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Varieties of nanostructured carbon grown by expanding radiofrequency plasma beam

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Results regarding the growth of carbon nanostructures by using a low-pressure expanding radiofrequency plasma jet are reported. The growth was performed in an argon plasma injected with acetylene precursor, in the presence of ammonia or hydrogen, on a substrate covered with nickel or cobalt catalysts. Various forms of nanostructured carbon material were obtained, depending on the catalyst size, ammonia or hydrogen / acetylene ratio and substrate temperature. The results exemplified in the paper describe nickel nanoparticles coated in highly ordered graphite shells, granular carbon, two dimensional carbon nanoflakes, nanowires and nanorods.

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1. Introduction

Due to their unique properties [1], the carbon nanostructures have a wide range of possible applications in nanotechnology. Laser ablation, arc discharge, Chemical Vapor Deposition (CVD) and Plasma Assisted Chemical Vapor Deposition (PECVD) are the most spread methods for the growth of carbon nanostructures. PECVD is becoming one of the most promising techniques, due to advantages such as a lower temperature operation, and an easier control of the material morphology [2].

A versatile PECVD technique for growing carbon nanostructures is described in this contribution. The technique uses acetylene as carbon precursor, which is injected remotely in a radiofrequency generated argon plasma, in the presence of ammonia or hydrogen gases. Depending on the radiofrequency discharge power, the $Ar/NH_3/C_2H_2$ or $Ar/H_2/C_2H_2$ gases ratio and the distance between the substrate and the acetylene injection point, various carbon containing radicals, like CH, CH_2, CH_3, C_2, are formed. These radicals are transported at to the substrate, sustaining the growth of the carbonic material.

In the first part of the paper results concerning the formation of gaseous radicals during the decomposition of acetylene by plasma, as resulted from Optical Emission Spectroscopy (OES) are presented. The characterization of carbon containing films is presented in the last part of this article. During the investigations, we have identified the influence of ammonia or hydrogen as catalyst gases and the importance of temperature for the formation of carbon nanostructures.

2. Experimental

For the growth of carbon nanostructure, we used a variant of PECVD. More information about the setup and the deposition steps can be found in [3] and [4]. Prior to carbon deposition the metallic catalyst was deposited by sputtering on oxidized silicon substrates, with a small size DC magnetron mounted on the PECVD chamber, at controllable, low deposition rate of ~10 nm/min. The Ni catalyst was transformed in particles by heating the thin film and treatment in ammonia. The radiofrequency plasma jet was generated in flowing argon, at powers up to 500 W. The hydrocarbon gas (acetylene) was introduced in the expanding Ar plasma beam, in the presence of ammonia or hydrogen acting as catalytic gases. The pressure, during deposition, was in the range 10^{-1}-3 mbar. The mass flow rate of the main gas (Ar) ranged between 200÷1000 sccm, and of the other gases (C_2H_2, NH_3 or H_2) between 1-20 sccm. The hydrocarbon gas dissociated in non-equilibrium plasma jet and the carbonic radicals reached the Ni catalyst heated up to ~700^{o}C where the nanostructures grew.

The chemical composition of plasma beam during the deposition process was investigated by Optical Emission Spectroscopy using a setup consisting of a spectral chain containing a focusing lens, an optical fiber, an optical multi-channel analyzer (OMA) and an acquisition card. The morphology of the materials deposited in hydrogen or ammonia environments, at different distances (5÷10 cm) and temperatures (400÷750^{o}C), was investigated by electron microscopy methods, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) using a JEOL-200 CX electron microscope.

3. Results and discussion

3.1. Plasma investigation

By Optical Emission Spectroscopy (OES) technique one can obtain useful information regarding the emissive species in plasma, and the possible radicals leading to the growth of thin films.

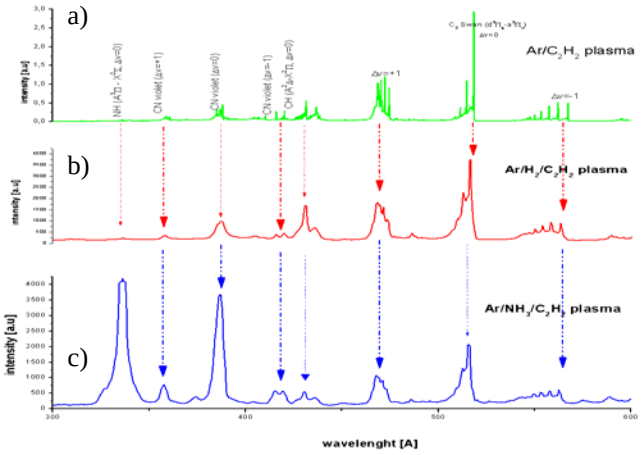

Fig. 1. Spectra emitted by expanding plasma in various gaseous mixtures a) Ar/C_2H_2, b) $Ar/C_2H_2/H_2$, c)$Ar/C_2H_2/NH_3$.

The optical spectra emitted by plasma used for deposition in the Ar/C_2H_2 *(a)* $Ar/C_2H_2/H_2$ *b)* and $Ar/C_2H_2/NH_3$ *c)* environments are presented in Fig. 1. They indicate a strong decomposition of acetylene, which is realized in the plasma by electronic collisions. Carbon-related species, the most important being the C_2, CH, CN, radicals, are showing their very presence by the corresponding spectral systems, as follows. The molecular bands of the carbonic radicals CH ($A^2\Delta$-$X^2\Pi$, Δv=0) and C_2 (Swan system, $d^3\Pi_g$-$a^3\Pi_u$, Δv= -1, 0, +1) are prominent. Also, the emission of the CN Violet system ($B^2\Sigma^+$-$X^2\Sigma^+$, Δv= -1, 0, +1) is present, whether we inject ammonia or not, proving the reaction between the carbon radicals and the residual nitrogen from the chamber. The presence of these radicals suggests that they can contribute to the material growth. The effect of the NH_3 addition in the plasma beam on the emission spectra, as presented in Figure 1b), is the appearance of the NH($A^3\Pi$ – $X^3\Sigma$) spectral system and the enhancement of the CN emission, while the emission of CH and C_2 radicals diminishes. The ammonia addition shifts the dominance of the carbon related bands (C_2, CH) into the dominance of the nitrogen related bands (NH, CN). The amount of hydrogen added in the injection reveals the increasing of C_2 and CH emissions (Fig. 1b).

3.2 Material investigation

In our experiments, the parameters with strong influence on the formation of carbon nanostructures were the substrate temperature, the metal catalyst size, the substrate to carbon source distance, the ammonia or hydrogen to acetylene ratio, the mass flow rates and the pressure.

3.2.1. The influence of substrate temperature

Without additionally heating of the substrate, only amorphous hydrogenated carbon-containing films were obtained on bare silicon substrates and without catalytic gases [4]. The key role of ~~the~~ temperature in nanostructuring the carbonic films can be observed from the morphologies of the film deposited at temperatures ranging between 400÷750°C. Comparing the carbonic films deposited in the same conditions - Ni catalyst, RF power, ratio of gas flows, pressure - but at different temperatures, we found that the morphologies vary from a compact film ((Fig. 2a) to a film with columnar morphology ((Fig. 2b).

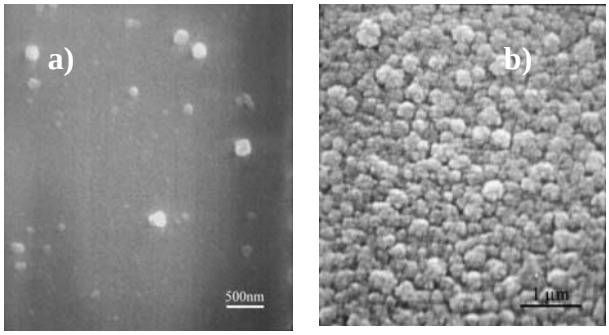

Fig. 2. SEM images of films deposited in similar conditions (catalyst sputtering: 3.5kV, $p=9x10^{-2}$ mbar, 20 sccm Ar, time=1 min; catalyst formation: treatment in argon-ammonia plasma, 5 min, 250 W, 1 mbar; carbon deposition: 250W, 1 mbar, Ar flow rate 500 sccm, C_2H_2 flow rate 1 sccm, 1 h) but at different temperatures: a) 400 °C and b) 750 °C.

The top view in the SEM investigation of the film deposited at high temperature (Fig. 2b) suggests a granular morphology. Nevertheless, the morphology is columnar, with conical columns of ~100-200 nm average diameters, quite well separated as can be seen in SEM images from Fig. 3. A top view and a tilted view of the scratched film are presented in Figs. 3 a and b, respectively. The images were obtained from a sample obtained in similar conditions as the one presented in Fig. 2, but the substrate temperature was 500 °C.

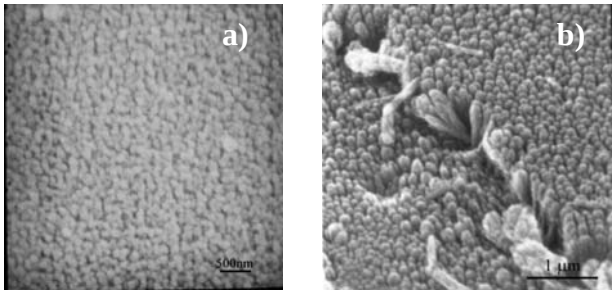

Fig. 3. SEM image of sample deposited basically in same conditions as samples from Fig. 2, but at 500 °C. a) top view and b) tilted view.

If the Ni catalyst islands are large, between 100÷200 nm, the high resolution TEM investigations have shown that the Ni is covered with graphitic layers having the graphene sheets aligned parallel to the metal surface [5].

3.2.2. The influence of the NH_3/C_2H_2 ratio

Different morphologies of the structured carbon films were obtained by changing the NH_3/C_2H_2 ratio. Such aspects are presented in Fig. 4a and 4b, where, a comparative view of deposits obtained at NH_3/C_2H_2: 4/1 (sccm) and 8/1 (sccm), respectively, is presented. In case of a higher amount of ammonia, the films are more porous, with a better separation of the nanostructures, denoting an individual mechanism of growth, controlled by the small size Ni seeds.

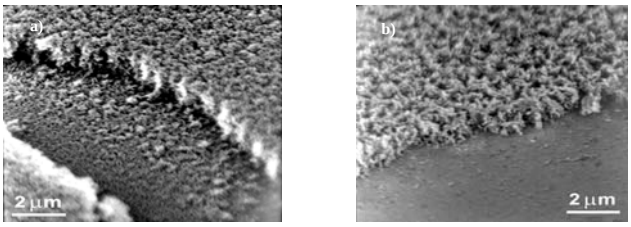

*Fig. 4. SEM images of films obtained on nickel catalyst in similar conditions (same substrate with Ni catalyst was divided in 4 parts) treated in ammonia plasma 5 min at 250 W at a pressure of 9*10-1 mbar; after being exposed to Ar plasma jet fed with acetylene in ammonia environment ½ h at (RF power 250W, pressure $9.5*10^{-1}$ mbar, Ar flow rate 500 sccm, NH_3/C_2H_2 ratio at a) 4:1 and b) 8:1.*

3.2.3 The influence of changing ammonia with hydrogen

In another set of experiments, we have used hydrogen injection in the main Ar discharge. Comparing the results of nanostructures deposition in the environments with ammonia (Fig. 5a) with those of hydrogen (Fig. 5b) deposition (similar conditions of RF power, temperature, pressure and gases ratio), one can see very different morphologies. The carbon structures are well separated and better defined in the case of hydrogen assisted deposition. The morphology of carbon nanostructures changed considerably, and we can trace the formation of flake-like nanostructures (Fig. 5b), having large surface area and sharp edges. More details (not shown here) were obtained from transmission electron microscopy studies. They revealed the formation of graphene sheet pieces, as a continuous network with sp^2 bonds. This proves again that hydrogen helps to etch away the disordered forms of carbon and plays an important role in the production of sp^2 bonded carbons [1].

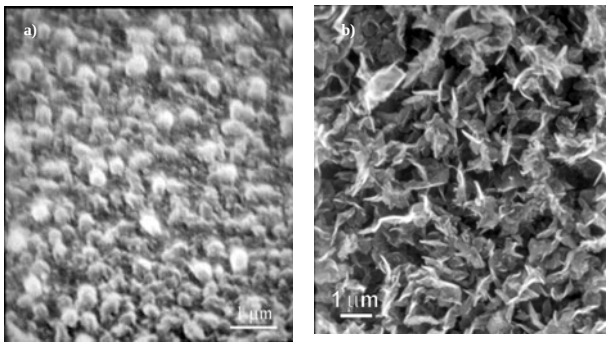

*Fig. 5. SEM images of films obtained in almost similar conditions (Catalyst depositions (3,5KV, at p=9*10-2mbar, in 20 sccm Ar, time=1 min), treated 5 min in: a) ammonia plasma and b) Hydrogen plasma at 250 W at pres 1 mbar; (Carbon deposition conditions:RF 250W, T~700°C, Ratio of gases a) $Ar/NH_3/C_2H_2$ 1000/18/1, p = 2.2 mbar and for b) $Ar/H_2/C_2H_2$ 1000/18/1, ,p=2.1 mbar).*

4. Conclusions

A simple and efficient method to produce carbon nanostructures, which may offers wide-area production possibilities at relatively low temperatures, was established. We have shown that different types of carbon nanostructures can be obtained by using the expanding *RF* PECVD for carbon deposition and the magnetron sputtering for metal catalyst deposition in the same reactor. Temperature has a key role in the nanostructured carbon growth process. At high temperatures (700° C) and in the presence of nickel as metal catalyst, the structure and of the morphology of deposited films are significantly modified, in comparison with the growth at low temperature on bare silicon substrate. The presence of gases (with role of catalytic gases - ammonia or hydrogen) has also a strong influence in the formation of carbon nanostructures. In the absence of NH_3 or H_2, amorphous hydrogenated films are deposited. At high ratio of NH_3 (or H_2)/ C_2H_2, the structures in the deposited films exhibit a separate individual growth. We observed that hydrogen is more efficient than ammonia in nanostructuring of the deposits. In this case, two dimensional graphene-like pellets are present.

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