N-graphene synthesis using N_2-Ar remote plasmas

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1. Introduction

Plasma environments constitute powerful tools in materials science by allowing the creation of innovative materials and the enhancement of long existing materials that would not otherwise be achievable[1]. In particular, N_2-Ar large-scale plasma sources driven by microwaves demonstrate advantageous properties for plasma processing techniques. In the present work graphene sheets were N-doped using a N_2-Ar large-scale remote plasma treatment. The samples were treated at different compositions of N_2-Ar gas mixture. The N-doped graphene sheets have been analysed applying scanning electron microscopy (SEM), Raman and Fourier transform infrared (FT-IR) spectroscopy. Optical emission spectroscopy was also performed to detect the emission of excited nitrogen atoms.

2. Experimental

A slot antenna excited, surface wave sustained N_2-Ar plasma source described in [2,3] has been used (see Figure 1). The discharge vessel consists in a tube with ~70 cm of length and closed at the top by a quartz window. Gases are injected in the chamber, considering a total flow of tens of sccm. The slot-antennas are cut in the broad wall of the feeding rectangular waveguide shown in the figure. Microwave power of 600 W at 2.45 GHz is fed to the chamber. The plasma is created by the energy carried by surface waves propagating radially and azimuthally along the interface between the plasma and a quartz dielectric plate. A pure TM_{140} surface mode, i.e. an evanescent wave along z, is excited. The graphene sheets with few atomic layers (1-5), synthesized previously applying microwave plasma-based method as described in [4,5], are placed in a remote plasma zone to be doped with nitrogen.

Two set of samples were produced to study the influence of N_2 percentage in N_2-Ar gas mixture (5-20 %) on the process of graphene doping.

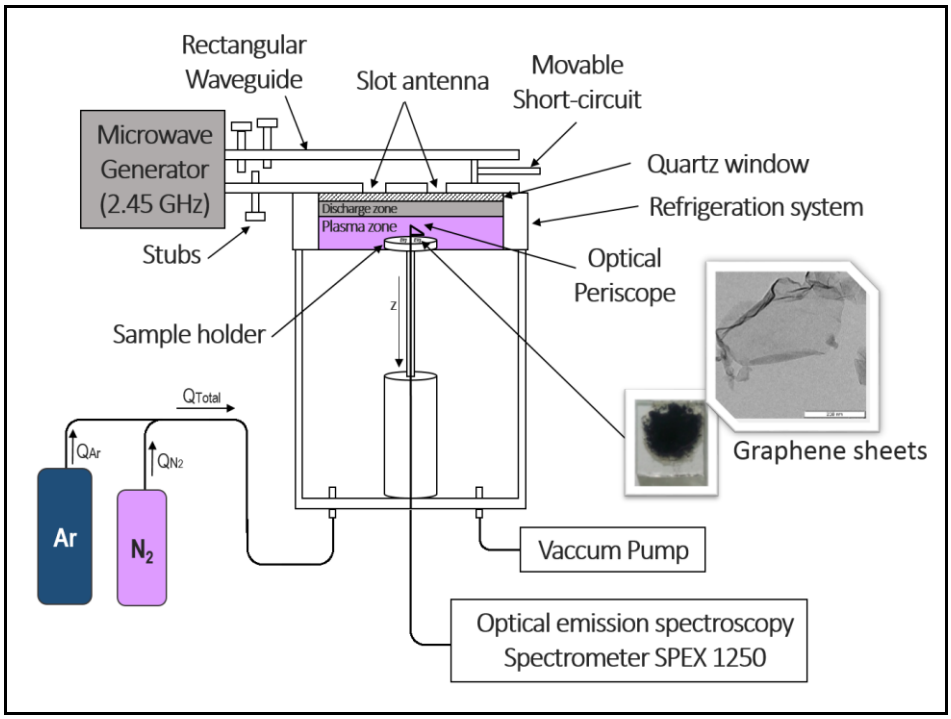

Figure 1 – Experimental setup.

3. Results and discussion

The plasma emission spectra in the 300-900 nm range detected at the axial distance where the substrate with the free-standing graphene sheets were placed are shown in Fig. 2. As observed the spectrum is dominated by Ar atomic lines. Intense nitrogen atomic lines at 821.6 nm and 822.3 nm belonging to the transition N (3p→3s) have been detected. The lines intensity decreases as the N_2 percentage in the N_2-Ar gas mixture increases from 5-20 %.

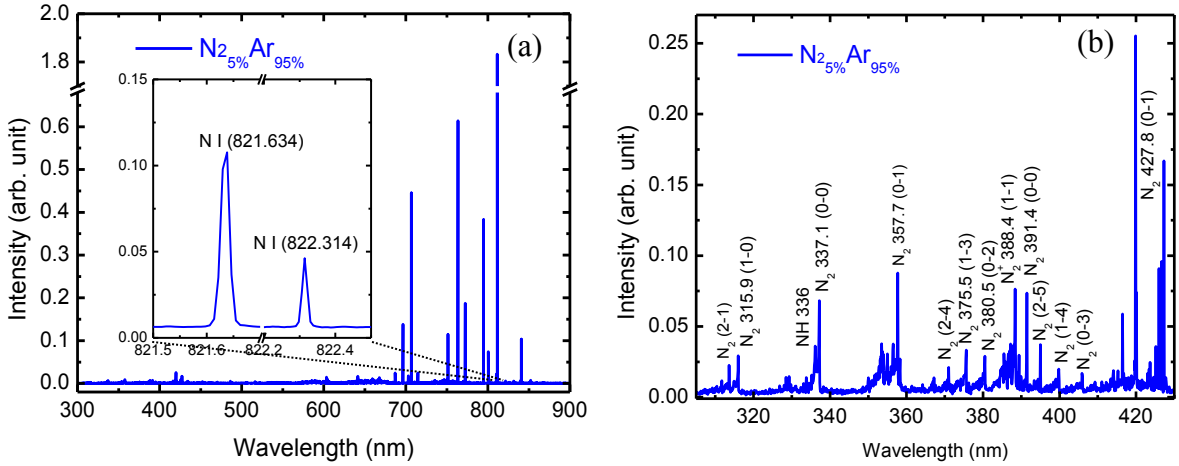

Figure 2 – (a) Optical emission spectra emitted by N_2-Ar plasma with 5% of N_2 in the gas mixture. Experimental conditions: P= 600 W, p= 1 mbar; (inset) Nitrogen atomic lines. (b) Emission spectra of the N_2 first negative system.

The rotational temperatures corresponding to the N_2 first negative system are commonly used as a measure of the gas temperature. To this end, the rovibronic bands in the 389-391 nm range, have been used. The rotational temperature has been determined using LIFBASE code [6]. The

gas temperature varies in the limits 900 K-1400 K when the percentage of N_2 in the N_2-Ar gas mixture increases from 5 to 20%. Therefore, energetic heavy particles could be present at the location of samples processing.

Fig. 3 shows the Raman spectra of ´pure` graphene sheets and the evolution of the Raman spectrum with the nitrogen percentage in N_2-Ar remote plasma. As seen there are three dominant peaks in the spectra. The three peaks are attributed to the G band at ~ 1585 cm^{-1}, 2D band at ~ 2662 cm^{-1}, and D band at ~1333 cm^{-1}. Taking into account the ratio between the 2D and G peak integral intensities (~2) and the full width at half maximum of the 2D-band (~45 cm^{-1}) of graphene sheets before plasma treatment the result is an indication of few-layer graphene sheets. As seen from Fig. 3(a) the D/G peaks intensity ratio increases with the N_2 percentage (from ~0.76 to ~1.19). Fig. 3(b) shows a SEM image of N_2-Ar plasma treated graphene sheets at 5% of N_2 in the gas mixture.

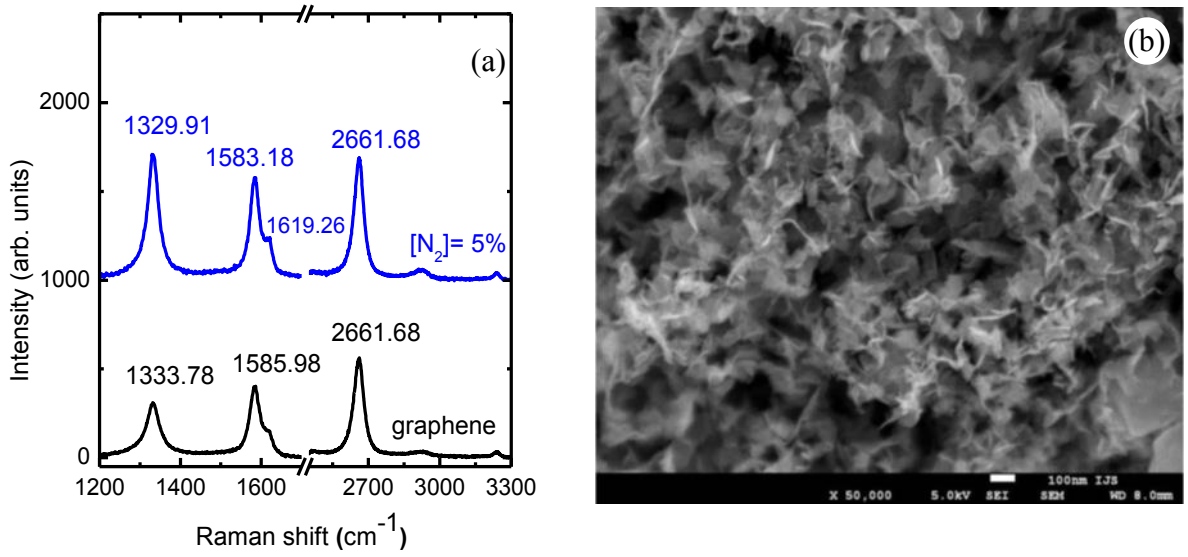

Figure 3 – (a) Raman spectra of graphene and N_2-Ar plasma treated graphene sheets with 5% of N_2 in the gas mixture. (b) SEM image of graphene sheets treated with a N_2-Ar plasma with 5% of N_2 in the gas mixture. (P = 600 W, p = 1mbar.

FT-IR spectra were used to investigate the bonding difference between graphene and N-graphene (see Fig. 4). The FT-IR spectrum of graphene shows some characteristic bands of surface oxidized groups at ~1733 cm^{-1} which most likely corresponds to C=O bond. The peak at ~2360 cm^{-1} corresponds to the C–O bonds and the features between 2841 and 3000 cm^{-1} are consistent with C–H_x stretching vibrations of chemisorbed hydrogen of various types present in all carbon films. In the case of the N-graphene sample a new peak at ~1244 cm^{-1}, corresponding to the C–N stretching vibrations appears.

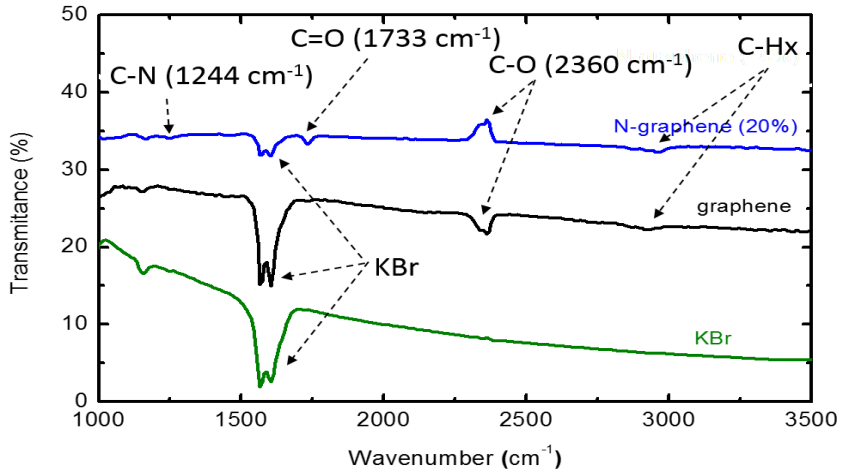

Figure 4 – FT-IR spectra of KBr, graphene and N_2-Ar plasma treated graphene sheets with 20 % of N_2 in the mixture of N_2-Ar (P = 600 W, p = 1mbar).

4. Conclusions

It was demonstrated the production of N-graphene by means of microwave N_2-Ar plasma based nitrogen doping of free standing graphene sheets. The plasma treatment of the graphene sheets was performed at different N_2 percentages in the N_2-Ar gas mixture while keeping constant the microwave power (P = 600 W), pressure (p = 1 mbar), exposure time and spatial position in the remote plasma zone. The results obtained demonstrate that the level of doping and type of functional groups attached to graphene scaffold can be controlled by percentage of N_2 in the N_2-Ar gas mixture. The work is in progress to make further optimization of the process by tailoring the plasma environment and fluxes of nitrogen atoms towards targeted nanostructures.

Acknowledgements. Work partially funded by Portuguese FCT - Fundação para a Ciência e a Tecnologia, under Project UID/FIS/50010/2013 and grant SFRH/BD/52413/2013 (PD-F APPLAuSE).

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