Supplementary information for
## "Plasma-assisted catalytic formation of ammonia in $N_2$-$H_2$ plasma on tungsten surface"

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## MEMORY EFFECT OF THE SYSTEM

The study of ammonia formation from nitrogen-hydrogen plasma was performed in the newly built setup described in the main manuscript with the purpose of avoiding the memory effect of conventional SS UHV chambers where the ammonia molecules are trapped on the walls. For that, investigating this memory effect of the new system (i.e. its storage over the time for $NH_3$) was the first measure carried out via two sets of experiments. $NH_3$ gas was first introduced in the system at a fixed pressure of $5 \times 10^{-3}$ mbar (a pressure that will be shown later to correspond to the highest ammonia produced in the system). The gas was then fully pumped and RGA spectra were recorded during the full process. Figure 1a shows the RGA current intensity variation for the major ammonia peak at 17 amu. As can be seen, the full pumping of $NH_3$ from the gas phase takes a few seconds. However, this does not indicate a complete removal of ammonia from the vacuum chamber but only in the gas phase as long as a possible residual part of ammonia can be sticking to the walls. Therefore, a second experiment was performed consisting of degassing the ammonia by an Ar plasma. Figure 1b shows the start of the ammonia degassing process by the impact of Ar atoms from the gas phase already before starting the plasma. When the Ar plasma was then ignited, an ammonia peak reaches its highest values at $1.4 \times 10^{-11}$ Amps, a value that represents 3 % from the initially introduced ammonia. The peak was then continuously decreasing and the $NH_3$ was almost fully removed in less than 10 min indicating therefore that the system storage is very low and the degassing of the residual ammonia can be performed through an argon plasma.
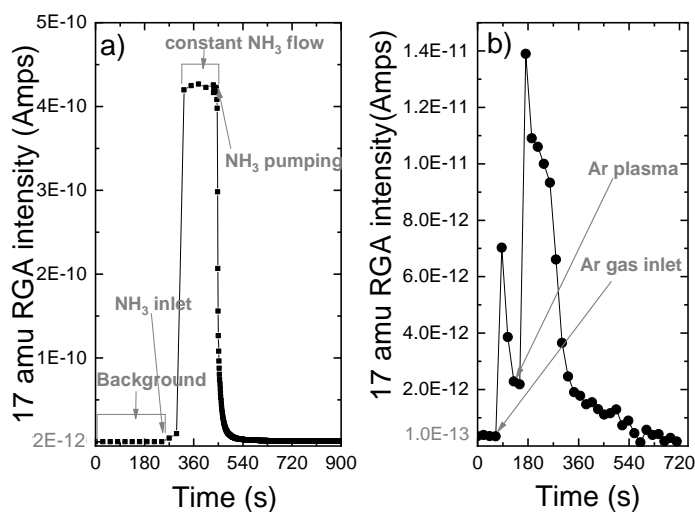


FIG. 1: Time evolution of the major ammonia peak at 17 amu following a) $NH_3$ inlet and pumping b) Ar gas inlet and plasma ignition

## WALL CONDITIONING

A wall conditioning step was carried out before each experiment consisting of cleaning of the quartz tube wall as well as the sample surface with pure Ar RF plasma at 120 W and $5 \times 10^{-3}$ mbar for two hours. Inert Ar gas has in fact the advantage of cleaning organic contamination from the surface without causing a chemical reaction or oxidation.

As the sample is floating its potential is set by the plasma potential ($V_P$). The floating potential ($V_F$) is defined by $V_P$-$V_F$ = 5 kTe so that ions are accelerated with 15 eV on the samples (with measured kTe=3 eV [1]).

Figure 2 shows the RGA spectra recorded at the beginning and the end of the Ar plasma cleaning procedure. As can be seen, the two hours Ar plasma completely removes hydrocarbons and carbon dioxide contaminants. Besides, more than 80 % of the initial water intensity was removed. Although during the process the water intensity represents less than 2 % of the total gas mixture, the peak will be taken into account during the deconvolution of the RGA measurements.

Note that the contaminants and specifically water molecules were removed from the surface not only by Ar atoms sputtering but also by thermal effect i.e. after 2 hours the measured temperature of the outer tube was around 90 degree promoting, therefore, the desorption of impurities from the surface.

An additional precaution to avoid the sample surface contamination consists of placing an alumina tube inside the surfatron plasma source to prevent the $SiO_2$ (from the tube wall) etching and redeposition on the W (an effect that we have observed for a long exposure to hydrogen plasma). The alumina tube was therefore used in this purpose to bypass the plasma-silica surface interaction in the most energetic place of the discharge. This inserted $Al_2O_3$ surface was verified to not affect the ammonia production results by performing an $NH_3$ formation experiment with and without adding the tube. Furthermore, all the W samples were analyzed by XPS after the experiments to confirm the absence of silicon on the surface.
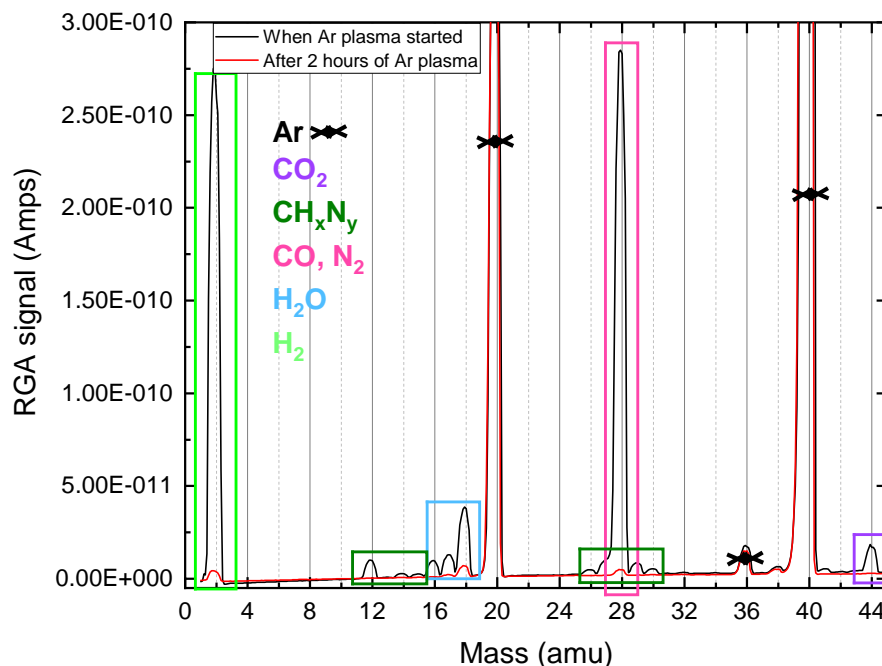


FIG. 2: RGA spectra recorded at the beginning and the end of the Ar plasma cleaning procedure identifying the major impurities

# RGA CALIBRATIONS

After the cleaning step, an RGA calibration was performed. It consists in determining the cracking patterns (CP) and the calibration factors (CF) for the different plasma species ($N_2$, $H_2$, $NH_3$ and $H_2O$). Electron impact ionization of a gas creates an array of ion fragments that make up the RGA spectra. The ratio between the major peak intensity and the other fragments intensity is referred as the cracking pattern. As an example, the $NH_3$ molecule presents 4 peaks in the RGA spectra: the main one at 17 amu for $NH_3^+$, one peak at 16 amu for $NH_2^+$, one at 15 amu for $NH^+$ and the last at 14 amu for $N^+$. The relative intensity of the different peaks for a given mass to charge ratio (m/q) constitutes the ammonia CP. Although the ratio of the peak heights in the cracking patterns can be found in tables of standard spectra, quantitative analysis of mixed gases generally requires accurate calibration of the cracking patterns (ionisation energy, but also on details of the individual instruments) with pure gases. Therefore pure $N_2$, $H_2$, $NH_3$

and $H_2O$ (introduced through a leak valve to the system) were injected separately in the quartz tube and their CPs were determined and summarized in table I. By varying the pure gas pressure, CPs were verified not to depend on the pressure.

TABLE I: Cracking patterns (CPs) of nitrogen, hydrogen, ammonia and water

|        | 1 | 14 | 15 | 16 | 17 | 18 | 28 |
|--------|---|----|----|----|----|----|----|
| $H_2$  | 1 |    |    |    |    |    |    |
| $N_2$  |   | 0.05 |    |    |    |    | 1 |
| $NH_3$ |   | 0.01 | 0.05 | 0.77 | 1 |    |    |
| $H_2O$ |   |    |    | 0.04 | 0.26 | 1 |    |

Calibration factor, on the other hand, represents the sensitivity of the RGA to a specific gas. It is, in fact, the proportionality factor of the measured detected current and the known partial pressure. Similar calibration procedure was reported by Malyshev and Middleman [2] and others [3–5]. Each gas CF was determined by relating the output current of the RGA to the known pressure of the gas measured by Baratron which is a capacitance manometer delivering direct absolute and gas independent measurement of pressure. CF of $N_2$, $H_2$ and $NH_3$ were extracted by introducing a controlled mixture of the 3 gases at known partial pressures. The choice of mixing the 3 gases together rather than introducing pure gases is justified by the detected change in the calibration factor when measuring pure gases or mixtures. This effect is probably resulting from the change in the preferential ionization of one gas over another when mixed together. Only the CF of $H_2O$ was determined for pure gas because of its high reactivity with $NH_3$ to form $NH_4^+$ (through acid-base reaction) that can contaminate the system. Besides, the water peak contributes less less than 2 % to the total pressure and its presence is assumed not to affect the other species CFs. Moreover, CF and CP calibration are performed before each experiment as the ageing of the RGA filament can affect these values.

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