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ON NOVEL MERITS OF (PLASMA-ASSISTED) ATOMIC LAYER DEPOSITION FOR NEXT-GENERATION ENERGY APPLICATIONS

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NiO and Co_3O_4 find major application in energy conversion and storage devices, such as photovoltaics, batteries and electrocatalysis. We have recently shown that combining these chemistries is beneficial for selected applications. We synthesize these layers by atomic layer deposition, which enables accurate control over film conformality, uniformity and stoichiometry, opto-electrical properties, crystal orientation and texture.

In this contribution, we will review selected merits of ALD when combined with plasma processing by presenting case studies where the above mentioned chemistries are investigated for the preparation of NiO hole transport layers for metal halide perovskite devices and of NiO and $NiCoO_x$ electrocatalysts for H_2O splitting.

Specifically, plasma-assisted ALD NiO is found to outperform the thermal ALD counterpart in terms of current density during the oxygen evolution reaction [1], because the plasma-ALD NiO layer is efficiently converted to the β-NiOOH phase. At the same time, plasma-assisted ALD NiO films are characterized by a Ni-to-O ratio of 0.82 ± 0.04, lower than the thermal ALD counterpart (0.94 ± 0.04). This comparison indicates that the plasma-assisted NiO films rich in Ni^{3+} acceptor states: while inducing an improvement in film conductivity, these are also responsible for redox reactions with the metal perovskite absorbed in photovoltaic devices, thereby negatively affecting the device performance.

The plasma-assisted ALD approach for the synthesis of $NiCoO_x$ with tunable chemical composition and crystallographic structure between rock-salt and spinel, enables to unravel the dual electrochemical behavior of these films [2]. In detail, Co-rich spinel type films display an electrochemical behavior which is confined at their surface, whereas Ni-rich rock-salt films exhibit a dynamic bulk-activation. Moreover, the plasma-ALD approach leads to film texture control, when NiO and Co_3O_4 are combined in heterostructures: Co_3O_4 adapts its growth direction to align with the <100> texture of NiO, while NiO similarly mimics the <111> textured Co_3O_4 [3].

References :

[1] S. Haghverdi Khamene, C.A.A. van Helvoirt, M. Tsampas, M. Creatore, J. Phys. Chem. C 127, 22570 (2023)
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