Plasma deposition of carbon-based materials: diagnostic studies

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The present work focuses on the characterization of a RF expanding plasma working in Ar/(C_2H_2 or CH_4)/(H_2 or NH_3) admixture, typically used for nanostructured carbon synthesis. The methodology includes the Optical Emission Spectroscopy, Langmuir probe and Mass Spectrometry investigations. A discussion regarding the species assisting the carbon nanowalls synthesis will be provided in correlation to the material properties.

The potential of carbon atoms of getting hybridized in sp, sp^2, or sp^3 offer to carbon based structures an wide potential of organization in various forms. Besides the natural forms of carbon, e.g. graphite and diamond, the research community has developed numerous other materials from amorphous to diamond-like carbon and even nanostructured carbon, for applications as protective coatings [1] or lubricants [2], in micro and optoelectronics [3] or biomedicine [4]. In particular, the sp^2 hybridized carbon, specifically the fullerenes (0D), carbon nanotubes (CNT) (1D) and, more recently, carbon nanowalls (CNWs) and graphene (2D), provided for several decades already the hot topics in various fields. The material properties, especially electronic, magnetic and optical, strongly depend on the size, dimensionality, and shape of the structure. Therefore, the process diagnostic and control during synthesis of nanostructured carbon is a key issue for obtaining advanced materials with improved performances and new functionalities.

Among the most studied techniques for the nanostructured carbon synthesis are those using plasmas, in which the ions, electrons, neutrals, reactive species and photons are assisting the deposition. Successful nanostructured carbon synthesis was reported by using various plasma sources and experimental configurations, like arc discharge [5], plasma torches [6] or plasma enhanced chemical vapor deposition (PECVD) [7], using DC [8], RF [9] or microwave [10] excitation. Although in most of the studies the authors are reporting the use of similar gaseous mixture (based on a hydrocarbon – methane or acetylene, - or fluorocarbon, an etching gas – ammonia or hydrogen, and a carrier gas – mostly argon), the variety of approaches leads to processing plasmas characterized by different kinds and amounts of reactive species, electronic temperatures, densities, and so on. At the same time, especially in the CNWs case, there are only a few reports which are correlating the plasma characteristics to the material properties.

The present work focuses on the characterization of a capacitively coupled radiofrequency expanding RF plasma jet system used for the synthesis of carbon based materials. The plasma is generated in argon flow, in a small interelectrodic space, and expands in the processing chamber as a plasma jet through a nozzle performed in the grounded electrode. The precursors injected in the nozzle proximity are fragmented by the plasma beam and are transported by the flowing plasma toward the substrate. Depending on the plasma parameters and the substrate properties, various materials can be synthesized, several examples including:

a) amorphous hydrogenated carbon films on unheated silicon substrates when Ar/C_2H_2 plasma is used [11];
b) Ni/graphite core-shell nanostructures in Ar/C_2H_2 plasma if large Ni grains were covering the heated Si substrate (700 °C) [12];
c) CNTs, carbon nanofibers and CNWs, as well as their combined growth [13] on heated substrates (500–700 °C) of oxidized silicon, either bare [14] or coated with Ni catalyst [15], by using an Ar/(NH_3 or H_2)/C_2H_2 plasma jet at RF power values in the range 200–400W.

The material synthesis process is discussed in relation to the plasma species assisting the deposition, as revealed by Optical Emission Spectroscopy (OES), Langmuir probe measurements and Mass Spectrometry (MS) investigations. Thus, an attempt to provide an extended characterization of the neutral, excited and ionized species generated upon the interaction of the Ar plasma jet with the injected hydrocarbon (acetylene or methane) and etching gas (hydrogen or ammonia) will be done. The plasma properties are determined in relation to the experimental parameters which were proved to influence drastically the material's growth and structuring. Thus, the influence of the substrate positioning in respect to the nozzle both along and aside the plasma jet symmetry axis will be correlated to the nature and energy of the species reaching it. Also, the discussion will focus on the influence of the carrier gas flow and of the pressure on the generation and transport of the species involved in the carbon nanowalls synthesis.

Finally, comments will be given in respect to the behavior of species identified in other configurations as critical for CNWs synthesis, and their influence on the growth in the RF expanding plasma.

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