Influence of substrate temperature on the plasma and carbon material properties in a low pressure RF plasma jet deposition system

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The present study aims to investigate the effect of the substrate temperature on the characteristics of plasma grown carbon nanowalls and to correlate them with the plasma species present during the synthesis. The plasma process was analysed with respect to the excited species by Optical Emission Spectroscopy performed at the substrate level. The material morphology was studied by Scanning Electron Microscopy and the degree of ordering by Raman spectroscopy.

1. General

The most advanced nanostructured materials are the carbon ones and they can be classified by their dimensionality [1, 2, 3, 4].

Previously, we have developed a method [5] for carbon nanowalls (CNW) growth based on downstream deposition from an expanding radiofrequency argon plasma beam discharge injected with acetylene in the presence of hydrogen.

Carbon radicals obtained from the dissociation of the precursor (C_2H_2) are transported by expanding plasma to the heated substrate, where they sustain the growth process. The method used is an application of plasma enhanced chemical vapour deposition technique.

In order to understand the principal mechanisms that intervene in species generation and lead to carbon materials synthesis is necessary to investigate the plasma and to obtain information about neutral and charged particles flows at substrate vicinity, plasma species temperatures and densities, etc. To do this, we can use complementarily various diagnose methods as OES (optical emission spectroscopy), Langmuir probe and MS (mass spectrometry) measurements [4]. In this paper we focus on the study of the emissive species by optical emission spectroscopy technique.

Among species considered to be important in the synthesis and nano-structuring processes are C_2 dimers, which we suppose to enter in carbon-carbon bonds and form cores that evolve in bi-dimensional graphitic sheet [6], CH carbon radicals that contribute to deposition of amorphous carbon and H atoms which activate the free bonds at the substrate surface and remove amorphous phase of carbon [7].

Carbon radicals responsible for material growth are influenced by the experimental conditions (nature and precursor flow, gas flow ratios, power injected in plasma). These factors bring complexity and versatility to the system. Exploiting this versatility we managed to synthesise different types of carbon materials, in the same experimental set-up, by changing the experimental parameters [8, 9, 10] (see Figure 5).

At a first sight the substrate temperature does not influence the plasma species, which are created separately by the plasma source. This contribution is intended to check this assumption and, in addition to investigate the influence of the substrate temperature on the CNW properties.

2. Experimental results

2.1. Substrate temperature influence on the plasma characteristics

The optical spectroscopy measurements were made at the substrate level with Ocean Optics HR 4000 spectrograph with a spectral resolution of 0.5 nm, equipped with a CCD camera detector with a 3648 px linear resolution. The parameters used for spectra recording were: entrance slit width of 30μm, spectral range of 200 – 1100 nm, 600 lines/mm, fiber opening of 600 μm and acceptance angle of 31°. The measurements were taken just above the substrate level at a height of 1 mm.

A typical emission spectrum recorded in our experimental configuration, in typical deposition conditions [8] is presented in Figure 1.

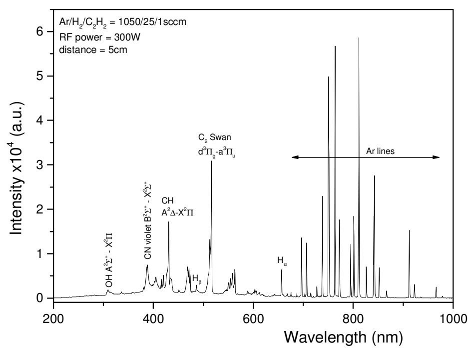

Figure 1: Typical emission spectrum recorded at substrate level

The most important signatures in an OES spectrum come from molecular radicals C_2, CH, OH, N_2 molecules and Ar and H_2 atoms. The presence of N_2, and emission of CN and OH is explained by the presence in the synthesis environment of water vapours or gas impurities from the admission gas or leakage from atmosphere. The presence of C_2 radicals allows us to determine the rotational temperature, which assumes that is an estimation of the gas temperature.

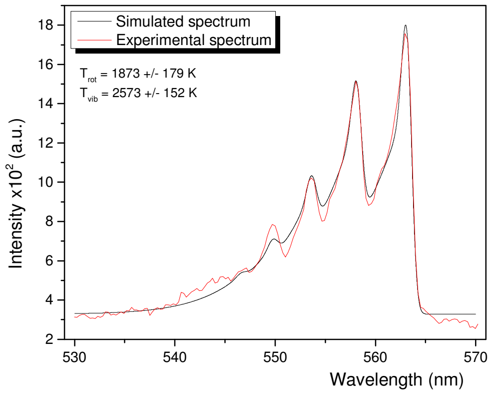

Figure 2: Temperature (rotational and vibrational) determination from C_2 bands (swan system, degraded to violet)

In Figure 2 are presented the simulated and experimental spectra of C_2 radicals in optimal conditions for carbon nanowalls deposition. The fitting procedure is discussed in reference [11].

Further, is presented the evolution of the emissive species intensities, considered to be important in the synthesis process as function of the substrate temperature.

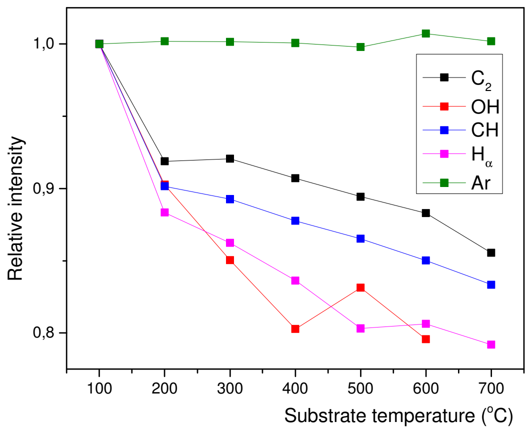

Figure 3: Dependence of the relative intensities of emissive species as function of substrate temperature

From the above graph it can be observed that the relative intensities of the emissive species have a slight descendent trend with increasing the substrate temperature.

Also, we followed the evolution of temperatures in plasma at variation of the substrate temperature. The behaviour of rotational and vibrational temperatures obtained from the simulation of molecular spectra belonging to C_2 sequence ($d^3\Pi g - a^3\Pi u$) $\Delta v = -1$ as function of substrate temperature is presented in Figure 4.

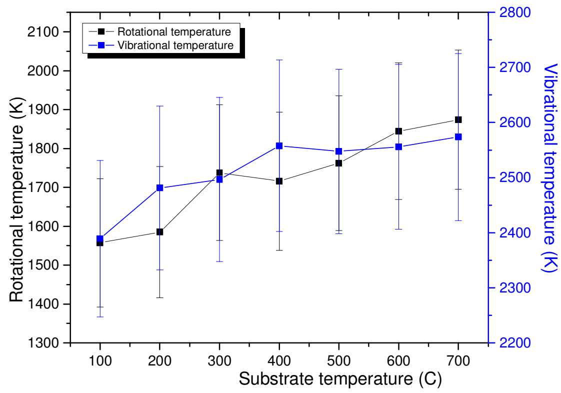

Figure 4: Rotational and vibrational temperatures as function of substrate temperature

As can be observed in the figure, both rotational and vibrational temperatures have an ascendant trend with the increase of the substrate temperature, thing that shows a heating of the gas near the substrate.

2.2. Substrate temperature influence on the material characteristics

For the study of the substrate temperature influence on the formation of carbonic nanostructures, the depositions were made by keeping constant all the other parameters that influence the deposited material properties, and varied only the substrate temperature in the domain 200°C (temperature obtained only from the heat provided by the plasma jet) to 700°C. The morphology of the obtained carbon nanostructures can be observed in Figure 5.

From the SEM images can be observed that the morphology of the deposited carbon nanomaterial on the substrate is different from one temperature to another. Thus, at a temperature of 200°C carbon nanofibers like structures can be observed. By increasing the temperature carbon nanowalls are being formed. Their density increases with the temperature, and their edges become more and more visible and sharper.

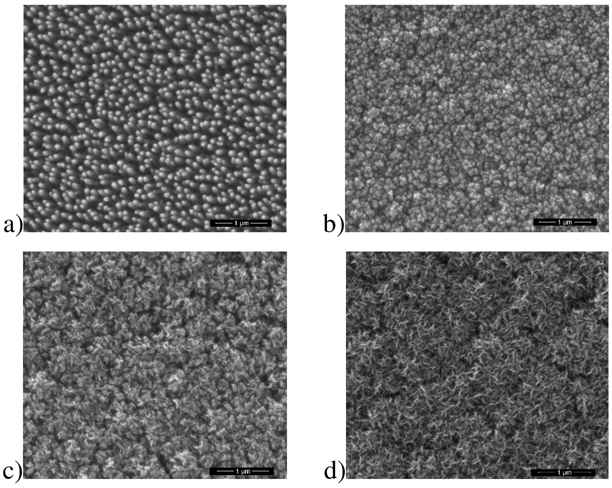

Figure 5. Top-view SEM images of the carbonic material deposited at different substrate temperatures: a) 200ºC; b) 400ºC; c) 500ºC; d) 700ºC. Length of scale bar is 1μm

The carbon nanostructures deposited at 200ºC and 700ºC were also studied by Raman spectroscopy, to see the ordered phase in the material, and the differences between the two materials. In these spectra we expected to see the D and G bands specific for carbonic materials, as well as the second order of these bands, on samples with a high content of graphenes. In Figure 6 are presented Raman spectra of these samples.

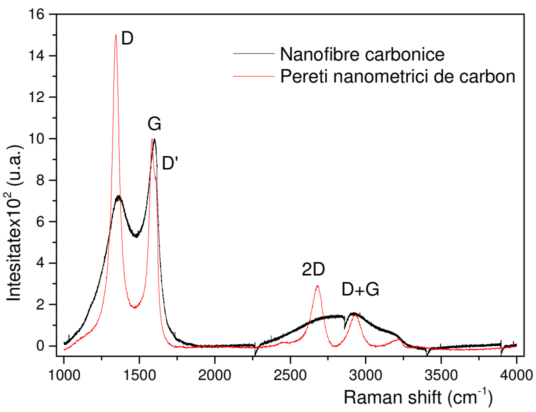

Figure 6: Raman spectra of carbonic structures like CNF and CNW obtained at variation of substrate temperature

In both spectra the D and G bands are distinct. The D band (1345 cm^{-1}) is assigned to disorder and defects in the structure of the material, being also associated with the presence of amorphous carbon fragments, and partially to the imperfections in the structure. The band is shifted toward smaller wavelengths for the carbon nanowalls to carbon nanofibers, corresponding to the structural transition from one material to the other. The G band appear close to 1590 cm^{-1} and is due to vibrations from graphitic structure, indicating a well graphitized carbonic structure. For carbon nanowalls one can observe the presence of D' (1608 cm^{-1}) and 2D bands well structured, indicating a high graphene content [12].

These very clear differences in the material properties are assigned mostly to the difference in the surface temperature. Temperature of surface influences adsorption, migration and reconstruction of chemical bonds from arriving species. On the other hand the present results shows that the temperatures of species in plasma are also influenced by the substrate temperature. Therefore a thermal activation of species in the boundary layer formed around substrate should also be considered. Still, the present experiments do not provide information to distinguish between the two influences. It would be interesting to have an investigation in which these effects are separated.

3. Conclusions

We showed that the deposited material is constituted of graphitized carbon fibres or walls with nanometre dimensions.

We demonstrated that we can obtain a transition from nanofibers to nanowalls through variation of substrate temperature.

The raising of the substrate temperature has an effect on the surrounding plasma.

Acknowledgments

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