

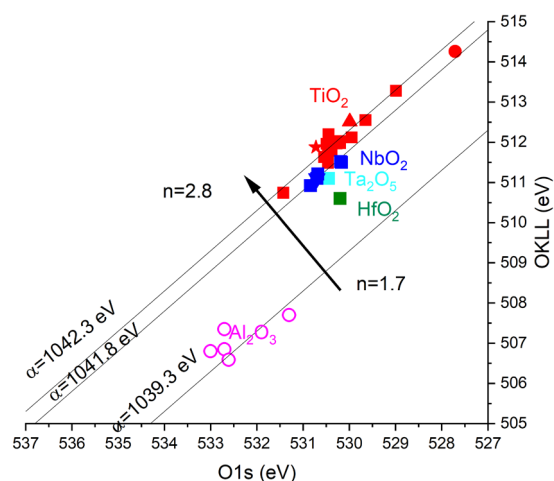
## Chemical state analysis of functional oxide thin films by combining soft and hard X-ray Photoelectron Spectroscopy

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As demonstrated in the present study, the recent development of commercial lab-based HAXPES systems, equipped with both a soft Al-K $\alpha$  and hard Cr-K $\alpha$  scanning X-ray source, opens up unique opportunities for monitoring the local chemical states of the cations and anions in functional oxides and catalysts, in a routine laboratory environment [1,2]. Surface-sensitive deep core-level photoelectron lines and respective Auger transitions can be measured using the hard X-ray source, whereas more bulk-sensitive shallow core-levels can be excited using either the hard or soft X-ray source. As demonstrated for thin Al<sub>2</sub>O<sub>3</sub> films, the local chemical state of the constituting ions in the oxide may even be probed at near constant probing depth by smart selection of sets of photoelectron and Auger lines, as excited with the combined soft and hard X-ray sources [1]. Exemplary cases are given for the combined chemical state analysis of cations and anions in different amorphous and crystalline TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> polymorphs, as prepared in the form of a thin film (~10-50 nm) by various synthesis methods, including thermal oxidation, anodization and atomic layer deposition (ALD) [1,3]. By careful selection of sets of photoelectron and Auger lines, as excited with the combined soft and hard X-ray sources, the Auger parameters (AP) for the respective cations and anions were derived at various probing depths [1]. The depth-resolved AP values for the thin (amorphous) oxide films were compared to their respective bulk crystalline reference phase(s). The resolved shifts in the cation and anion AP values as function of the synthesis conditions could be linked to tiny changes in the local electronic polarizability around the core-ionized atoms between the different oxide polymorphs, which originate from differences in the local coordination spheres (short-range order) around the constituting cations and anions. Moreover, the local chemical state of oxygen in various technologically-relevant oxides could be correlated to the optical/dielectrical properties, such as the refractive index (see Fig. 1).



**Fig.1** Oxygen Auger parameter derived for different oxides, showing a clear correlation with the respective refractive index.

### References

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