

Mass spectrometric studies of the mechanism of film inhibition in hydrogen/methane plasmas in the presence of nitrogen.

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Abstract:

Complete suppression of amorphous C:H film deposition has been reported for N₂/CH₄ ratios ~1, in low-pressure technical plasmas. This finding has been recently used by the authors for the proposal of a possible technique for the inhibition of re-deposited T-containing carbon films at the divertor region of fusion devices. Although several works aiming to the understanding of the underlying physicochemical processes have been published, the complexity of the system is far from being properly described by the proposed models. In the present work, experiments in DC glow discharges at low pressure of H₂/CH₄/N₂ admixtures (90:0-5:0-5) are described. Mass spectrometry of neutral species as well as plasma mass spectrometry for ion detection have been used as the main diagnostics. Several plasma conditions (plasma current, gas composition, etc) as well as isotopic exchange (H/D) have been investigated. Also, the effect of progressive film growing on the metal walls of the reactor in the composition of gas phase species has been investigated. It is concluded that wall carbonisation is required to trigger the inhibition process. Ethylene and acetylene are found as the main reaction products.

1. Introduction.

The plasma deposition of nitrogenated amorphous carbon films, of high interest due to their mechanical properties [1] has traditionally faced the difficulty of low deposition rates and low N incorporation into the a-C: H film [2]. These facts have motivated a rather strong effort oriented to the understanding of the basic processes responsible for the deposition/inhibition in the presence of nitrogen into the plasmas. Several mechanisms are presently under debate. Thus, the so-called scavenger effect due to fast reactions between plasma active species and film precursors has been claimed in the absence of energetic particles [3] whereas direct sputtering of the growing film by the N-bearing ions from the plasma could be essential when high voltages are created near the substrate [4]. Among the first hypothesis, either ions or radical species have been proposed as scavengers [5]. On the completely different topic of fusion plasmas, the authors have recently proposed the use of this effect to preclude the re-deposition of tritiated carbon films in hidden areas of fusion devices [6] and some experiments have been already initiated to validate the technique. Since plasma conditions in which redeposition takes place are extremely varied and hardly adjustable, a deep understanding of the inhibition of film deposition by nitrogen injection is urgently needed. This work is focused on the important issue of the surface vs. gas phase dominated mechanisms of interest for the extrapolation of the technical plasma observations to the fusion plasmas.

2. Experimental set-up

The experimental set-up has been previously described [6]. Briefly, carbon films are deposited in a glow discharge reactor consisting of a cylindrical chamber (inner area $\sim 2000 \text{ cm}^2$) continuously pumped by a 450 l/s turbomolecular pump to a base pressure of $< 3 \times 10^{-7}$ mbar. DC glow discharges of methane/hydrogen admixtures (5/100) are produced and nitrogen is added to the plasma in relative concentrations of $\text{N}_2/\text{CH}_4 < 1$. The film deposition was monitored by inserting metal and silicon samples into the plasma at room temperature. XPS depth profile and profilometry were used for the characterization of the film growth. Mass spectrometry (Balzers QMS125), in a differentially pumped chamber, $P_0 = 5 \times 10^{-9}$ mbar, is used to characterize the gas composition during the deposition process. A diaphragm with constant conductance is used to reach a pressure reduction factor of ~ 200 for most species. Calibration of the cracking patterns and absolute sensitivity was performed for some relevant species only. In a twin system, mass spectrometry of neutrals and ions was performed by differentially pumped spectrometers (PPM 421). Optical emission spectra in the range of 370 to 500 nm were recorded by means of an OMA (Oriel) through a glass window. The discharges were readily initiated at the operation pressure by means of an electron gun. At the total pressure of $P < 3 \times 10^{-2}$ mbar typically used, a residence time of ~ 50 -100 ms for methane and nitrogen was estimated. Plasma current $50 < I_p < 400$ mA and discharge voltages between 300 and 550 V are routinely used for the film deposition. For the metal-to-carbon wall transition experiments, a stainless steel sheet was inserted coaxially into the reactor. Extensive conditioning in pure H_2 plasmas was used prior to the experiments.

3. Results

The addition of nitrogen to the H_2 /methane glow discharge plasma, in concentrations comparable to that of methane and in the presence of a previously carbonised wall, leads to important changes in the mass spectrum of the neutral species, even when the plasma conditions are adjusted in order to keep a constant current, and only minor variations in the discharge voltage are eventually observed. In fact, no modification in the cracking fraction of the injected methane is typically seen upon the addition, as far as the total pressure variation does not change the effective pumping speed of the turbo pump. Figure 1 shows two examples of the mass spectra recorded during the experiment. Plasma on-off conditions for pure methane and N_2 seeded plasmas are displayed. Peaks corresponding to C_1 and C_2 hydrocarbons and some N-related species are shown. Among all the changes, the most conspicuous one corresponds to that of masses 26 and 27, both rising as N_2 is added to the plasma. The increment of the peaks after switching on the discharge indicates that also mass 28 and 29 (N_2H^+ produced at the ioniser region of the RGA under the simultaneous presence of N_2 and H_2) are significantly produced in the N_2 containing plasmas, while mass 14 insensitivity ($\sim 10\%$ of the 28 peak for nitrogen in our RGA) is consistent with a constant value of the nitrogen concentration at any plasma current. Note that, due to the relative detection sensitivity, variations of few percent in mass 28 in the N_2 -containing plasmas are comparable to the range of the absolute values for some other peaks. All the findings above reported are in agreement with observations from other type of diagnostics. So, no significant nitrogen incorporation to the carbon film could be detected by XPS analysis of the samples. Also, optical emission spectroscopy of the plasmas indicates little or no influence of the molecular nitrogen in the decomposition of methane in the discharge [5]. Characterization of the methane/hydrogen discharges by Langmuir probes (double probe configuration) yields characteristic values for electron density and temperature of $\sim 10^{10} \text{ cm}^{-3}$ and 4

eV, respectively, and no significant effect of N₂ addition in these parameters was detected.

As it is well known, mass assignment is a rather challenging task in this type of plasmas. Table I shows most of the relevant information for the cracking pattern of the possible stable species. The data are taken from the NIST data basis [7] and they are arranged in the scheme used by Davis et al [8] for the simulation of similar hydrocarbon mixtures. Each species is assigned to a main peak, with little interference from the rest. Only C₃ hydrocarbons have been included in the upper limit of the hydrocarbon series. Mass 52 has been chosen as a possible indicator of C₂N₂ formation and, together with HCN represents the only molecular species bearing both types of atoms expected in the spectra. The reconstruction of the chemical composition by the present method is obviously not free from some ambiguities. The signals to be handled span several orders of magnitude in the residual spectra and all peaks are subjected to contamination from several species to some extent. In this work, several tests have been run in order to get confidence in the method. First, some peaks that are not directly involved in the calculation of the hydrocarbon composition are used as consistency checks, when available. This is the case for the peaks 25 and 28, among others. So, a rather constant ratio amu26/amu25 ~5 holds for the C₂ hydrocarbon cracking pattern. This allows for the crosscheck of the total C₂ contribution to mass 26, and eventually, and in combination with the information provided by other masses, the detection of significant CO production. It also allows to some extent to assess the possible presence of HCN in the peaks 27 and 26 as well. The other important tool employed is isotope exchange. Plasmas of deuterated methane diluted in deuterium have been produced under the same conditions as those above reported. This allows, for example, for the separation of the possible contributions from ethylene and HCN to peak 27 in the hydrogenic plasmas. In figure 2, the method has been applied to the deposition plasmas. Three examples are given, corresponding to pure methane/H₂, a methane/N₂ containing plasma, with relative concentrations of 4% and 3%, respectively and, from a different run, a deuterated, nitrogen containing plasma, with CD₄/N₂ relative concentrations of 5 and 2% respectively. While in the first two cases, the cracking of methane into the plasma is the same, a lower value was observed in the latter. Typical hydrocarbons are given as a function of their characteristic peaks, although absolute amounts are only partially available through the RGA calibration (see above). For the deuterated case, the overlapping of the CO and the acetylene peaks at amu 28 can lead to an overestimate of the hydrocarbon production. Information from mass 44 in fact points to the presence of a significant contribution of carbon oxides in these plasmas. The displayed spectra preclude any strong contribution of HCN in the plasma, and a dominant production of ethylene and acetylene in general. As seen, the addition of nitrogen into the discharge enhances the production of both unsaturated, C₂ hydrocarbons, but the effect on ethylene is stronger. It also leads to a remarkable enhancement of C₃ hydrocarbons, the total effect being a drastic increase of C in the gas phase. Although not shown, it must be noted here that some increase, but in lower extent, is also seen in the interaction between the film and N₂/H₂ plasmas [6], as one may expect from the sputtering effect in the presence of energetic (300-400 eV) ions. The energy and composition of these plasma ions has been also analysed by means of the PPM. Although a full report of the observations will be given elsewhere, it must be said that fairly monoenergetic ion distributions, corresponding to the cathode fall potential are seen. However, little change in the ion composition has been recorded when methane is added to the nitrogen-containing plasma. One exception of this trend is the conspicuous rise of the ion at mass 42, together with a simultaneous

decrement of ion masses 18 and 29, both having a strong contribution from the non-hydrogenic ions in the N₂/H₂ plasmas (NH₄ and N₂H components, respectively).

As stated above, the wall conditions have an important effect on the phenomena here described. In fact, little hydrocarbon production is observed when the plasma is started on a clean, metallic wall. This behaviour is displayed in figure 3, where the evolution of some significant peaks during the gradual growing of the film is shown. A first plasma of CH₄/N₂/H₂ (4% and 6% respectively) is kept running. Then an 8-minute period (from 28' to 36') of deposition in pure methane/H₂ plasmas is inserted, and the N-containing plasma is again produced. Three spectra, corresponding to different times after the initiation of the process are shown. The initial deposition rate, under no C re-emission, is estimated in 5.4x10¹⁴Ccm⁻²s⁻¹. As seen, a steady increase of the unsaturated C₂ hydrocarbons takes place, but with little evolution of their relative proportion. Interestingly, and within the reconstruction errors, ethane and n-propane show little or no increase at all. Also, some mass 52, ascribed to the cyanogen molecule, can be seen at long deposition times.

4. Discussion.

One of the long-standing controversies in the carbon-deposition plasma research is the relative role of surface and gas phase processes and their interplay [9]. In the case of the N-containing C deposition plasmas, an ample experience exists about the phenomenology of the film inhibition, but as expected, little agreement on the underlying physico-chemical processes has been achieved to date. Thus for example, Clay et al. [4] proposed the direct etching of the growing film by N₂ ion bombardment as the responsible mechanism of film inhibition in methane/nitrogen RF plasmas, while other authors have claimed gas phase scavenger effects of either molecular ions [3] or neutral nitrogen-containing molecules [5] on the film precursors. Although the plasma characteristics and particle energies are significantly different in RF, MW and DC glow discharge plasmas, the results here presented can reveal some aspects of these complex systems. Thus for example, mass spectra analysis of the etching of the C films in our DC-N₂/H₂ plasmas showed that at least a 25 to 30% of the re-emitted hydrocarbons are directly produced by sputtering of the film. On the light of these observations, and the strict proportionality found between the CH and N₂⁺ emissions with the cracked methane and molecular nitrogen ion concentration respectively, previously reported [6]

$$I_{CH} = a (\Delta CH_4) \sim (I_p)[CH_4] \quad 1a)$$

$$\text{with } I_{N_2^*} = b (I_p)[N_2] \quad 1b)$$

the contributions of both type of sources, hydrocarbon conversion and sputtering, to the C₂ hydrocarbon production can be expressed as

$$\Delta C_2 = f_{(N_2)} (\Delta CH_4) + c(I_p)[N_2] \quad 2)$$

where the left side term stands for the production of any C₂ hydrocarbon in the plasma, a-c are constants and f depends on the N₂ plasma concentration. Note that no change in the relative fraction of H/N ions is assumed as the current (I_p) is changed, in agreement with the observations. If one assumes that the fraction of cracked methane converted into C₂ species has the functional form

$$f_{(N_2)} = 0.5 [N_2]/[CH_4] + d \quad 3)$$

where a factor of 0.5 accounts for the stoichiometry and d for the C₂ produced during pure methane deposition [13], and using the relations given in 1a,b, equation 2 can be rewritten as

$$\Delta C_2 / I_{CH} = 0.5 [N_2]/[CH_4] + d + I_{N_2}/I_{CH} \quad 4)$$

Finally, since I_{N₂}/I_{CH} is proportional to [N₂]/[CH₄](at constant Te) one finally gets a linear expression of the form

$$\Delta C_2 / I_{CH} = A. I_{N_2}/I_{CH} + d \quad 5)$$

In figure 4, the type of plot suggested by eq. 5 is shown for a wide range of discharge conditions. High regression coefficients for the fitting of both C₂ main peaks, amu 26 and 27, are obtained, thus providing good evidence of the hypothesis of the model for N₂/CH₄<1 mixtures. At higher N₂ values, a smaller slope of the lines would be expected, due to saturation of the scavenger effect. Unfortunately, no data are presently available to fully verify this behaviour. Under the light of the double contribution for the re-emission of hydrocarbons, the results presented in figure 2 deserve some comments. First, although C₂N₂ molecules, typically produced in the interaction between nitrogen plasmas and the film [3] are produced once a given thickness of the film is grown, no evidence of significant HCN (nor DCN) formation, that would also be expected from film sputtering and some gas phase reactions [10] is obtained in the de-convolution of the mass spectra. A significant production of this species can be directly excluded from the constancy of molecular nitrogen in the plasma, and suggests that the scavenger effect of the N₂-derived species in the plasma takes place through the recombination of the film precursors rather than the production of N-bearing, stable species as HCN, probably in a similar way as the one responsible for the Huels process in arc discharges [11]. It is also worth noting that the chemical composition of the released hydrocarbons is similar to that found by Vietzke et al [12] in the sputtering of carbon films by thermal and energetic H particles. However, a stronger contribution of acetylene is expected during the film bombardment by heavier species, as seen in our etching plasmas. All these observations lead us to suggest that, during the deposition of carbon from N₂/H₂ mixtures, gas phase reactions are the main mechanism for C₂ production.

The wall conditions do have, however, an important role. This is clearly seen in the time evolution of the mass spectra displayed in figure 3b. There are several reports on the early stages of the film deposition describing the need of an initial C implantation on the metal as a pre-requisite for film growing. This was correlated with the evolution of hydrocarbon re-emission in a previous work in very similar deposition conditions [13] The most striking observation, however, is that no film inhibition effect is seen until a given thickness of C film is grown on top of the metal surface. This fact again provides evidence for the complex interplay between gas phase and surface mediated processes taking place in this kind of systems. An obvious conclusion from this is that the intermediate product responsible for the recombination of film precursors could decompose upon impinging on a bare metal surface, as opposed to the carbonised one. It must be noted here that this type of behaviour has clearly been observed in mass and energy resolved hydrocarbon and fluorocarbon ion beam experiments by Mitsuoka et al [14] at energies in the range of those measured in our plasmas. Although the extrapolation of these data to our, more complex system could be somehow speculative at this stage, work in this direction is presently in progress.

Conclusions.

The mass spectra of the neutral species produced during the deposition of carbon films in nitrogen-containing methane/hydrogen plasmas have been investigated in a DC glow discharge reactor. The de-convolution of the spectra shows that ethylene and acetylene are the main re-emitted hydrocarbons in the plasma, with little contribution from HCN molecules. A simple model based in the spectroscopic observations previously reported indicates that the main hydrocarbon production channels in the plasmas are gas phase recombination of film precursors and sputtering of the carbon film by the plasma ions, this channel accounting for a moderate (<30%) fraction. Surface conditions are critical for the development of the film inhibition mechanism, possibly due to the likely fragmentation of the reaction intermediates on the initial metallic surface. All these observations lead to the conclusion of a "catalytic-like" effect of some nitrogenated species on the gas-phase recombination of the film precursors for the mechanism of film inhibition in N₂/CH₄/H₂ DC low-pressure plasmas.

Acknowledgement

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Figure captions.

Fig1. Typical mass spectra of deposition plasmas. Units: amu 14,15,16 and 28, 10⁻⁶ torr, amu 25,26,27 and 29, 10⁻⁷ torr and amu 30 and 52, 10⁻⁸ torr.

Fig.2. Reconstructed chemical composition of the species produced in the plasmas from the spectra shown in fig.1 (cases 1 and 2), together with those from a deuterium run (case 3). Uncertainties on the partial contribution of CO to the deuterated acetylene are shown.

Figure 3.

a) Time history of some RGA peaks during the deposition of C film from a N-containing methane/H₂ plasma on a clean metallic surface.

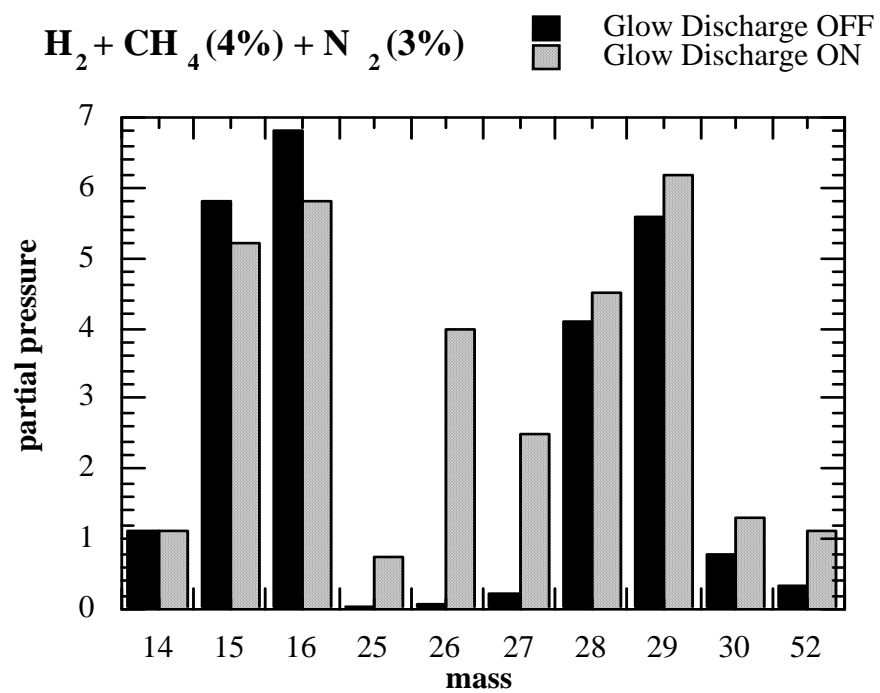
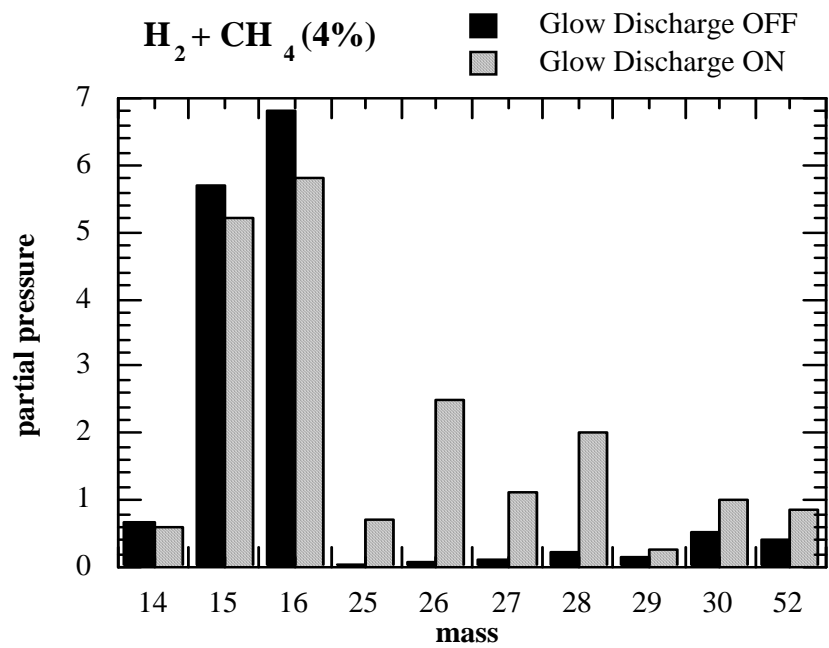


Figure.1

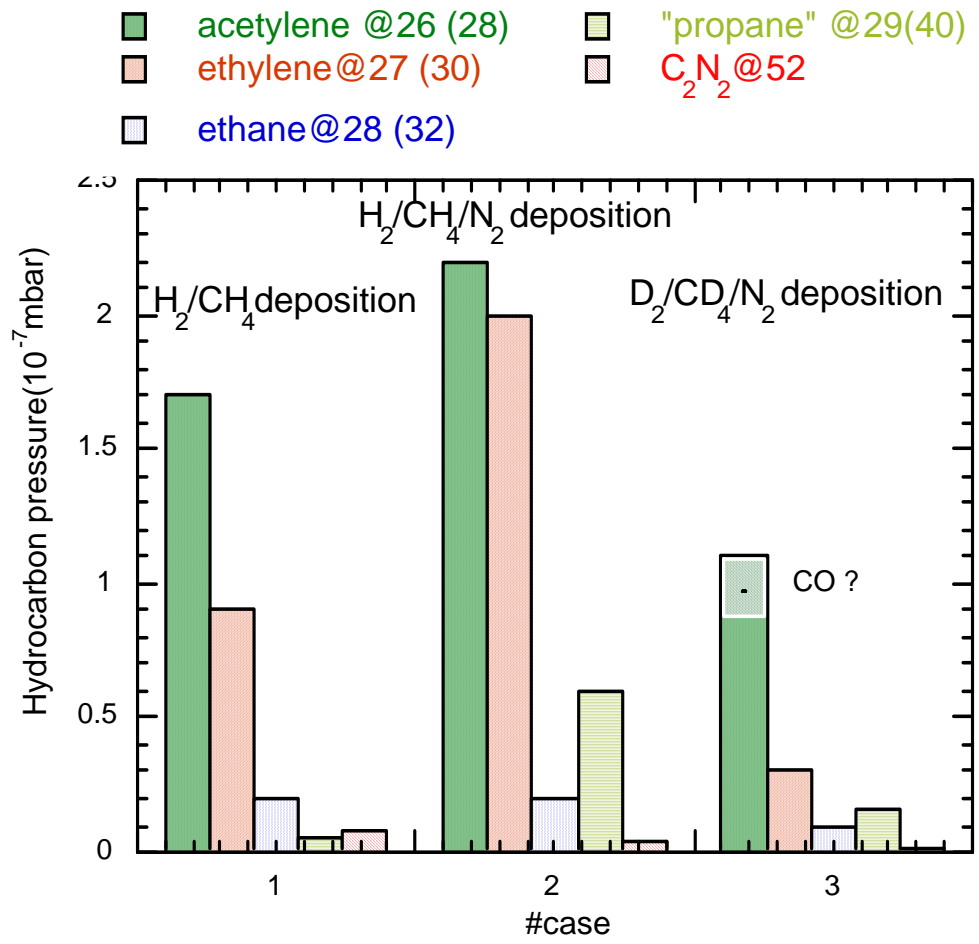


Figure2.

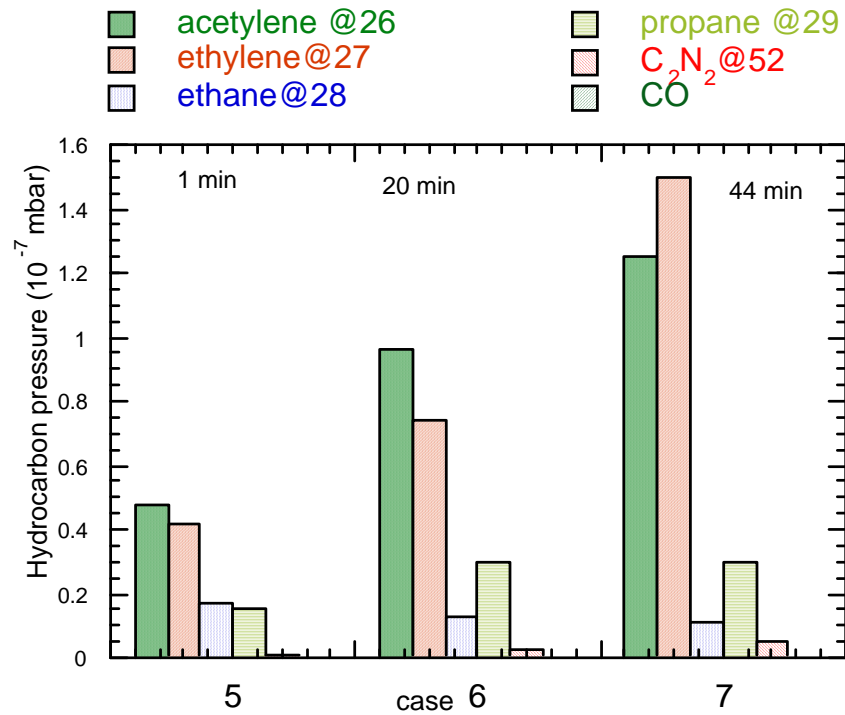
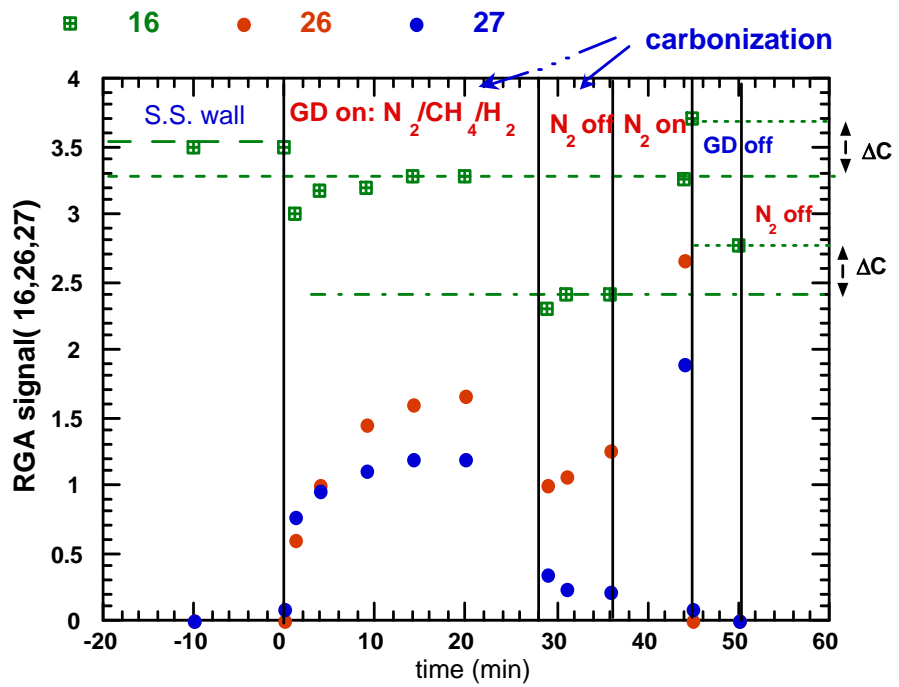


Figure3.

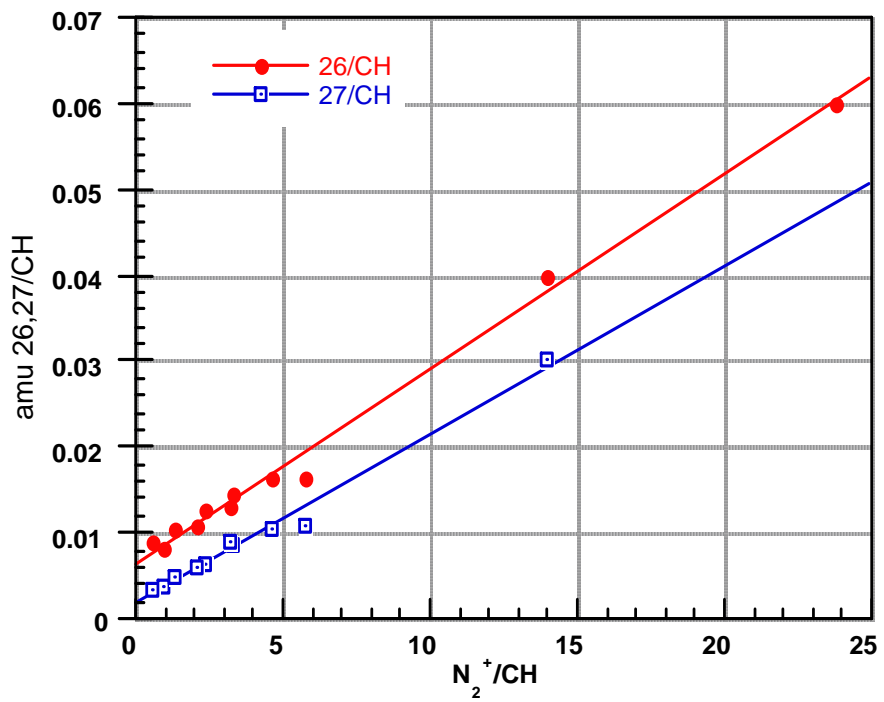


Figure 4.