DEPENDENCE OF CARBON NANOWALLS QUALITY UPON PLASMA AND SUBSTRATE CONDITIONS

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Introduction

The carbon nanostructures, including carbon nanowalls-CNWs, exhibit special physical and chemical properties due to their unique morphology, structure, size, shape, dimensionality, asymmetry and composition. Particularly, their features resulting from the shape (2D dimensionality, sharp edges boundary, high surface to volume ratio) and structure (containing superimposed packed graphene multi-layers) recommend them as good materials in various applications [1]: field emission at low voltages [2], superhydrophobic/ superhydrophilic surfaces [3], cells repellent surfaces [4], gas [5] and bio-sensors [6], supports for metal nanoparticles, membranes for fuel cells and electrodes for battery and supercapacitors [7].

We have previously developed and reported [8, 9] a method for synthesis of carbon nanowalls (CNW) using a PECVD process based on downstream growth from a low-pressure radiofrequency argon plasma jet injected with acetylene in presence of hydrogen. The parameters which control the density, the size, the shape and the structure of nanowalls were explored in relation with the obtaining of high quality CNW material. Thus, the influence of plasma conditions (RF power, $Ar/H_2/C_2H_2$ gas flow ratios, pressure) on the structure, morphology, and chemical composition of the CNW layers were investigated.

One of the most important properties of CNWs materials is their large surface area, reported to be from hundreds to up one thousand m^2/g [10], depending on the deposition methods and the substrate (flat-2D or 3D architectures).

In this respect we searched for methods to control the length and height of carbon nanowalls, and we report in this contribution some of the results. Also, we have investigated the possibility to combine the growth with various substrates, which is of high relevance for applications.

Experimental

The procedure of CNWs synthesis in the radiofrequency plasma jet was described extensively elsewhere [8, 9]. In the previous studies we defined the so named "standard" values of the deposition parameters leading to good quality CNWs (large length and height, small thickness, well individualized and isolated nanowalls). They were established to be: gas flow ratios $Ar/H_2/C_2H_2$: 1050/25/1 sccm, pressure p~1,2 mbar, T=700^{o}C, RF power 300W, distance between the substrate and the acetylene injection ring 5 cm, and 30 minutes deposition time. In the present experiments the growth conditions were varied starting with these optimal values established before by changing the Ar main flow in a range of 1400-2000 sccm, while the ratio H_2/C_2H_2 was kept constant at 25/1 (sccm). This set of samples was done to extend the previous study performed at of 300-1400 sccm range of Ar flow [9]. In addition, the synthesis was done this time onto substrates of different nature (gold plackets, polished steel and Cu tablets, graphite, ceramics, etc.), thus complementing the previous study which referred to Ti, stainless steel, quartz, MgO, carbon paper, Si and oxidized silicon SiO_2/Si. All the samples studied here (at the above mentioned values of gas flow ratios) were obtained without any catalyst.

In all cases the CNWs growth was performed after a preliminary plasma pre-treatment in Ar/H2 (1050/25 sccm), 300 W, for 5-10 minutes. This pretreatment had the role of substrates cleaning and activation.

The samples have been investigated by SEM, TEM, SAED, XPS, Raman and FTIR.

For an easy identification of the samples they were labeled as bellow in table 1.

Table 1. Experimental conditions used CNWs synthesis

sample code	pressure	Ar flow	substrate
CNWs standard	1.2	1050	Si, Cu, Au, ceramics
CNW_1400	1.4	1400	Si/SiO_2
CNW_1400_steel	1.4	1400	polished steel
CNW_1600	1.5	1600	Si/SiO_2
CNW_1600_steel	1.5	1600	polished steel
CNW_1700	1.6	1700	Si/SiO_2

Results and Discussion

Figure 1 presents the morphologies of CNWs deposited on SiO_2/Si substrate, at different flow ratio, without metal catalyst. The change of morphology is vey clear: the size is higher and individualization of each CNW is better when the argon flow rate increases. Nevertheless, at about 2000 sccm Ar flow the obtained CNWs are no longer homogeneous as others. The height of CNWs, as observed in cross section SEM investigations (not shown here), revealed that CNW 1050 have about 3.7 μm in height, CNW 1400 about 4.4 μm and CNW 1600 around 7.7 μm, respectively. This trend of increase of dimensions (i.e length or height) was observed also in the case of using other substrates as mentioned before in the experimental section.

The structure of standard CNWs (1050) layers was investigated by TEM and SAED. The images are shown in Figure 2. In figure 2 a) we can observe the veil morphology of

CNWs. The SAED image proves the presence of graphitic structures. In the figure 2b) is presented a very thin foil of CNW. It shows a grey region with several black dots. This image reveals the intimate structure of CNWs consisting in a superposition of graphitic nano-domains with different orientations, some of them being oriented in respect with the electron beam direction. Such graphitic domains, indicated by SAED, are consisting of small grain sizes about 5 nm .

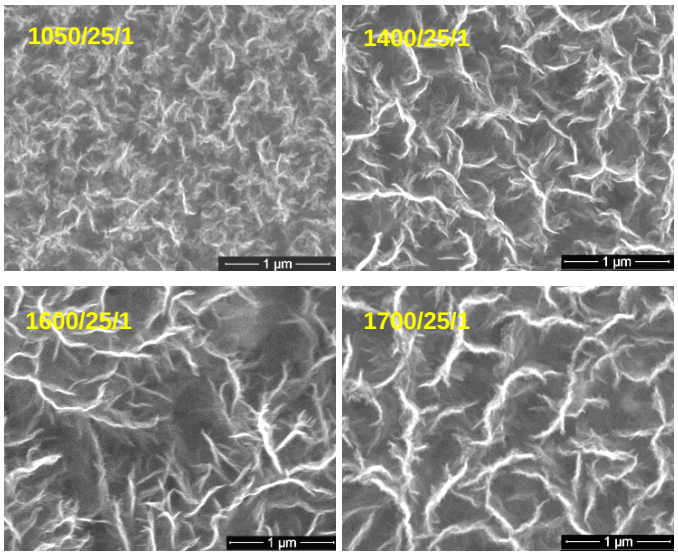

Fig. 1 Morphologies of CNWs deposited onto SiO_2/Si at different flow ratio without catalyst .

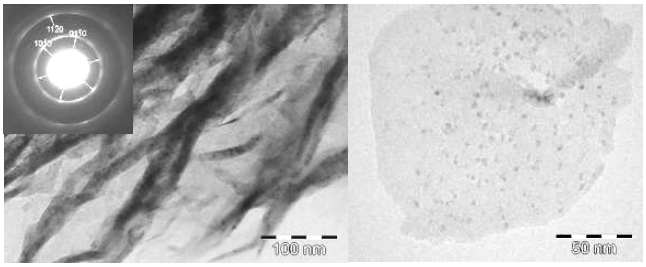

Fig. 2 TEM and SAED images of standard CNWs (1050)

The presence of ordered structures in CNWs deposited without catalyst was proved also by Raman spectroscopy. In Figure 3 can be observed a Raman spectrum of a sample of this type (1050). This spectrum indicates a typical multi-graphene-like structure [11], assembled from small grains with some degree of disorder, where we can find D and G (including D' shoulder) bands and their second resonance order as a combination of 2D, D+G and 2D' band.

X-ray photoelectron spectroscopy (XPS) was used to determine the elemental composition and chemical bonding at CNWs surface. This XPS results show the presence of the elements in the CNWs as follows: C, O, N. Their concentrations are: 85% (C), 3.3% (N) and 11.7% (O).

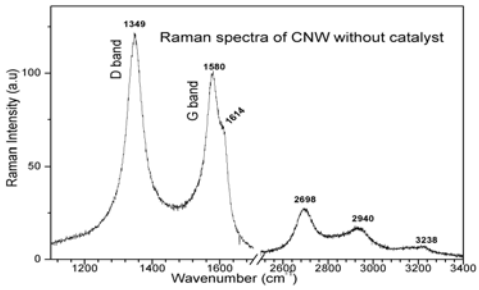

Fig. 3 Raman spectra of standard CNWs (1050)

Figure 4 presents a FTIR spectrum of standard CNWs (1050) deposited on Si wafer without catalyst.

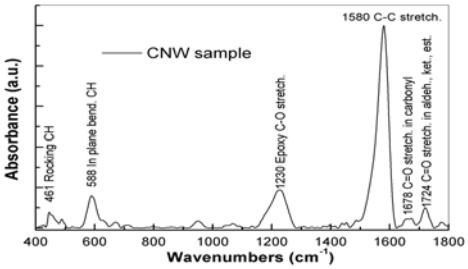

Fig. 4 FTIR spectra of standard CNWs (1050) onto Si substrate

The FTIR spectrum shows the most intense absorption band at about 1580 cm^{-1} associated with the C-C stretching vibrational mode in poly-aromatic carbonic structures and other weaker absorption bands situated at cca. 567, 644, 688, 1232, 1419, 1452, 1495 and 1697 cm-1, assigned to functional groups which contain hydrogen and oxygen (see Figure 4). The attribution of all FTIR absorption bands of standard CNWs was discussed in [3].

In Figure 5 are shown the SEM images of CNWs synthesized on polished stainless steel.

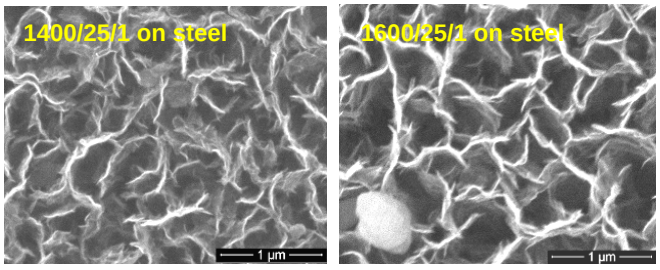

Fig. 5 Morphologies of CNWs deposited at different flow ratio onto polished steel without catalyst.

The appearance of CNWs is the same as in Figure 1. These images prove the growth on non-expensive and conductive substrates.

Conclusions

We successfully demonstrated the extending of the previously established [9] experimental parameter domain in terms of gas flow ratio to higher argon flows, having as results higher deposition rates and larger size nanostructures, as example of about 8 μm height.

In addition we have used non-expensive and conductive substrates, obtaining on them high quality CNWs (morphologies and structures). By using conductive substrates for CNWs synthesis, some characteristics of CNWs (thermal and electrical conductivity) can be easily investigated immediately after synthesis without any other subsequent preparation.

The identification of the experimental conditions (gas flow ratio) for CNWs synthesis in absence of catalyst shortened substantially the duration of the synthesis procedure.

The presented results obtained by SEM, TEM, SAED, XPS, Raman and FTIR indicate that the radiofrequency plasma jet method can be used to obtain reproducible CNWs layers with tailored characteristics. This method can be easily scaled up to large mass production of this kind of nanomaterials.

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