Thin Films prepared by PLD: model systems for studies using large facilities techniques

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A number of methods from large scale facilities require the application of well-defined samples, controlling crystallinity, roughness to interface quality, requirements which can be fulfilled by thin films. We apply pulsed laser deposition (PLD) to create these thin films to utilize complementary techniques, ranging from neutron reflectometry (NR) to grazing incidence X-ray absorption spectroscopy (GIXAS), and angle resolved photon emission spectroscopy (ARPES). The material system which we study are oxynitrides which are applied as photoanodes in photo-electrochemical water splitting. Shortcomings of this material class are a fast decay in activity over the first few electrochemical cycles (Fig. 1) and a decay on the long term[1]. While the long-term decay is possibly related to a degradation of the material, i.e., a loss of nitrogen, the fast decay is not really understood, and therefore also no approach can be envisioned how to overcome this problem. We studied the fast decay of the material (and first approaches how to prevent this) by using thin films as model system. For this approach we developed a method on:

- How to deposit oxynitrides with well-defined oxygen content and crystallographic orientation by PLD using NH_3 as reactive gas component on conducting substrates.
- Design a cell for in-situ NR and in-situ/operando GIXAS (and modulation excitation, ME-XAS) (Fig. 1).
- Measure the thin films before/after photoelectrochemical operation with NR and ARPES and before/after/during operation using GIXAS and ME-XAS.

We could detect a surface modification, i.e., a change in density, by NR in the range of 3 nm, while XAS was utilized to analyze changes in oxidation state (order) for the different elements[2]. A change of oxidation state of the A cation was detected, while the B cation (here for $LaTiO_xN_y$), which is normally assumed to be the active site, undergoes local disordering. This surface modification reduces the overall water splitting activity, but we could identify a co-catalyst, which supresses these modifications. We could also identify critical steps in the water splitting mechanisms, where during surface modifications the formation of NO_x competes with the oxygen evolution[3]. Using ARPES we could finally identify an electron accumulation layer at the surface[4] as another mechanism for decreasing the activity.
Now we are working on approaches to mitigate the identified degradation mechanisms.
Without highly defined, high quality PLD films it would have not been possible to utilize the large facilities, and therefore to identify (mitigate) the origins of activity decay of these oxynitrides for water splitting.

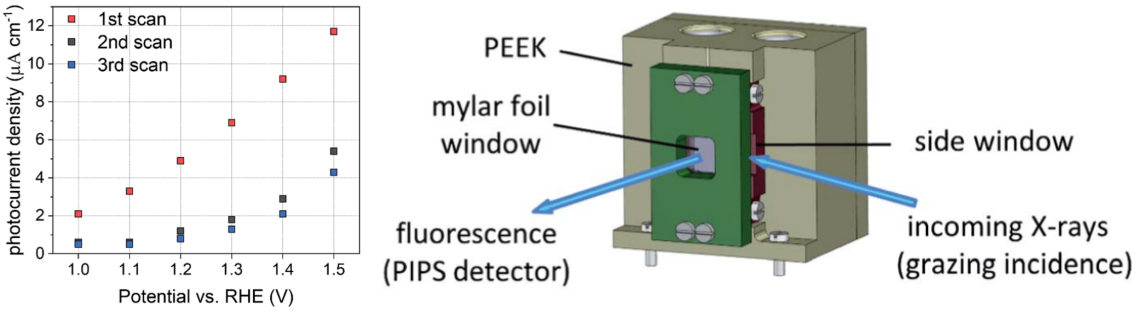

Figure 1: photocurrent densities for the first three potentiodynamic measurements, showing initial degradation (left), Operando reactor cell for surface sensitive GIXAS measurements.

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