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Study of a radio frequency plasma for production of equivalents of Titan's aerosols

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In Titan's atmosphere, solid aerosols are produced mainly by photochemistry reactions. In order to produce analogues of these aerosols, a capacitively coupled RF discharge in a N_2/CH_4 mixture is used. This paper reports plasma measurements done using optical emission spectroscopy, microwave resonant cavity and Langmuir probe. In steady-state conditions, electron density is measured as function of pressure and gas mixture. It is shown that an add of methane reduces the electron density. The formation and growth of the solid aerosols (dust) produced in the plasma are studied thanks to their influence on the self-bias voltage of the discharge, and on the intensity of a neutral nitrogen line. In transient regime, the self-bias voltage of the powered electrode is strongly coupled with the line intensity. It is shown that the characteristic time of dust formation is about one minute.

1. Introduction

The atmosphere of Titan, the largest satellite of Saturn, is principally composed of nitrogen (98%) and methane (2%). Photochemistry by solar photons induces the formation of solid aerosols. The descent of the European probe Huygens into the Titan's atmosphere in 2005 enables us to collect much more data on these aerosols than ever. Among these data, the most interesting were produced by : i) the DISR (Direct Imager/Spectral Radiometer) experiment that provided optical data on the aerosols and reflectance spectra of the satellite surface which is partly composed of aerosols [1]; ii) the ACP (Aerosol Collector and Pyroliser) experiment, designed at Service d'Aéronomie (SA), that provided compositional data on the aerosols [2]. However, these data remain difficult to explain without reference data, and the information retrieved from the only the Huygens data do not allow to understand the formation of solid particles in the Titan's atmosphere.

These are the reasons why laboratory simulations of the chemical-physics of the Titan's atmosphere are of primary interest, to better constrain its properties. Up to now, most of the tholins produced in laboratory are films deposited on solid surfaces. These solid films do not reproduce the fractal form of the Titan's aerosols, and solid substrate can influence the chemistry producing tholins. This is the reason why the SA team has started to produce analogues of Titan's aerosols in laboratory, using a Radio-Frequency (RF) Capacitively Coupled Plasma (CCP). This type of plasma, widely used in the field of micro electronic processes, is known to produce solid particles in the gas phase. This property makes this experiment original compared with experiments existing in Europe and on the USA studying Titan's tholins. It also allows producing large amounts of tholins which can be provided to laboratories collaborating in the field of planetology and astrobiology.

2. Experimental set-up

The experimental set up is a RF Capacitively Coupled Plasmas in agreement with the *"GEC reference cell"*. The experimental set up is named PAMPRE (a French acronym Production d'Aérosols en Microgravité par Plasma REactif) [3]. The plasma is generated by a radio frequency discharge (13,56 MHz) through a tuning match box and confined by a grounded metallic grid cage of 10cm in diameter. Various proportions of nitrogen-methane are obtained by mixing high purity nitrogen with a N_2-CH_4 (0.90-0.1). Pumping speed is controlled by a throttle valve and pressure measured by a capacitance gauge. Into the plasma, solid aerosols are directly produced from the gas mixture, are maintained in levitation by electrostatic force, and are ejected trough the confining metallic grid. Thus, solid particles are produced without any surface interaction.

The plasma is studied using Optical Emission Spectroscopy (OES) done in the UV visible range, using a 60cm monochromator fitted with a photomultiplier. The second positive and the first negative system of nitrogen and the CN band are observed. The metallic grid confining the plasma is used as a resonant cavity in the microwave range. The electron density is determined from the shift of the resonant frequency of this cavity. The TM_{210} mode, the most intense one, is used.

In order to validate the electron density measurements, an electrostatic probe is also used. As the probe is not compensated, only the ionic saturation current is measured.

Moreover, during the dust formation, the self-bia voltage (V_{dc}) of the powered electrode is measured.

3. Results and discussion in steady-stat conditions

3.1. Spectroscopy

Figure 1 presents an example of line intensit measurement as function of pressure done in stead state conditions. Two bands (0-2 and 1-3) of th second positive system of N_2, the (0-0) band of N_2 and of a CN band are presented. We observe that al these intensities increase with pressure, reach a maximum for 0.8 mbar and then decrease.

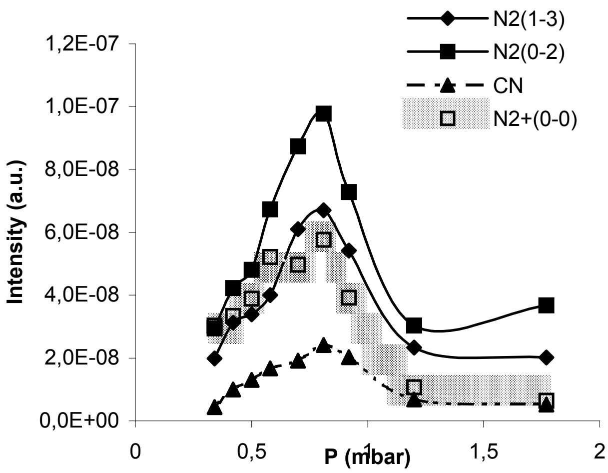

Fig. 1: Lines intensities as function of total pressure for a N_2-CH_4 (0.98-0.02) mixture.

3.2. Electron density measurements

The electron density is measured as function of the pressure in pure N_2 plasma, and in N_2-CH_4 mixtures. All results are presented in figure 2.

i. Pure nitrogen

In pure nitrogen (empty diamonds), the electronic density, measured by microwave resonant cavity, increases with pressure, reaches a maximum for 0.4 mbar and decreases. The decay of electron density for pressure higher than 0.4 mbar is confirmed by Langmuir probe measurements (full diamonds). The electron density is deduced from ionic saturation current, assuming the equality between electrons and positive ions densities and an electron temperature of 2eV. This electron temperature has to be validated by plasma modelling. Even if an uncertainty exists on the electron temperature, the decay of electron density for pressure over 0.4 mbar is confirmed. For pressures below 0.4 mbar, many uncertainties exist (size of the sheath, electron temperature, accuracy of current measurement,...).

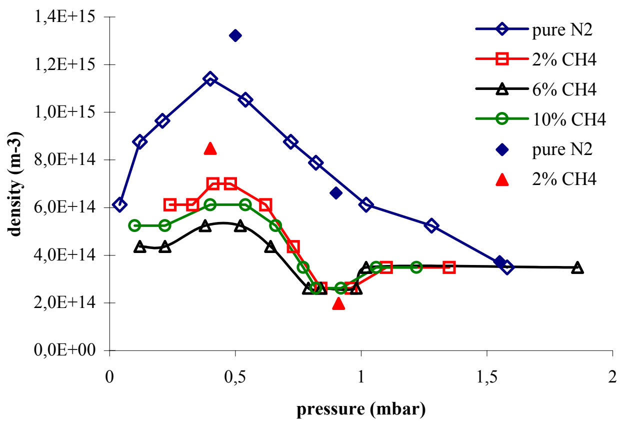

Fig.. 2. Evolution of the electronic density (cavity measurements, empty symbols) and ionic density (probe measurements, full symbols) with pressure in different mixture plasmas and pure nitrogen.

ii. Mixtures of nitrogen and methane

As electron density measurements are validated in pure nitrogen, mixtures are now studied. Results are also presented in figure 2 for three different methane percentages: 2%, 6% and 10%.

Electron densities measurements are done by microwave resonant cavity method. We observe similar variations with pressure as in pure nitrogen, but electron densities are lower than in pure nitrogen. For all the studied mixtures, a minimum is observed at a pressure of 0.8 mbar. This minimum is not understood, but, we have observed that at 0.8 mbar, the production of tholins is efficient.

The decay of electron density for pressure over 0.4 mbar is also observed by probe measurements. But, only the N_2-CH_4 (0.98-0.02) mixture has been used and only for two pressures. As a matter of fact, in N_2-CH_4 mixtures, the probe remains conductive during few seconds, because organic material is deposited. For these two pressures, it was not possible to point out a difference between ions and electrons densities. Then, electron attachment on tholins is not measurable using this technique.

3.3. Discussion

OES and electron density presents the same variations as function of pressure: an increase with pressure, a maximum and a decay. Even if these variations are similar, the maximum of line intensity is obtained for pressures higher than for electron density. These results are up to now not well understood and have to be explained using a modelling of the RF-plasma discharge.

4. Results and discussion in transient regime

4.1. Optical spectroscopy and V_{dc}

In the transient regime, the self bias voltage (V_{dc}) and the intensity of the (0-0) transition of the second positive system of nitrogen (at 337 nm) are recorded during the beginning of the RF plasma discharge in order to point out the dust formation.

i. Comparison between V_{dc} and I_{337}

In the following, the dust particle formation and growth is monitored thanks to the time evolution of the self-bias voltage of the discharge. This parameter is correlated with the time evolution of the nitrogen line at 337 nm (fig.3).

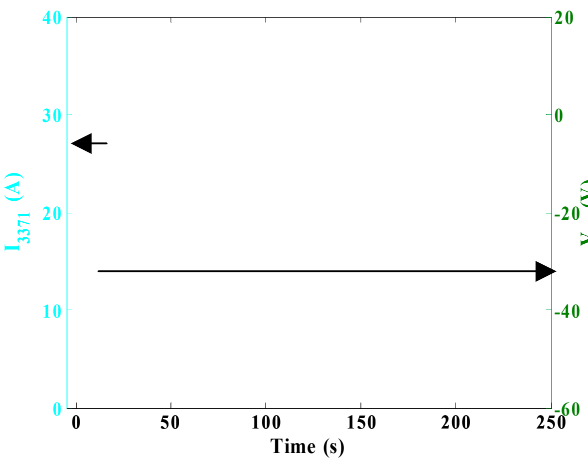

Fig.3. Time evolution of V_{dc} and I_{337} in a N_2/CH_4 dust forming plasma.

A self-bias voltage is set at the driven electrode of a Capacitively Coupled Radio Frequency (CC-RF) discharge if both electrodes differ in size and when a coupling capacitor (here the match box) is inserted between the RF generator and the electrode (or when the electrode is non-conductive). If one considers a given sinusoidal voltage, applied to the capacitor formed by the electrodes, first the voltage over the plasma is the same as the applied voltage. During the first half-period, when the voltage is positive, electrons are accelerated toward the driven electrode. The capacitor is charged up by the electron current, and the voltage over the plasma drops. On the second part of the cycle, the applied voltage changes polarity, hence the voltage over the plasma as well. The capacitor is now charged up by the ion current, and the voltage over the plasma drops as well. The charging process occurs until the capacitor is sufficiently negatively charged (due to higher mobility of the electrons) so that the electron and ion fluxes (integrated over a RF cycle) are equal. This process finally results in a time-averaged dc bias at the driven electrode [4]. Thus the self-bias (V_{dc}) evolution gives an idea of the evolution of the couple electron density/electron temperature.

As can be seen in figure 3, in a dust forming plasma, the value of V_{dc} is not constant in time. V_{dc} exhibits a well-defined time evolution, linked to dust particle formation in the plasma. On the first part of the curve, we can identify a slightly decreasing part (between 0 and 10 s). It can be explained by the formation and accumulation of very small dust particles (few nanometers), that modify the electron collision frequency. In a second part, a drastic decrease in the amplitude of V_{dc} indicates that dust particles are big enough to attach electrons and thus modify the value of the self-bias voltage. This fast decrease can be compared to the aggregation phenomenon, well-known in silane-based plasmas [5]. Moreover, after around 100 s, V_{dc} seems to tend to a stable regime. In some cases, slow oscillations of V_{dc} are observed. The evolution of Vdc for few minutes for two RF powers is presented in fig.4. These oscillations correspond to successive generations of dust produced into the plasma.

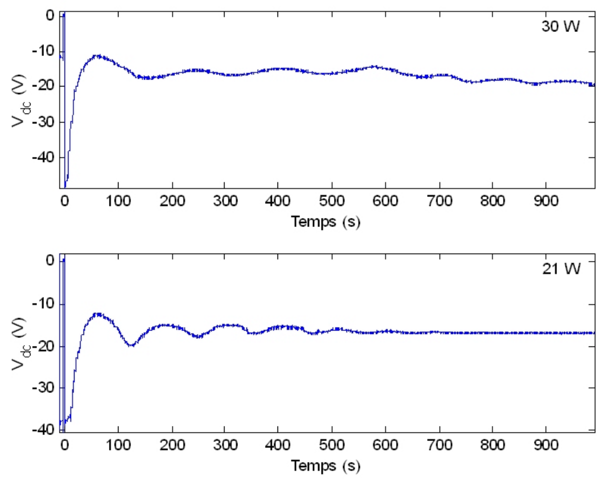

Fig.4. Time evolution of V_{dc} for two RF powers.

By looking at the time evolution of I_{337} (fig.3) we can observe that it also responds to the modifications in the plasma. We can notice that both V_{dc} and I_{337} respond to the plasma modifications, but not in the same way. At the plasma ignition, $|V_{dc}|$ increases while I_{337} increases too. This behaviour is due to the large amount of free electrons in the plasma. In a second time, $|V_{dc}|$ exhibits a slightly decreasing plateau and then decreases while I_{337} begins to decrease. Both V_{dc} and I_{337} reflect evolution of electron density and temperature. The line intensity of the second positive system can also be linked with the pooling reaction:

$$N_2(A) + N_2(A) \rightarrow N_2(C) + N_2(X)$$

where $N_2(A)$ is a nitrogen metastable state depending on the physico-chemistry of the plasma .

ii Parametric study

A parametric study of the evolution of V_{dc} has been performed. First, different dilutions of CH_4 in N_2 are studied. A V_{dc} measurement for a given total pressure (P = 1 mbar) and a given RF power (30 W) for different CH_4 dilutions from 1 to 7% is presented in fig.5. We observe that as the amount of methane increases, the characteristic time for dust production increases too. In the case of a 10% dilution (not shown here), the corresponding curve is quite similar to the one of 0% methane, where no dust can be formed. However, dust particles are known to be synthesised from this dilution. This result only means that they don't affect the discharge enough to be detected in the self-bias voltage.

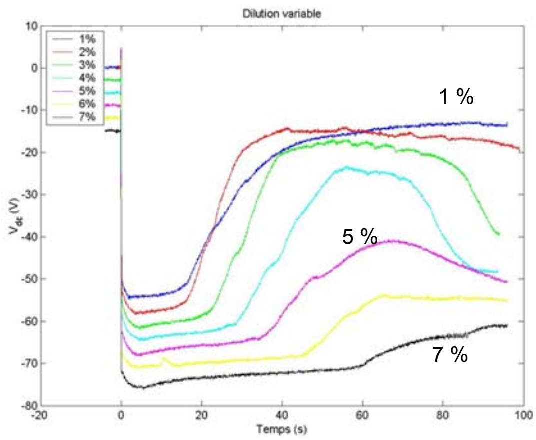

Fig.5. Influence of CH_4 amount on dust formation

The total pressure has also an influence on the characteristic time of dust particle production. Fig. 6 presents the characteristic time of dust formation for a dilution of 2% of methane and a RF power of 30W. Dust formation is evidenced to be faster when pressure increases. In the same way (by the RF power), we showed an injected power of 30W leads to an optimal fast kinetics allowing to produce huge quantities of particles. Finally, this parametric study allowed us to confirm which experimental conditions are the optimal to dust particle formation.

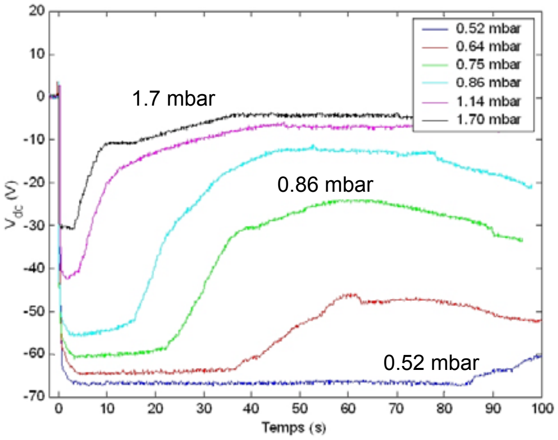

Fig.6. Dust formation as function of pressure

5. Conclusion

The RF capacitively coupled plasma is a good tool for the production of solid particles in a N_2/CH_4 mixture. In this paper, we have shown that electron density is strongly coupled with the amount of methane. From OES and microwave resonant cavity measurements, we have shown that nitrogen radiative states have similar behaviours.

The dust formation is pointed out by the self-bias voltage that can be used as a monitoring tool. The characteristic time of dust formation is as more short as the amount of methane is weak and as the pressure is high. The parametric study of dust formation shows that Titan's conditions (2% methane) are favourable to obtain particles. Moreover, in our experiment, dust production is more efficient for a pressure about 1mbar.

As plasma properties vary with pressure, these presented results have to be explained using a plasma modelling. This work is in progress [6].

6. References

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Acknowledgments

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