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## Mass spectrometry of Ar/H<sub>2</sub>/C<sub>2</sub>H<sub>2</sub> expanding RF plasma used for synthesis of carbon nanowalls

B. Mitu, S.D. Stoica, S. Vizireanu, G. Dinescu

<sup>(1)</sup> National Institute for Lasers, Plasma and Radiation Physics

Atomistilor 409, PO Box MG 36 Magurele – Bucharest, 077125, Romania

(\*) [mitub@infim.ro](mailto:mitub@infim.ro)

### 1. Introduction

The carbon nanowalls materials are mostly synthesized by plasma assisted techniques [1]; therefore understanding the plasma species and chemistry is a key issue for controlling CNW properties. The present paper deals with the investigation by mass spectrometry of the neutral and ionic species generated in an expanding RF plasma beam used for the deposition of carbon nanowalls. The influence of the distance between the hydrocarbon injection point and the mass spectrometer entrance on the species density and their energy is reported.

### 2. Experimental

The expanding RF (13.56 MHz) plasma beam source was working at 200 W RF power, in Ar gas (99.9999% purity) at constant flow of 630 sccm, while the active gas (H<sub>2</sub>, 25 sccm) and the hydrocarbon precursor (C<sub>2</sub>H<sub>2</sub>, 1 sccm) were introduced in the deposition chamber through an injection ring situated in the proximity of the nozzle [2]. The mass spectrometer (EQP 1000, Hiden Analytical) was mounted on the symmetry axis of the plasma beam, the distance between the precursor injection point and its aperture being varied in the range 2-10 cm. It corresponds to the substrate positioning during the carbon nanowalls synthesis, allowing measuring the number and energy of the plasma species (ions and neutrals) which contribute to the deposition.

### 3. Results and discussion

The mass spectra of neutral and ionic species recorded at 5 cm from the injection point (which corresponds to the synthesis of the best CNW material), are presented in Figure 1. The spectrum of neutrals is dominated by the Ar – containing species, while only small peaks associated to H<sub>2</sub>, and C<sub>2</sub>H<sub>2</sub> could be measured.

The mass spectrum of the ionic species (recorded at 3 eV) clearly shows, besides the peaks associated to H<sub>3</sub><sup>+</sup> and ArH<sup>+</sup> ions, the formation of various carbonic clusters, up to C<sub>8</sub>H<sub>x</sub>-related species. Clusters with odd number of carbons are also observed in the present experiments. This is in contrast to most of the reports related to low pressure RF direct discharge plasmas [3] injected with acetylene, but is similar to the measurements reported for expanding thermal plasma [4] in argon/acetylene. The present measurements show that besides the acetylene fragmentation via electrons

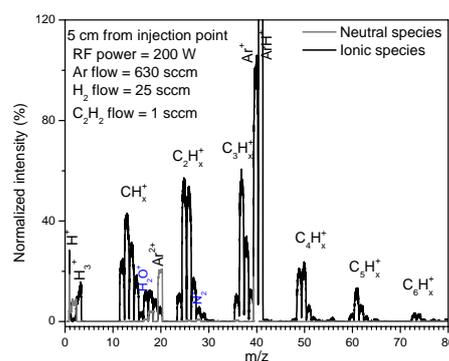


Figure 1. Mass spectra of neutrals and ions for expanding RF plasma in Ar/H<sub>2</sub>/C<sub>2</sub>H<sub>2</sub> admixture

collisions, in our plasma is active a dissociation channel based on charge transfer from the Ar ions. They are provided by the main discharge running upstream the nozzle. Last process leads to the formation of C, CH neutral and ionic species, observed both by mass spectrometry and optical emission spectroscopy. These species can generate an alternative polymerization reaction chain that generates  $C_{2n+1}H_x^+$  carbonic clusters, in addition to the one which lead to  $C_{2m}H_y^+$  ones.

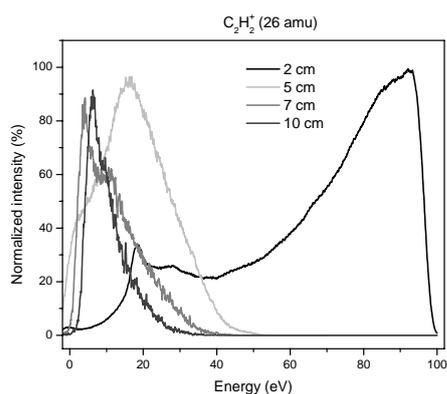


Figure 2. Normalized ion energy distribution of  $C_2H_2^+$  for various distances from the injection point

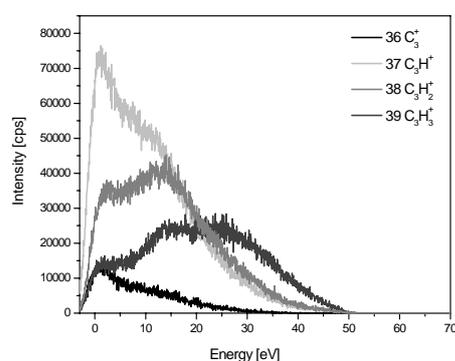


Figure 3. Energy distribution of  $C_3H_x^+$ -related cluster at 5 cm from the injection point

via electrons collisions, in our plasma is active a dissociation channel based on charge transfer from the Ar ions, followed by polymerization. The energy distribution of the ionic clusters depends on the position and the number of carbon and hydrogen atoms.

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The energy distributions of all important peaks appearing in the mass spectra have been investigated for various distances from the injection point. The most energetic species are  $H^+$  and  $H_3^+$ , with energies extending up to 120 eV, at 2 cm from the injection point (curve not shown).

The normalized intensities of the  $C_2H_2^+$  peak obtained for all the investigated distances are presented in Figure 2. In the nozzle proximity, the energy distribution is bimodal, with energies extending up to 90 eV, while moving further from the nozzle, the maximum energy value is decreasing and the distribution is moving toward one having only one peak, with a maximum around 6 eV.

The dependence of the energy distribution upon the number of hydrogen atoms in  $C_3H_x^+$ -related cluster is presented in Figure 3. It shows a clear tendency of moving its second maximum toward higher energies, as the number of hydrogen atoms attached to the cluster is higher, pointing out towards an association energy transfer from the  $H^+$ .

## 4. Conclusions

The expanding RF plasma generated in Ar/ $H_2$ / $C_2H_2$  mixture under conditions favorable for carbon nanowalls growth was investigated by mass spectrometry. The ionic spectra show both odd and even carbon clusters, up to  $C_8H_x^+$ . Their presence indicates that besides the acetylene fragmentation