MASS SPECTROMETRY MEASUREMENT IN CH_4/N_2 DC PLASMA

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Amorphous hydrogenated carbon (*a*-C:H) films have received considerable attention over the last years due to their unique chemical, electrical, optical and mechanical properties. The most common method recently used for the carbon film deposition is plasma-enhanced chemical-vapour deposition (PECVD). To date results of numerous investigations in this field could be found. Its analysis shows that the structure and properties of hard-carbon films do not strongly depend on the choice of the source hydrocarbon gas (CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_8, C_4H_{10}, C_6H_6, $C(CH_3)_4$) [1], but both the deposition rate and layer characteristics could be changed by gas-admixture inserting. So addition of N_2 to methane results in the formation of nitrogen-doped hydrogenated carbon film (*a*-C:H:N), which is a superior electronic material to *a*-C:H [2].

In contrast with investigations of film deposition and film properties, mechanistic studies of the film deposition process are not so numerous. Accordingly, many questions remain open as to the deposition mechanism and hard-film formation in DC PECVDs. In particular, the knowledge of relative importance of ions and radicals in this process is far from complete. For this reason, study of the heavy charged species composition of the nitrogen-methane low-temperature DC plasma is the main objective of this work.

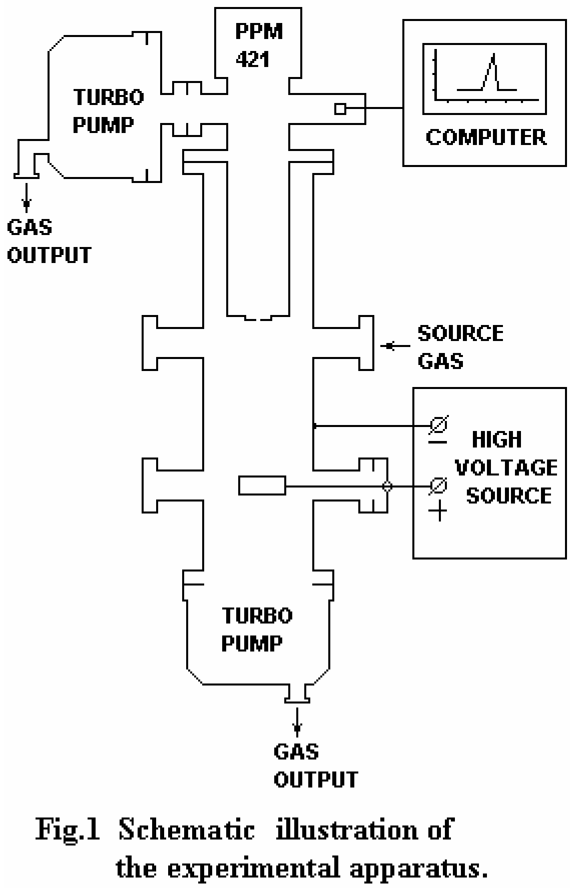

Fig.1 Schematic illustration of the experimental apparatus.

N_2/CH_4 (N_2 vol. abundance 0-100%) plasmas were produced in a DC glow discharge reactor (stainless steel tube with inner diameter 10 cm), at total current I_D=100 mA (typical discharge voltage was between 350 and 450 V) and pressure P=0,04Torr (Fig.1). The vacuum chamber of the discharge reactor was evacuated by means of a turbomolecular pump. Gas input flow rates were controlled by needle valves. Ions and stable neutral compounds proceeding from the discharge were studied by mass spectrometry. A quadrupole mass spectrometer Balzers PPM-421 equipped with a cylindrical mirror energy analyzer was employed for neutrals (electron impact ionisation) and ions registration. The energy distributions of ions were analysed too. The front hood of the mass spectrometer was connected with the discharge vessel and was operated with ground potential.

Typical ion energy distribution functions for several ions were found to have a double-peak "saddle structure" (Fig. 2). It should be noted that the relative intensity of the peaks depends on the source gas composition. The origin of the low energy peak is at present obscure but may be in some complex collision and/or charge exchange process.

The experimental results of the N_2-CH_4 plasma ion composition investigations are shown on the Figures 3, 4. Mass signals are normalised to total ion current for each measurement.

The main ions for the pure methane plasma are the ions with m/e = 17 (CH_5^+) and m/e = 29 ($C_2H_5^+$). These particles result from the following processes [1]:

$$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$$
$$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$$

Rate constants of the reactions for our experimental conditions are of the order of 10^{-9} cm^3s^{-1} [3]. Thus the primary ions CH_4^+ and CH_3^+, produced by the electron impact in the methane plasma, rapidly convert to CH_5^+ and $C_2H_5^+$. A notable amount of ions with m/e = 27 ($C_2H_3^+$) is registered too.

The nitrogen addition significantly changes the methane plasma ion composition: for the N_2 content in the precursor gas mixture more than 12%, the dominant charged particles are the ions with m/e = 28 ($C_2H_4^+$, CH_2N^+, N_2^+). At the same time it could be seen that amount of NH_4^+ increases significantly. This effect is the result of the following reactions:

$$C_2H_5^+ + NH_3 \rightarrow NH_4^+ + C_2H_4$$
$$CH_5^+ + NH_3 \rightarrow NH_4^+ + CH_4$$
$$CH_3^+ + NH_3 \rightarrow CH_4N^+ + H_2$$
$$CH_4^+ + NH_3 \rightarrow NH_4^+ + CH_3$$

Ammonia, participating in these processes, is a product of the heterogeneous reactions of nitrogen and hydrogen [4]. Because of its high proton affinity the protonated ammonia NH_4^+ is chemically unreactive toward hydrocarbons. Decreasing of $C_2H_5^+$ concentration in its turn entails the lessening of the formation probability of heavy hydrocarbon ions in the reactions as following:

$$C_2H_5^+ + CH_4 \rightarrow C_3H_7^+ + H_2$$
$$C_2H_5^+ + C_2H_4 \rightarrow C_3H_5^+ + CH_4$$

Thus nitrogen acts as a very effective hydrocarbon ion scavenger in the methane plasma.

For the pure nitrogen plasma it is characteristic the prevalence of the ions N^+ and N_2^+. A small amount of N_2H^+ should be considered as a result of interaction between charged and neutral particles of plasma and hydrocarbon film deposited on the reactor wall. The data received are generally in good agreement with results obtained by N.Mutsukura [4] in a RF discharge.

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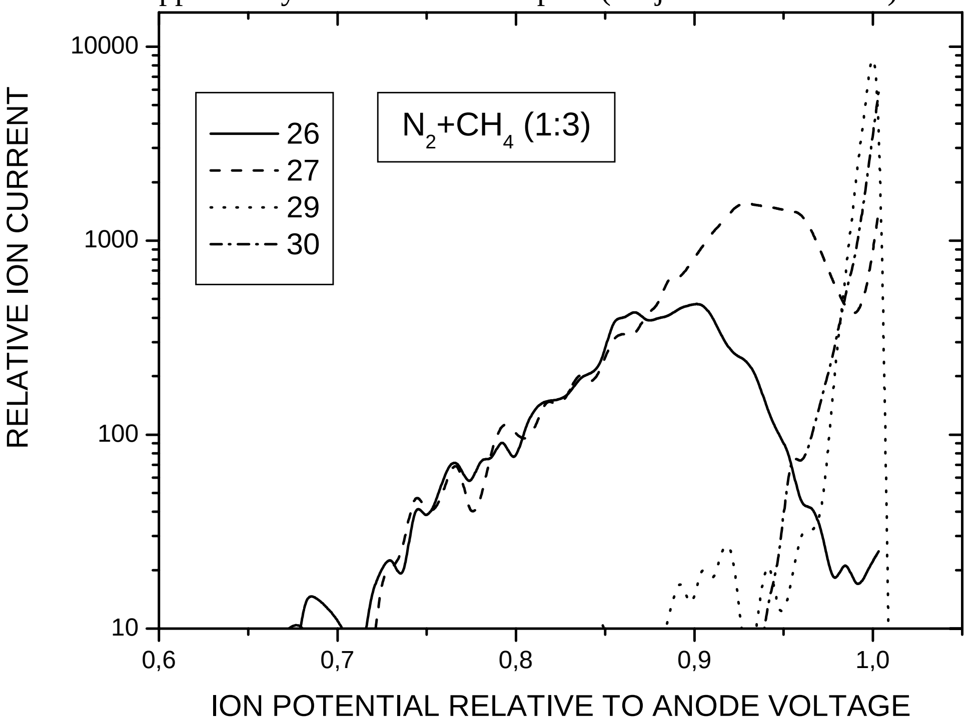

Fig. 2. Ion potential distribution relative to the anode in N_2/CH_4 plasma. Numbers are in line with *m/e* of corresponding ions (Table 1).

Table 1. Assignments of Predominant Mass Signals in N_2/CH_4 Plasmas

m/e	Ionic species	*m/e*	Ionic species	*m/e*	Ionic species
1	H^+	17	CH_5^+, NH_3^+	40	$C_3H_4^+$, $C_2H_2N^+$
2	H_2^+	18	NH_4^+	41	$C_3H_5^+$
3	H_3^+	26	$C_2H_2^+$	42	$C_3H_6^+$, CH_4N^+
12	C^+	27	$C_2H_3^+$, CHN^+	43	$C_3H_7^+$
13	CH^+	28	$C_2H_4^+$, CH_2N^+, N_2^+	44	$C_3H_8^+$, $CH_4N_2^+$
14	CH_2^+, N^+	29	$C_2H_5^+$, N_2H^+	52	$C_4H_4^+$, $C_2N_2^+$
15	CH_3^+, NH^+	30	$C_2H_6^+$, CH_4N^+	54	$C_4H_6^+$, $C_2H_2N_2^+$
16	CH_4^+, NH_2^+	39	$C_3H_3^+$	55	$C_4H_7^+$

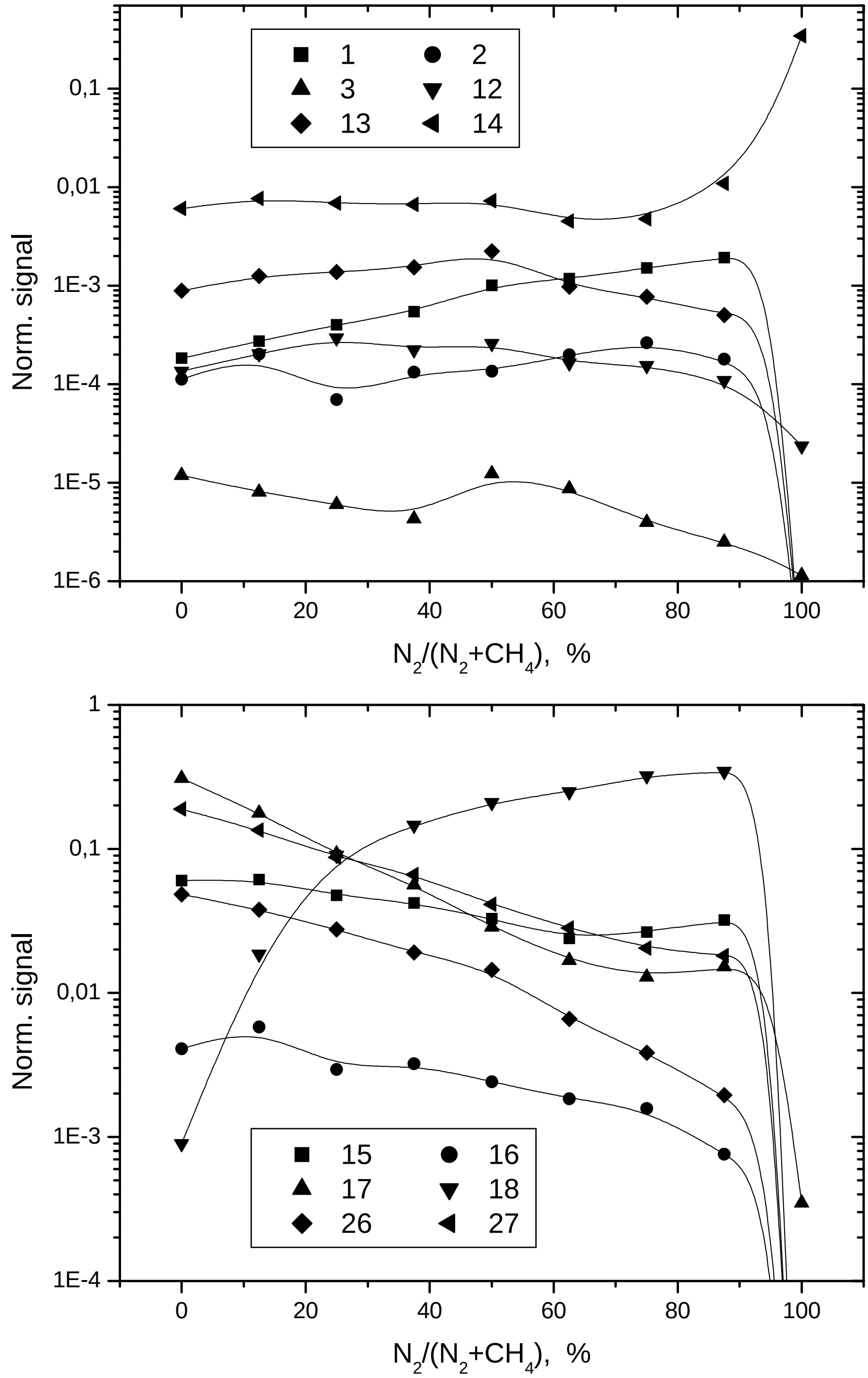

Fig. 3. Normalized mass currents of several kinds of ions in N_2/CH_4 plasma. Numbers are in line with *m/e* of corresponding ions (Table 1).

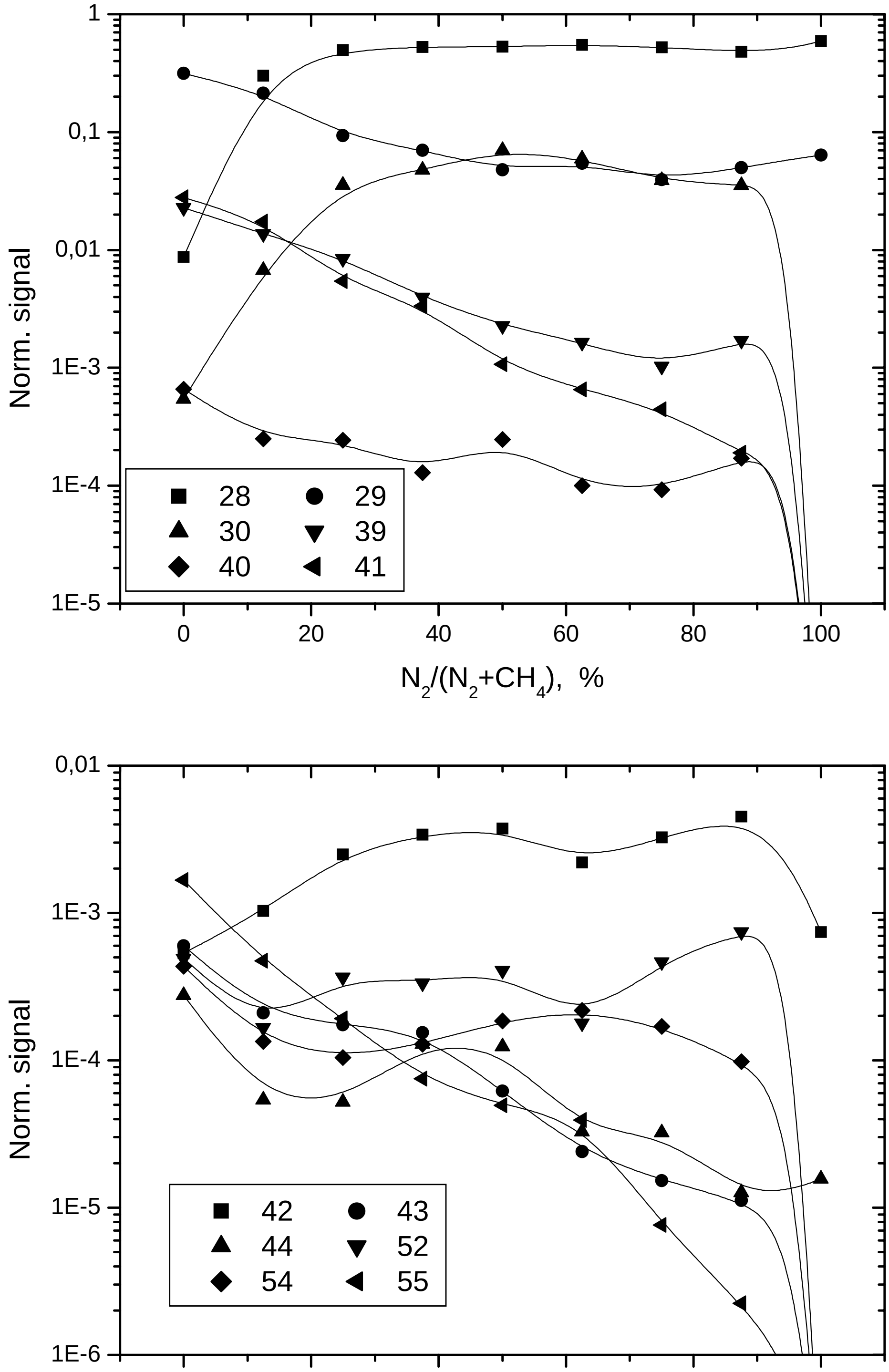

Fig. 4. Normalized mass currents of several kinds of ions in N_2/CH_4 plasma. Numbers are in line with *m/e* of corresponding ions (Table 1).

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