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

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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