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Laboratory analogues simulating Titan's atmospheric aerosols: Compared chemical compositions of grains and thin films

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ABSTRACT

Two sorts of solid organic samples can be produced in laboratory experiments simulating Titan's atmospheric reactivity: grains in the volume and thin films on the reactor walls. We expect that grains are more representative of Titan's atmospheric aerosols, but films are used to provide optical indices for radiative models of Titan's atmosphere.

The aim of the present study is to address if these two sorts of analogues are chemically equivalent or not, when produced in the same N_2–CH_4 plasma discharge. The chemical compositions of both these materials are measured by using elemental analysis, XPS analysis and Secondary Ion Mass Spectrometry. The main parameter probed is the CH_4/N_2 ratio to explore various possible chemical regimes. We find that films are homogeneous but significantly less rich in nitrogen and hydrogen than grains produced in the same experimental conditions. This surprising difference in their chemical compositions could be explained by the efficient etching occurring on the films, which stay in the discharge during the whole plasma duration, whereas the grains are ejected after a few minutes. The higher nitrogen content in the grains possibly involves a higher optical absorption than the one measured on the films, with a possible impact on Titan's radiative models.

1. Introduction

Titan, the largest satellite of Saturn, is surrounded by a brownish opaque photochemical smog. This smog is made of solid organic aggregates of a few hundreds of nanometers, rich in nitrogen, and with a global $C_xH_yN_z$ composition (Israel et al., 2005; Tomasko et al., 2005; Tomasko et al., 2008). The chemical complexity of this smog is far from being understood despite the numerous *in situ* data by the ongoing Cassini-Huygens mission (Israel et al., 2005; Lavvas et al., 2013; Vinatier et al., 2012; Waite et al., 2007). Several experiments have been developed to infer their chemical composition by studying laboratory analogues (Cable et al., 2012; Coll et al., 2013; Tran et al., 2003). According to the experimental setups, the analogues (also named tholins in the following) are produced on the wall of the reactor, or in the volume, producing respectively organic thin films or spherical shaped individual grains of a few thousands nanometers in diameter (Coll et al., 1999; Hadamcik et al., 2009).

Little attention has been drawn to the possible effect of such different growth pathways on the chemical composition of the analogues. Individual grains and thin films are usually considered as equivalent materials in terms of their chemical signatures, and used alternatively depending on the involved analysis technique. Ellipsometry for example requires exclusively thin films to determine the optical indices of the material (Mahjoub et al., 2012; Sciamma-O'Brien et al., 2012), whereas high-resolution mass spectrometry analysis has been performed on grains only (Pernot et al., 2010; Somogyi et al., 2012). However an infrared spectroscopic comparative study showed some differences between grains and thin films produced in the same experimental conditions (Quirico et al., 2008).

The aim of this work is to address this common paradigm by comparing the chemical composition of both solid materials produced simultaneously in a plasma experiment simulating the formation of solid organic aerosols in the atmosphere of Titan (Alcouffe et al., 2010; Szopa et al., 2006). The chemical

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composition of these tholins grains has been extensively studied in the past by infrared absorption spectroscopy, mass spectrometry and elemental analysis (Quirico et al., 2008; Carrasco et al., 2009; Sciamma-O'Brien et al., 2010). The chemical composition of the tholins thin films has to date only been globally characterized by infrared absorption spectroscopy (Gautier et al., 2012). The present work provides the first chemical analysis of tholins thin films along their depth profile, using XPS (X-ray Photoemission Spectroscopy) and SIMS (Secondary Ion Mass Spectrometry) analysis. Those two techniques are commonly used for organic films analysis in general, (Johnston and Ratner, 1996; Retzko et al., 2001; Sabbatini and Zambonin, 1996; Shi, 1996) and are well adapted for nitrogen containing films in particular (Hanuš et al., 2012; Maurau et al., 2012; Vogelsang et al., 2011). Moreover two kinds of substrates are used, made of CaF_2 and SiO_2, to analyze the sensitivity of the solid deposition to the nature of the substrate.

2. Experimental section

2.1. Sample production

Experiments are carried out with the PAMPRE set-up, based on a Radio-Frequency Capacitively Coupled Plasma (RF CCP) at 13.56 MHz (Szopa et al., 2006). RF plasmas are also used in nitrogen methane mixtures for the production of CNx hard films (Hao et al., 2007) or hydrogenated amorphous carbon films (a-C:H) (Géraud-Grenier et al., 2004). Their efficiency to produce solid material explains their interest to simulate the formation of Titan's aerosols.

The plasma discharge is produced between a polarized cathode and a grounded metallic grid (anode) surrounding and confining the plasma. The same power discharge of 30 W is injected in the whole electric circuit for all the experiments. Half of the injected power is effectively consumed to produce the discharge itself (Alves et al., 2012). 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. Two high purity gas bottles are used, one of pure N_2 and one containing a N_2–CH_4 mixture with 10% CH_4 (Sciamma-O'Brien et al., 2010). Four mixtures conditions are chosen here to scan chemical conditions in agreement with the methane concentration profile in the atmosphere of Titan (Waite et al., 2005): 1, 2, 5 and 10% of CH_4 diluted in N_2. Experiments are performed at room temperature and a 0.9 mbar pressure. The gas in the reactor is slightly warmed by the plasma discharge reaching a stable temperature of 315 and 340 K for methane amounts of 2 and 10% respectively (Alcouffe et al., 2010). The reactor walls are slowly warmed accordingly but no change is observed in the 2-hrs experiments performed here.

RF CCP discharges are well-known for producing simultaneously thin films on substrates and solid particles (grains) in the volume of reactive gas mixtures (Bouchoule, 1999). In our experimental set up, the thin organic films are produced on the grounded anode, whereas levitating grains are produced simultaneously in the gas volume without interaction with the walls (Berndt et al., 2009). To collect the films on the grounded electrode, two optical disks with a 1 cm diameter and a 1 mm thickness made of respectively CaF_2 and SiO_2 are symmetrically placed in the reactor to provide comparable substrates for thin film deposition. These two substrate materials are chosen to be chemically different but with similar geometry and similar electric properties in the plasma discharge. A 2 h experiment duration is chosen, to limit the thickness of the films below 1 μm (Mahjoub et al., 2012).

The film synthesis is a reproducible process. In previous studies we chose the same experimental conditions: silicon substrates, 5% of injected CH_4, 55 sccm gas flow, 30 W of injected power (Mahjoub et al., 2012; Gautier et al., 2012). Gautier et al. (2012) synthesized three films in a 3 h-duration experiment, and Mahjoub et al. (2012) synthesized a film in a 2 h-duration experiment. The obtained thicknesses are reported in Table 1. The growth rates are in agreement for the four samples showing that the films grow linearly, at least in the few-hours duration range of the experiments, and are well reproducible.

Table 1
Films thicknesses obtained in various synthesis, using the same experimental conditions: Silicon substrates, 5% of injected CH_4, 55 sccm gas flow, 30 W of injected power. Three substrates were placed in the plasma box for the same experiment in (Gautier et al., 2012). The uncertainty of the film thickness is given by the non-uniformity calculated by Complete-EASE™ software (Mahjoub et al., 2012).

Synthesis duration (h)	Thickness	Thickness/h	Reference
3	1250 ± 40	417 ± 13	Gautier et al. (2012)
3	1340 ± 40	447 ± 13	Gautier et al. (2012)
3	1300 ± 40	433 ± 13	Gautier et al. (2012)
2	850 ± 30	425 ± 15	Mahjoub et al. (2012)

The films samples are carefully collected after air exposure of the reactor and stored in individual boxes. The syntheses are performed in a one single experimental campaign of a few weeks; just before the analysis of the films in order to limit as much as possible the time interval between the synthesis and the analysis. Films are analyzed here by X-ray Photoelectron Spectroscopy (XPS) and Secondary Ion Mass Spectrometry (SIMS). And solid grains have been previously analyzed by elemental analysis in (Sciamma-O'Brien et al., 2010).

2.2. X-ray Photoelectron Spectroscopy (XPS)

The first step of the analysis is a chemical probe by XPS along the depth of the films. This is achieved using a Thermo Scientific K-Alpha instrument, with a monochromatic Al–K α X-Ray source (1486.6 eV) located in the ILV laboratory. Charge compensation is used to overcome charging effects on the organic films. The X-ray spot is set at a 400×400 μm size on the substrate. The pass energy of the analyzer is used in Constant Analyzer Energy mode, with a 50.0 eV pass. The energy step size is set at 0.1 eV. 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 are performed. The data treatment is performed using a Shirley baseline and a 30% Lorentz-Gaussian distribution for the peak fitting. XPS measurement tracks every component of the organic film but hydrogen.

The elemental composition is therefore given as normalized results, taking into account the expected elements composing the films and possible contributions of the substrate (Ca and F for films deposited on CaF_2 substrates; and Si and O for SiO_2 substrates), but no hydrogen. Therefore 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 by this only technique.

2.3. Secondary Ion Mass Spectrometry (SIMS)

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 located in the GEMAC laboratory. The organic film is bombarded by a 14.5 keV Cs^+ ion beam, of 10 μm diameter. The etch time can reach 3000 s.