



Entropy tailoring in oxynitride coatings by colliding plasmas approach

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The increase in fossil fuel demand worldwide, due to rapid socioeconomic development, has impacted on the environment and contributed to climate change. Addressing these issues requires the development of green technologies aimed at creating sustainable and eco-friendly energy systems. We propose a strategy based on entropy control of oxynitride thin films which consist in tuning multicomponent systems and increasing the structural and compositional complexity coupled during the deposition process. Our approach focuses on a dual-PLD system that utilizes colliding plasmas to produce complex nanocrystalline structures with both structural and compositional gradients.

In this work we used 248 nm KrF excimer laser sources operated at a repetition rate of 10 Hz and 2 J/cm² fluence were synchronized by an external pulse generator signal used to ablate TiN/ZrN and HfN targets placed at an angle of 30° with respect to the substrate central axis. Chemical and structural control was achieved by controlling the surface oxidation reaction and gas phase reaction by adding O₂ pressures (1×10^{-4} up to 10 Pa). Using this approach to improve the photocatalytic properties, we controlled the photocatalytic activity of selected system by local clustering, surface reconstruction, and formation of interface and vacancy in the multiphase state. The deposited films were investigated with Atomic Force Microscopy, Scanning Electron Microscopy, X-ray Diffraction, X-ray Photoelectron Spectroscopy and thermo-stimulated desorption and emission.

In-situ monitoring of the process plays an essential role towards building plasma-thin film correlation and thus complementary in-depth analysis of oxidation scenarios was performed by electrical (angle- and time-resolved dual electrical probe) and optical monitoring during pulsed laser deposition of TiON, HfON and ZrON. The investigations revealed that gas phase oxidation for Zr system can occur as low as 10⁻³ Pa O₂ while the Ti and Hf systems are characterized by another oxidation threshold. The gas phase oxidation was quantified by analysis the special signature in the charge particle density distribution. A time-resolved study uncovered intricate dynamics within a plasma-temperature, characterized by unique angular structuring. A complete correlation between the acceleration dynamics and O⁺ presence in the plasma is given by comparison with structural analysis of the deposited films. Their effectiveness was investigated by catalytic redox processes.

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