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FTIR INVESTIGATION OF THE AGEING PROCESS OF CARBON NANOWALLS

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Abstract. In this paper we investigate the changes that occur in the chemical composition of carbon nanowalls due to ageing process in open atmosphere. Ageing process of the carbon nanowalls samples was monitored for about two years by FTIR spectroscopy. The carbon nanowalls were deposited in a low-pressure plasma jet expanding through a nozzle. The ageing behaviour of the samples is related to the time alteration of deformation and stretching of the sp^2 and sp^3 vibration bands.

Key words: ageing process, carbon nanowalls, FTIR, surface chemical change, low pressure plasma, radiofrequency plasma, nanostructures

1. INTRODUCTION

Carbon nanowalls (CNW) [1] can be described as networks of interconnected carbon walls, grown vertically on a substrate, having thicknesses of a few to tens of nanometres. They are assembled from superposed graphene domains. Because carbon nanowalls have a very large specific surface area and sharp edges, they can provide us many opportunities for various applications [2], such as interesting nanoscale electronic devices, batteries [3], supercapacitors [4], etc. Plasma-enhanced chemical vapour deposition technique is gradually becoming an established technique for synthesizing nanomaterials, having reasonable growth rates at low temperatures [5]. In the present case, the CNW layers were prepared by radiofrequency plasma-enhanced chemical vapour deposition (RF-PECVD) method using an argon plasma jet injected with acetylene and hydrogen. The morphology of the carbon nanowalls was investigated by Scanning Electron Microscopy (SEM) and their chemical composition by Fourier Transform Infrared (FTIR) spectroscopy. Depending on the deposition conditions the resulting CNW samples show different layer thicknesses and sizes of nanostructures. The ageing of the samples is characterized by the changes of deformation and stretching of the sp^2 and sp^3 vibration bands in three different regions (1000–1200 cm^{-1}, 1500–1600 cm^{-1}, and 2850–2950 cm^{-1}, respectively). In this paper we analyse and compare the ageing behaviour of carbon nanowalls samples for different gas flow rates (1050 sccm Ar and 1400 sccm Ar). The carbon nanowalls sample made at 1400 sccm gas flow rate was monitored for approximately 2 years.

2. EXPERIMENTAL

The procedure of deposition of carbon nanowalls layers was described previously, as example in [6]. The experimental system is shown in Fig. 1.

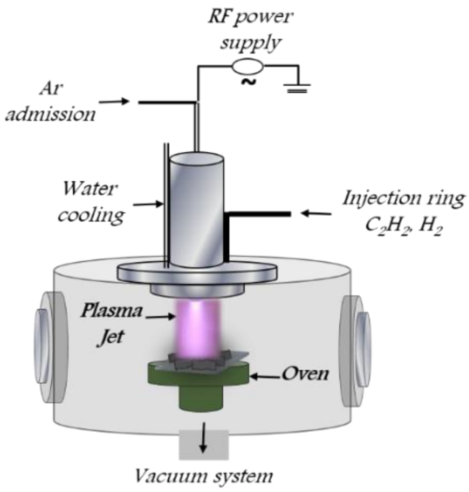

Fig. 1 – The experimental setup showing the deposition chamber.

It consists of two main parts: an active chamber (where the radiofrequency discharge, at 13.56 MHz, is generated) and the deposition chamber (where the substrate is placed over a heating oven). The plasma jet connects the two chambers through a nozzle, which can have various diameters and can be manufactured from different materials (molybdenum, in the present case). We employed argon (1050 sccm and 1400 sccm flow rates) as the main gas, while as precursor we injected downstream the nozzle a mixture of acetylene (1 sccm) and hydrogen (25 sccm) at a total pressure of 1.1 mbar for 300 W radiofrequency power, 15 minutes deposition time and a substrate temperature of 700 °C [7]. Furthermore, after the deposition process, the CNW samples were kept in special closed sample boxes for minimizing the interactions of CNW materials with the ambient conditions. The ageing behaviour of the CNW structures was monitored by means of a Jasco FTIR

6300 spectrometer. Examining the ageing behaviour consists in measuring the surface of the samples by means of FTIR spectroscopy. FTIR experiments were made in transmission mode, with 1024 accumulation numbers and having a 4 cm^{-1} resolution. For maintaining a steady atmosphere in the measurement chamber, we used silica gel and we regularly purged the spectrometer with argon gas. As known, the carbon nanowalls are strong light absorbent materials and for this reason, the employed substrate was a thin silicon wafer (transparent to infrared), in order to increase the signal. During ageing the acquired FTIR spectra indicate the appearance of the sp^3 bands in the range 2850–2950 cm^{-1} for all our samples. Moreover, the sp^2 aromatic band from 1580 cm^{-1} (which is characteristic for CNW samples) remains constant in time. For a better illustration of the ageing process, the FTIR spectra were plotted as 3D meshes in Matlab.

3. RESULTS AND DISCUSSIONS

3.1. STUDY OF CNW MORPHOLOGY

The ageing process of the carbon nanowalls samples was analysed for two gas flow rates. In Fig. 2(a, b) we present the Scanning Electron Microscope investigations of samples obtained in the following conditions: a) 1050 sccm of argon and b) 1400 sccm of argon.

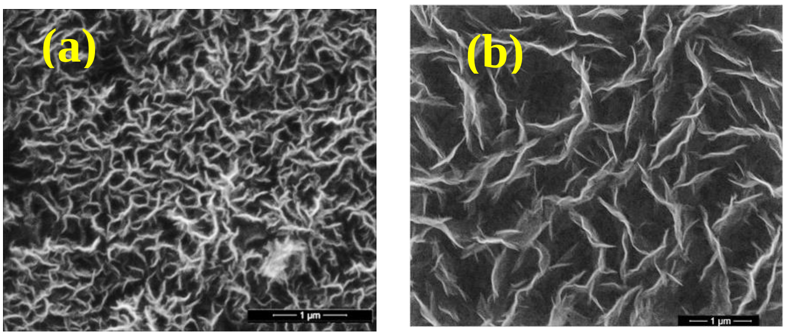

Fig. 2 – SEM images: a) CNW 1050 sccm; b) CNW 1400 sccm.

From the SEM measurements one can observe that the texture (size and the distance between nanowalls) of our carbon nanowalls can be highly influenced by gas flow. At 1050 sccm gas flow, the carbon nanowalls have a small size and high surface density. If we raise the gas flow up to 1400 sccm, the size of the nanowalls is increased with respect to the aforementioned case, and the density decreases.

We assign this change of morphology to the different chemical processes and radicals densities in plasma at different flow rates [7].

3.2. FTIR STUDY OF THE CNW SAMPLES

In Fig. 3 we present the initial FTIR spectra of the measured carbon nanowalls samples and in Fig. 4 we observe the FTIR spectra of the aged CNW materials. At the first glance, we could acknowledge that the carbon nanowalls materials represent samples with acceptable absorption band intensities in the infrared region.

In Table 1 we present the most important identified vibrational modes.

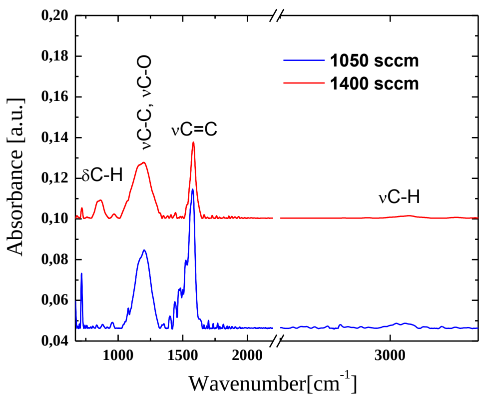

Fig. 3 – Initial FTIR spectra of the CNW samples.

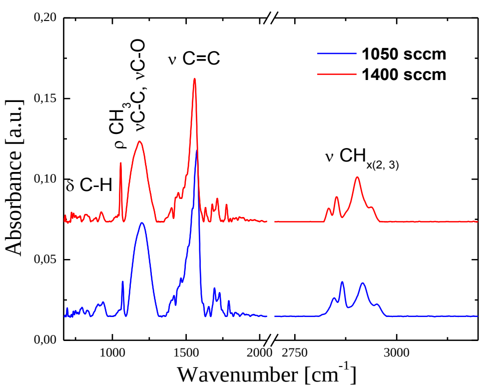

Fig. 4 – Aged FTIR spectra of the CNW samples.

Table 1

CNW IR vibrational modes

Wavenumber [cm^{-1}]	Absorbtions
900–1000	δ C-H
1070	ρ CH_3
1184, 1202	ν C-C, νC-O
1558, 1573	ν C=C
2832, 2903	ν CH_2
2852, 2936	ν CH_3
3050	ν C-H

In the initial spectrum of CNW sample (Fig. 3, blue spectrum), the sp^2 aromatic stretching absorption from 1570 cm^{-1}, νC=C, [8] presents a high intensity vibrational signal which dominates over the water absorption bands.

In addition, in the samples, we observe a sp^2 aromatic band in the range 3000–3050 cm^{-1} due to νC-H vibration band stretching [8]. In the range 1180–1200 cm^{-1} we identify the νC-C and νC-O stretching vibrations [8].

When studying the behaviour of our carbon nanowall samples in time, we can identify several important chemical changes of the aged CNW materials. Firstly, in Fig. 4, we can observe the appearance, in all our samples, of the sp^3 aliphatic absorptions in the range 2850–2950 cm^{-1}, due to asymmetric and symmetric stretching of $\nu CH_{x(2,\ 3)}$ vibration [9]; while, also, the aromatic νC-H stretching vibration band (from 3000–3050 cm^{-1}) disappears in time. In the old CNW samples, the ρCH_3 rocking vibration bands at 1070 cm^{-1} show up (in all spectra) , which were splatted during the ageing process, from the initial absorption bands at 1180–1200 cm^{-1} [8].

3.2.1. Effect of flow rate on deposited samples

Furthermore, in the aged CNW spectrum, the sp^2 aromatic band from 1570 cm^{-1} is clearly visible. Figs. 5, 6 and 7, show the FTIR spectra, plotted as 3D meshes in Matlab for three important regions (1000–1300 cm^{-1}, 1400–1800 cm^{-1} and 2700–3200 cm^{-1}).

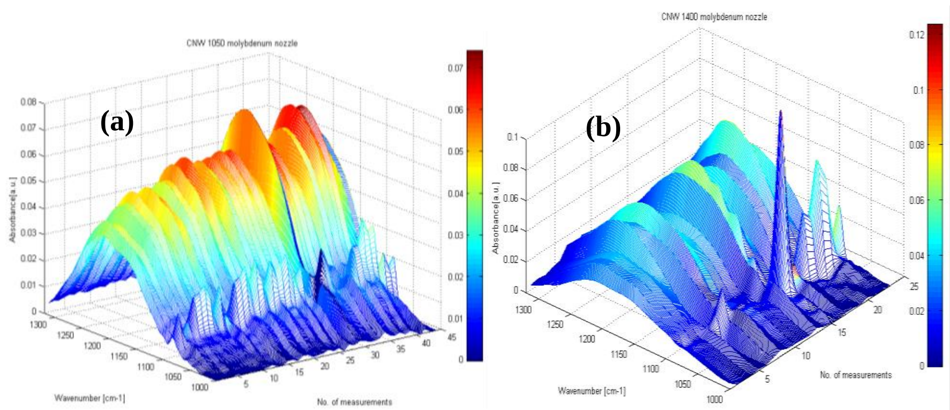

Fig. 5 – Ageing FTIR spectra of carbon nanowalls samples: 1000–1300 cm^{-1} range for:
a) CNW 1050 sccm; b) CNW 1400 sccm.

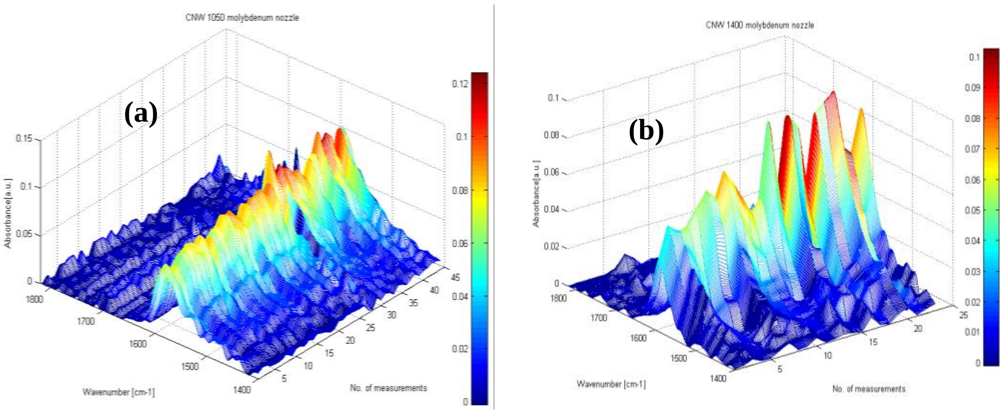

Fig. 6 – Ageing FTIR spectra of carbon nanowalls samples: 1400–1800 cm^{-1} range for: a) CNW 1050 sccm; b) CNW 1400 sccm.

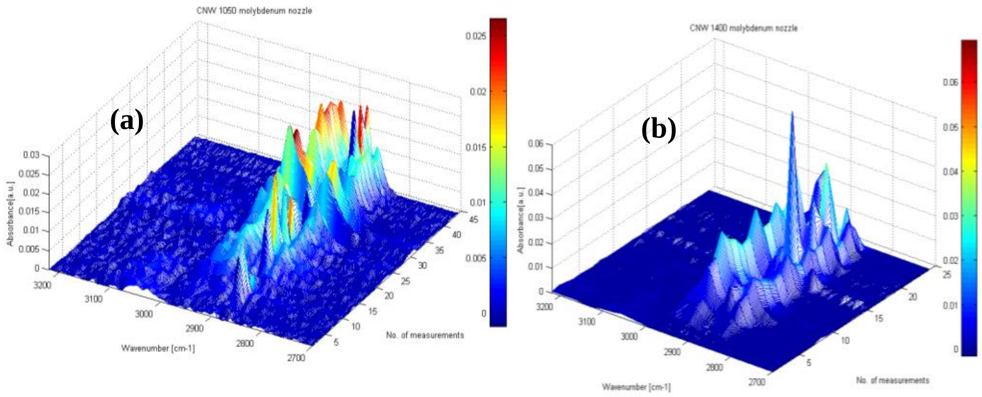

Fig. 7 – Ageing FTIR spectra of carbon nanowalls samples: 2700–3200 cm^{-1} range for: a) CNW 1050 sccm; b) CNW 1400 sccm.

An important observation is that the absorption band of sp^2 C-H, from 3000–3050 cm^{-1} is present in all carbon nanowalls samples and disappear during the ageing process. Also, another observation is that the ageing of the CNW made with 1400 sccm gas flow rate is faster compared to that made at 1050 sccm: it starts from the second day.

The aged FTIR spectra from Figs. 5, 6 and 7 present an oscillating signal intensity in time. These oscillations come from the fact that in the carbon nanowalls layers arise new chemical vibrations (in the absorbent nanostructures), being also combined with the atmospheric instabilities present in the FTIR chamber. Even when taking extra-safety precautions during the measurements, due to the high sensitivity of our FTIR spectrometer this behaviour is still present (*i.e*. in the above spectra).

4. CONCLUSIONS

We prepared carbon nanowalls layers by plasma jet enhanced chemical vapour deposition using argon as carrier gas and acetylene as precursor, in presence of hydrogen. We show that the morphology of the layers, specifically the size of nanostructures and their number density on surface is influenced by the the carrier gas flow rate.

By means of the FTIR spectroscopy technique, the chemical stability of carbon nanowalls material was investigated in time, aiming to reveal a possible ageing process. The ageing is indeed observed and it is characterized by modification of the vibrational bands structure in the infrared absorption spectra.

We were able to establish that different gas flow rates have distinct impacts on the ageing properties of the obtained nanometric systems. The use of lower argon flow rate, guarantees for keeping the CNW FTIR signal intensity constant in time for longer period.

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