



HAL
open science

Low pressure microwave plasma process from Zr and Ti metalorganicprecursors: A comparative study of metal oxide and metal/oxide/silica films

Patrice Raynaud, Ines Martinko, Alberto Palmero, Laurent Thomas, Audrey Soum-Glaude, Daniele Ngoue, Aïssatou Diop, Stéphanie Roualdès, V. Rouessac, Arie van Der Lee, et al.

► **To cite this version:**

Patrice Raynaud, Ines Martinko, Alberto Palmero, Laurent Thomas, Audrey Soum-Glaude, et al.. Low pressure microwave plasma process from Zr and Ti metalorganicprecursors: A comparative study of metal oxide and metal/oxide/silica films. 47th EPS Conference on Plasma Physics, Jun 2021, Sitges (Barcelona), Spain. <hal-04749011>

HAL Id: hal-04749011

<https://hal.science/hal-04749011v1>

Submitted on 22 Oct 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

Low pressure microwave plasma process from Zr and Ti metalorganic precursors: A comparative study of metal oxide and metal/oxide/silica films.

P. Raynaud¹, I. Martinko², A. Palmero³, R. Alvarez³, L. Thomas⁴, A. Soum-Glaude⁴, D. Ngoue⁴, A. Diop⁴, S. Roualdes⁵, V. Rouessac⁵, A. Van der Lee⁵, O. Antonin^{2,6}, T. Nelis⁶

¹CNRS – Laboratory of Plasma and Conversion of Energy (LAPLACE), Toulouse, France

²University of Toulouse, Toulouse, France

³Spanish Council of Research (CSIC), Materials Science Institute of Seville, Seville, Spain

⁴Laboratory of Processes, Material and Solar Energy (PROMES), Perpignan, France

⁵European Institute of Membranes (IEM), Montpellier, France

⁶Berner Fachhochschule (BFH), Institute ALPS, Biel-Bienne, Switzerland

In this work, metal oxide and metal oxide/silica « composite » thin films were obtained by PECV in multi-dipolar ECR Plasma reactor from gas mixture composed of oxygen gas and metalorganic precursors. [Zirconium (IV) tert-Butoxide (ZTB, $ZrO_4C_{16}H_{36}$) and Titanium (IV) Isopropoxide (TTIP, $TiO_4C_{12}H_{28}$)]. To investigate the plasma behavior, OES, FTIR and MS have been employed while the characteristics of the deposited thin films have been examined by FTIR, XPS, SEM, AFM, X-ray reflectivity (XRR) and ellipsometry porosimetry (EP).

In the first part of the work, the study focuses on thin film characteristics as a function of O_2 /precursor ratio. As O_2 /precursor ratio increased, analyzed properties evolve similarly in both zirconium and titanium oxide films. Composition of the films progresses from organic to almost inorganic with the addition of oxygen to plasma gas mixture. The growth mode evolves from homogeneous to columnar in highly oxidized plasma. From a fundamental point of view, columns obtained experimentally in ZTB and TTIP were compared with those obtained by theoretical simulation (Monte Carlo method) in order to understand the observed morphological differences (column width).

Further, we investigated the influence of the total gas pressure of plasma gas mixture composed of O_2 (95%)/metalorganic precursor (5%) on thin film growth. Chemical composition of the films does not change drastically with the increase in pressure. In the case of ZTB, total gas pressure has a strong influence on the morphological characteristics: columnar growth disappears at pressures above 8 mTorr. This phenomenon was not observed in films deposited in TTIP plasma.

In the third part of this work we have demonstrated the possibility of synthesizing $ZrSi_wO_xC_yH_z$ and $TiSi_wO_xC_yH_z$ homogeneous thin composite films by simultaneously introducing a metalorganic precursor and an organosilicon precursor [Hexamethyldisiloxane (HMDSO, $OSi_2C_6H_{18}$)] into the reactor. Increase in the fraction of HMDSO in the plasma gas mixture induces a change in growth mode from columnar growth mode (low HMDSO content) to uniform growth mode (higher HMDSO content). This work has highlighted the various possibilities of obtaining a large panel of thin film properties in terms of density, optical index and porosity.

Keywords: low pressure PECVD, Thin films, metal oxide, metal oxide/silica, ZTB, TTIP, HMDSO