Densities of active species in N_2/CH_4 afterglows with application to nitrogen and carbon doping of anatase nanocrystals and ALD TiO_2

A. Ricard[1], J.P. Sarrette[1], Y. Wang[2], Y.K. Kim[2]

[1] *LAPLACE, Université de Toulouse, CNRS, INPT, UPS, 118 route de Narbonne, 1062 Toulouse, France*
[2] *Departmentof Physics, Ajou University, Suwon 443-749, South Korea*

N_2 / 0-3$^0/_{00}CH_4$ microwave (HF) flowing afterglow emissions have been characterized by optical emission spectroscopy at pressure between 4 and 20 Torr in a tube of 18 mm internal diameter (i.d.) at constant flow rate (Q_{tot} = 0.5 slpm) and injected HF power (P_{HF} = 100 W). The N_2 1st pos at 580.4 nm and CN violet at 384.7 nm band system intensities were recorded along the tube in the late afterglow region. After calibration of the N atom density by NO titration, the absolute concentrations of N and C atoms were determined. The C-atom density shows a maximum value of 4.7 10^{13} cm^{-3} at 13 Torr for the N_2 / 0.04$^0/_0CH_4$ mixture. Anatase nanocrystals and ALD (Atomic Layer Deposition) TiO_2 samples were exposed to optimum afterglow conditions at temperatures ranging from 300 to 600 K. Surface-selective chemical modifications of TiO_2 samples are evaluated by XPS.

1. Introduction

In various applications such as photocatalysis, photovoltaics and sensors, the performance of TiO_2 is largely determined by the detailed chemical structure of the surface. For example, the introduction of nitrogen in TiO_2 can reduce the bandgap below 3.0 eV for a visible activity in photocatalysis. Nevertheless, the N-doped TiO_2 performance largely depends on the control of the nitrogen bonding structure and distribution between the surface and the bulk. In addition, carbon may also displace the lattice Ti to give C-doped TiO_2 which may show enhanced visible light absorption and photoactivity. However, the ultimate performance is strongly related with detailed bonding nature of carbon on the surface as well as within the TiO_2 matrix.

From this point of view, flowing afterglows at reduced pressure can be very useful because of their high concentrations in atoms and of their simplified chemistry, easily monitored through the operating parameters (pressure, gas flow rate, injected power).

The aim of the present study is to maximize the production of N and C-atoms in N_2/CH_4 afterglows and to expose anatase nanocrystals and ALD TiO_2 samples in optimal conditions. X-ray photoemission spectroscopy (XPS) is used to quantitatively evaluate the modifications induced on the extreme surface composition.

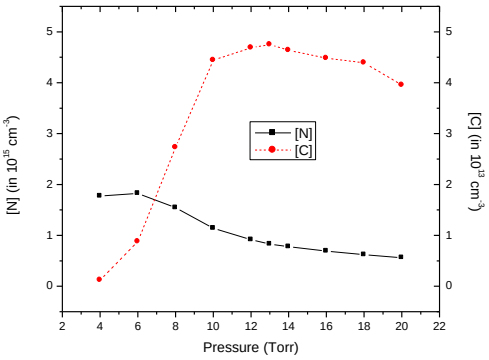
2. Results

In full late afterglow conditions, the N-atom gas phase chemistry is essentially reduced to the 3-body recombination process and the N-atom density [N] is related to the N_2 1st pos emission at 580nm I_{580} through relation (1):

$$I_{580} = k\,[N]^2, \qquad (1)$$

where the proportionality constant k can be obtained by NO titration [1]. Similarly, the emission intensity I_{385} of the CN violet system at 385 nm can be used to obtain the absolute C-atom concentration, once the N-atom density is known.

Varying the CH_4 amount (< 3$^0/_{00}$) and the pressure in the 4-20 Torr range, it is found that the [C]/[N] ratio shows a peak maximum for the N_2/0.4$^0/_{00}CH_4$ gas mixture and that a maximum [C] atom density of 4.7 10^{13} cm^{-3} is obtained at 13 Torr, with a corresponding N-atom density equal to 8.3 10^{14} cm^{-3}.



Pressure variation of N and C-atoms densities in the N_2/0.4$^0/_{00}CH_4$ late afterglow (0.5 slpm, 100 Watt)

Anatase nanocrystals and ALD TiO_2 samples were exposed in optimal afterglow conditions at temperatures ranging between 20 and 300°C and XPS analysis of the treated samples is in progress.

3. References

[1] H. Zerrouki, A. Ricard, J.P. Sarrette, Contrib. Plasma Phys. **54** (2014) 827.