the deposits formed in the AGD: (a) Graphite and (b) Graphene.](image)

4. Conclusions
Carbon deposits were formed on copper substrates by the AGD method in a stable atmosphere with acetylene contents at a temperature of 600 °C, obtaining different carbon structures, depending on the deposition parameters, which were identified by spectroscopy of the IR and Raman spectroscopy.

In atmospheres with 20% acetylene at a temperature of 600 °C and a time of 15 min. carbon was deposited with the graphite structure.

Graphene layers with large concentrations of defects were obtained in atmospheres with 5% acetylene during 5 s of treatment. These defects prevent the generation of the 2D signal of the flat graphene.

In atmospheres with 5% acetylene, during a deposition time of 120 s, polymer deposits were created on copper substrates previously subjected to sputtering. This polymer corresponds to an acetylene polymer reported in Radio Frequency discharges and in this case, was obtained in continuous current AGD resulting in a new acetylene polymer formation method. The signal of the OH functional group and the carbonyl group, obtained from the IR spectroscopy analysis, suggests the reaction of the deposit with the oxygen of the environment, after being removed from the reactor. Finally, in addition to the polymer having been obtained in direct current discharge, it is also deposited at an elevated temperature with respect to those commonly deposited in radiofrequency discharges.

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