

Tritium Inventory Control in ITER and the Chemistry of Carbon/Nitrogen Plasmas.

Francisco L. Tabarés.

Laboratorio Nacional de Fusion. CIEMAT. Av Complutense 22, 28040 Madrid
Tabares@ciemat.es

The physical and chemical processes taking place in cold plasmas of carbon and nitrogen-containing molecular species have received an outstanding interest in the last decades due to their application in many physical systems, ranging from thin film deposition to interstellar atmospheres. Moreover, studies of the gas phase and surface mediated processes of these reactive systems have been carried out in several types of plasmas within the Fusion community, leading to the development of the scavenger technique for tritium retention control in fusion devices.

Cold plasmas containing carbon and nitrogen-bearing species have been the topic of extensive research for decades. The reason for that has been the relevance that these plasmas have in fields so diverse as the PACVD growth of superhard carbon nitrides, both in film [1] or crystalline [2] states, pollution chemistry [3], extraterrestrial atmospheres and ice rocks [4] and, lately, tritium control in fusion devices [5]. The ample experience gained by the technical plasma community, in many instances through pure empirical knowledge, indicates that many factors can substantially modify the growing rate and physic-chemical properties of plasma-deposited films [1]. Well-known factors are substrate composition and temperature, bias voltage and the addition of reactive species to the precursor-generating plasma (hydrogen is a typical example). Both, gas phase and surface mediated processes play a key role in the underlying chemistry. However, the complexity of the underlying physio-chemical processes leading to the deposition/inhibition of carbon nitride films in technical plasmas is clearly reflected by the fact that no prediction of the film properties can be unambiguously made based on the deposition parameters alone. There are, nevertheless, some well established observations concerning these plasmas:

a) There is a strong contribution of chemical erosion processes of carbon (with a low energy threshold) in the presence the nitrogenic species. This erosion leads to the formation of highly stable, volatile products and it is enhanced by the presence of hydrogen and the substrate temperature. Among these products one can find N_2 , HCN, C_2N_2 , NH_3 , C_2H_2 , and C_2H_4 , although no systematic correlation has been yet reported between plasma conditions and the outcome of the chemical reactions involved.

b) Surface effects are paramount, and they appear to depend on the chemical environment. In that sense, free N-bearing radicals can possibly induce surface chemistry effects equivalent to those caused by low energy ions. However, conditions exist under which enhanced deposition of nitrogen-containing poor-quality carbon films can be formed.

c) At pressures in the range of a few Pascals ($1Pa = 7.5mTorr$) fast gas phase reactions (implying radical and ion scavengers) will contribute to the further depletion of carbonised film precursors. Ammonia, atomic nitrogen and molecular nitrogen ions have been proposed as radical or ion scavengers under these conditions.

From a pure thermodynamical point of view, carbon-nitrogen bonding is promoted by its superior strength compared to that of carbon-carbon, as summarized in Table I. When dealing with molecular ion chemistry, the strong proton affinity of species as ammonia or molecular nitrogen drives many charge transfer processes. While carbon ions have a high sticking coefficient on the growing film, these nitrogen-based molecular ions can act as film etchers. From the kinetics point of view, low activation energies are associated to the fast radical-radical or radical-molecule reactions taking place under a plasma background. Some of these reactions have their counterpart in radical-surface interaction processes, on which the creation of active sites at the surface by ion impingement are of crucial relevance.

Table I. Bond energies in N/C/H systems

| Bond type | Bond Energy KJmol ⁻¹ |
|-------------------|------------------------------------|
| H-H | 435.9 |
| N:N (triple) | 945.4 |
| C:C (triple) | 838.0 |
| H-NH ₂ | 442.0 |
| H-CH ₃ | 435.0 |
| C-N | 286.0 |
| C=N | 615.0 |
| C:N (triple) | 887.0 |
| C-C | 347.0 |

Perhaps, the most conspicuous example of the chemical systems here addressed in extraterrestrial atmospheres is Titan's. Depending on altitude, a mixture of hydrocarbons and nitrogen bearing molecules, mainly N₂ and ammonia, leads to an evolving mass spectra of the type shown in figure 1. Cosmic radiation in this case plays the role of the plasma in dissociating and exciting the molecular components, thus triggering a series of elemental reactions of difficult modeling in the complex parametric space existing over this Saturn's satellite surface.

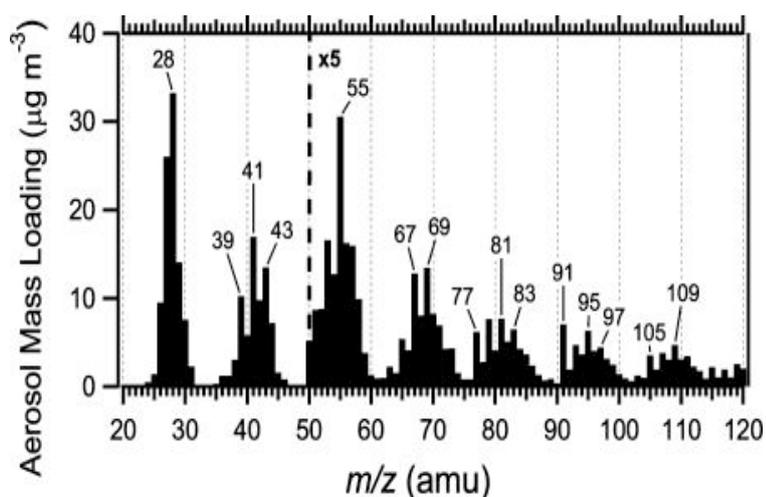


Fig. 1. Averaged mass spectrum for aerosols formed in 0.1% CH₄ in N₂. This spectrum is a representative spectrum for all aerosols produced in a range of mixtures of CH₄ in N₂. Data to the right of the dashed line at 50 amu are multiplied by 5 for ease of viewing.

Interestingly, a very similar mass spectrum can be recorded at the laboratory when a methane-diluted, nitrogen plasma is created at given condition of gas pressure and wall properties (see Fig 2). The reproduction of the chemical composition of the gas mixture under well-controlled lab conditions can obviously shed light into the underlying elemental processes taking place under the more stringent, hard to reach conditions prevailing on these extraterrestrial objects.

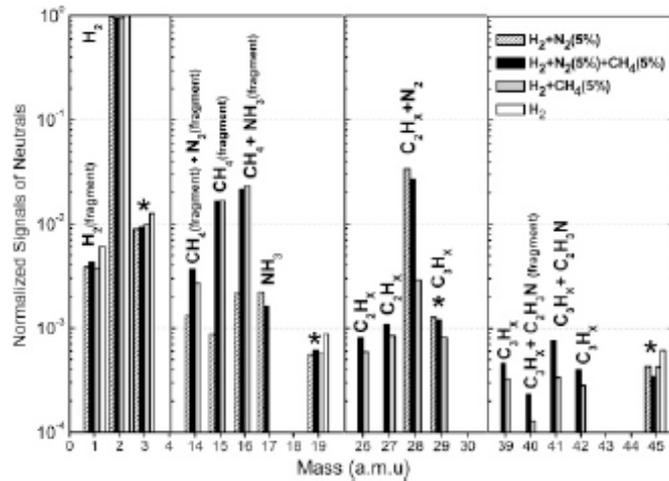


Fig.2. Mass spectrum of several reactive mixtures injected into a DC Glow discharge plasma (from Ref 10).

In the last years, our group in CIEMAT has worked in carbon/nitrogen bearing plasmas for the purpose of developing suitable techniques for the tritium inventory control in Fusion devices [6], directly associated to the formation of hydrocarbons and their plasma-driven decomposition into tritium rich films.

An exhaustive research has been done aimed at optimizing the conditions (pressure, power, gas mixture, wall composition, type of plasma...) of the so-called “scavenger technique”. A picture has arisen showing the possible paths for the formation of the detected products (HCN, acetylene, cyanogen, methylamine,...) and the role that wall conditions and gas mixture have on the final outcome of the plasma induced reactions. Although molecular nitrogen was initially selected as carbon-radical scavenger, it was soon discovered that recombination of nitrogen atoms with hydrogen on metal walls, leading to ammonia synthesis, could be the actual species playing the role. Therefore, direct ammonia injection experiments were performed in the divertor plasma simulator PILOT PSI on which methane seeded hydrogen plasmas under parametric conditions resembling those of ITER divertor (fig 3). Mass spectrometry and optical emission spectroscopy were used to analyze the outcome of the reaction, clearly dominated by HCN production. A complementary experiment was performed in an Inductively Coupled RF reactor, on which a physical separation between ammonia and the methane/H₂ plasma was possible. Analysis of the mass spectrometric data clearly indicated that direct reaction between ammonia and the carbon radicals produced in the plasmas was taking place.

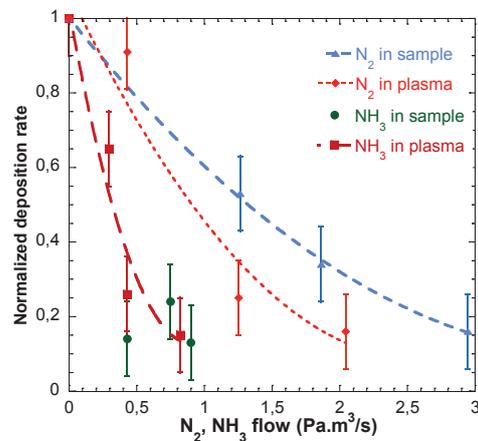


Fig 3. Effect of nitrogen and ammonia injection on the deposition of a carbon film from a hydrogen/methane plasma in Pilot PSI (see ref 6).

An obvious implication of this finding is that no ammonia decomposition, i.e., its injection into the plasma, is required for the scavenger effect.

Several techniques, aside from conventional mass spectrometry, have been developed or adapted to fully characterize the nitrogen carbon plasmas. Perhaps, the most efficient one has been Cryotrap Assisted Mass Spectrometry (CTAMS)[7]. By condensing the reaction products in a liquid nitrogen trap and looking at the associated perturbation into the recorded mass spectra, first, and to the mass spectra of the released products by slow TDS up to room temperature afterwards, a clear discrimination between the strongly overlapping cracking patterns of the involved species can be achieved with the help of the characteristic vapor pressure data at low temperatures.

One important finding concerning the heterogeneous reactions playing some role in the scavenger mechanism comes from the experiments dealing with the effect of the sampling characteristics in differentially pumped mass spectrometry. When the same chemical mixture (methane/nitrogen/hydrogen) was fed into the plasma reactor, a drastic effect of wall conditions and, in less extend, in the kind of walls of the connecting duct, was recorded. Thus, for example, metallic walls favor ammonia production while carbonized ones promote the formation of HCN and acetylene. The kind of wall in the connecting tube has an impact of the survival probability of the low sticking radicals conveyed from the plasma to the analysis regions as well. This is particularly evident when methyl or NH_x radicals are involved in the formation of the detected products.

Finally, deposition of carbon films in gaps existing in the first wall and divertor structures in ITER can account for up to half the total tritium retention. To date, thermooxidation or glow discharge in pure oxygen seems to be the most effective way of removing these deposits. However, several shortcomings of the technique exist. Besides the unwanted oxidation of other parts of the vessel, the production of, highly corrosive, tritiated water and the need of tritium recovery from it strongly complicates the design of the active gas handling system. For that reason, the use of nitrogen-containing chemical species (NH₃, N₂, NO₂) could represent an appealing alternative to the use of O₂. The results obtained by our group certainly point in this direction [8]. Together with ammonia as radical scavenger at the remote areas of ITER divertor, these techniques could be integrated into a single scheme [9] for the control of tritium inventory in a carbon-based material scenario in a fusion reactor.

References

- [1] Wang E.G., Prog Mater Sci. **41**, 241 (1997)
- [2] Zhang Y. et al. Appl. Phys Lett. **68**, 634-636 (2005)
- [3] Fraser M E et al. Plasma Chem Plasma Process. **5**, 163 (1985)
- [4] Trainer, Melissa G. et al. Proc Natl Acad Sci U S A. **28**; 18035–180421 (2006)
- [5] Tabarés F.L. et al. Plasma Phys. Control. Fusion. **44** L37-42 (2002)
- [6] F.L. Tabarés et al. “Suppression of tritium retention in remote areas of ITER by non-perturbative reactive gas injection”. Phys. Rev. Lett. **105**, 175006 (2010)
- [7] J.A. Ferreira and F.L. Tabarés “Characterization of minority species in reactive plasmas by cryotrap-assisted mass spectrometry” *Plasma Sources Sci. Technol.* **18** (2009) 034019
- [8] J.A. Ferreira, F.L. Tabarés, D. Tafalla “Optimization of non-oxidative carbon-removal techniques by nitrogen-containing plasmas”. J. Nucl. Mater. **390-391** (2009) 593-596
- [9] F.L. Tabarés et al. “Towards an Integrated Scenario for Tritium Inventory Control during ITER Operation under Carbon PFCs by Nitrogen-Based Chemistry” Proc IAEA Conference 2010 Daejeon, Ko. Paper #EXD/P3-33.
- [10] I. Tanarro...F.L. Tabarés, et al. “Ion Chemistry in Cold Plasmas of H₂ with CH₄ and N₂”. *J. Phys. Chem. A*, **111** (2007), 9003 -9012