Compared chemical compositions of grains and thin films produced in an N_2/CH_4 dusty plasma simulating Titan's aerosols

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Experiments are carried out with a Radio-Frequency Capacitively Coupled Plasma (RF CCP) at 13.56 MHz. The plasma discharge is produced between a polarized cathode and a grounded metallic grid (anode) surrounding and confining the plasma (Szopa et al. 2006). The gas mixture is continuously injected in the reactor at 55 sccm and pumped through a rotary valve vacuum pump. The gas flow composition is adjusted in order to introduce from 0% to 10% of CH_4 in N_2. Four mixtures conditions are chosen here to scan chemical conditions in agreement with the methane concentration profile in the atmosphere of Titan: 1, 2, 5 and 10 % of CH_4 diluted in N_2. Experiments are performed at room temperature and a 0.9 mbar pressure.

In our experimental set up, the thin organic films are produced on SiO_2 substrates placed on the grounded anode, whereas levitating grains are produced simultaneously in the gas volume without interaction with the walls. Films are analyzed by X-ray Photoelectron Spectroscopy (XPS) and Secondary Ion Mass Spectrometry (SIMS). The solid grains have been previously analyzed by elemental analysis in (Sciamma-O'Brien et al. 2010).

For XPS measurements, sputter depth profiling is performed using an Argon ion gun (2 keV energy, 10 µA current), with an etch time of 10 s. An etch time of 10 s is equivalent to an etching thickness of 15 nm, calibrated using Ta_2O_5. After each etching step, XPS measurements (C, N, O, Si) are performed. XPS analysis directly provides the C/N ratio of the films, but the hydrogen content, important for characterizing an organic material can unfortunately not be given solely by this technique.

After XPS analysis, the organic solid film is covered with a thin gold film for SIMS analyses. Those are performed using a Cameca IMS4F ion microscope. The organic film is bombarded by a 14.5 keV Cs^+ ion beam, of 10 µm diameter. The etch time can reach 3000 s. The ions monitored are therefore H^-, $^{12}C^-$, $^{16}O^-$ as film constituents.

XPS analysis shows that the first external layer, of about 20 nm thickness, has a higher oxygen content. Oxygen reaches up to 10% of the elemental ratio at the surface of the film. Below this oxidation layer, the film is homogenous in terms of its N/C ratio, confirmed by SIMS, which shows that the samples are homogeneous down to the film-substrate interface.

Table 1. Elemental analysis of both thin films and grains. Thin films N/C ratios are determined here from XPS data at a 150 nm depth; and thin films H/C ratios are taken from $Cs\text{-}M^+$ molecular ions from SIMS analysis. The grains elemental analysis has been made in (Sciamma-O'Brien et al. 2010).

Samples	Thin films		Grains	
	N/C (XPS)	H/C (SIMS)	N/C	H/C
1%	0.4	~0.1	0.9	1.1
2%	0.3	~0.1	0.8	1.1
5%	0.2	~0.1	0.6	1.2
10%	0.1	~0.1	0.4	1.4

Films are found less rich in nitrogen by a factor of 2 to 3, compared to grains. This lower nitrogen content explains the lower amine signature compared to the aliphatic one observed in a previous first study (Quirico et al. 2008) opposing films and grains by mid-infrared absorption spectroscopy.

The H/C ratio in the films is independent of the methane content, which is not the case for the levitating dust particles. The H/C ratio in grains was indeed found to increase with the initial methane amount: C was found constant by elemental analysis, meaning that this ratio increase corresponds to a higher H amount in the grains (in agreement with the suspected role of H as inhibitor for grains growth). Moreover, the similar ~0.1 H/C ratio obtained by SIMS for all films is much lower than the H/C observed in the grains.

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