

O 68: Poster: Oxide and Insulator Surfaces

Time: Wednesday 18:00–20:00

Location: P2/EG

O 68.1 Wed 18:00 P2/EG

Sub-nanometer depth profiling of native transition metal oxide layers within single XPS spectra — ●MARTIN WORTMANN, DOMINIK GRAULICH, NATALIE FRESE, and TIMO KUSCHEL — Bielefeld University, Bielefeld, Germany

Many transition metals form a thin oxide layer of only few nanometers upon exposure to the atmosphere, which affects their interfacial properties. Such native oxide layers are commonly analyzed using photoemission spectroscopy (PES) and X-ray photoelectron spectroscopy (XPS) in particular. The most common method to obtain compositional depth profiles in PES is based on gradual surface ablation by ion sputtering. However, it is known to affect the microstructure of the surface, compromising depth-resolution and compositional accuracy. Other methods such as angular-resolved, energy-resolved, or hard X-ray PES are associated with considerable experimental effort or demands on sample texture. Here we propose a simple and accessible approach for sub-nanometer depth profiling of native metal oxide layers within single lab-XPS spectra. Heavy transition metals usually have multiple orbital energies within the energy range of a lab-XPS giving rise to peak regions at various binding energies. The signal contributions of oxidized and elemental metals can be distinguished by peak deconvolution. The kinetic energy of the photoelectron determines its inelastic mean free path (IMFP) length, which is a measure for the depth from which information is obtained. Different binding energies can thus be assigned to different values for IMFP, so that an oxide concentration profile can be inferred from a single XPS spectrum.

O 68.2 Wed 18:00 P2/EG

Ab-initio investigations of the order of K^+ ions on cleaved muscovite mica — ●ANDREA CONTI, GIADA FRANCESCHI, MICHAEL SCHMID, ULRIKE DIEBOLD, and FLORIAN MITTENDORFER — Institute of Applied Physics, TU Wien, Wiedner Hauptstrasse 8-10/134, 1040 Vienna, Austria

Model systems based on single crystals can help to provide a better understanding of the chemistry and the catalytic activity of a given oxide surface. In this work, we present DFT calculations on the surface of muscovite mica, a common phyllosilicate whose structure consists of alternating layers of aluminosilicates and K^+ ions. This material easily splits into thin K-terminated sheets, yet the atomistic order of the surface K^+ ions has been, until recently, unknown [Franceschi *et al.*, *submitted* (2022)]. Calculations, using the “Vienna Ab-initio Simulation Package” (VASP) and the metaGGA (r²SCAN) exchange-correlation functional, indicate a close correlation between the distribution of the surface K^+ ions and the arrangements of the subsurface Al^{3+} ions: the K^+ ions preferentially occupy the Al-rich rings. In addition, the calculated diffusion barriers suggest that the K^+ ions are mobile enough at room temperature to jump to more favorable sites. AFM simulations, using the Probe Particle Model, are in good agreement with the experimental images.

O 68.3 Wed 18:00 P2/EG

Vanadium and iron intermixing in honeycomb oxides on Pt(111) and Ru(0001) — ●PIOTR WEMHOFF¹, CLAUDINE NOGUERA², JACEK GONIAKOWSKI², and NIKLAS NILIUS¹ — ¹Carl von Ossietzky University, Institute of Physics, D-26111 Oldenburg, Germany — ²CNRS-Sorbonne University, UMR 7588, INSP, F-75005 Paris, France

Whereas V and Fe are immiscible in bulk-type perovskite oxides, mixed oxide honeycomb layers can be prepared on Pt(111) and Ru(0001) surfaces. Their atomic composition is accessible from bias-dependent STM topographic images, as the Fe ions develop a protruding contrast

with respect to V when tunneling into their 3d(z²) orbitals at elevated bias. On Pt(111), up to 50% iron can be incorporated into a V₂O₃ host oxide, whereby the Fe runs through a series of distinct configurations evolving from isolated ions to pairs in 3rd neighbor positions, short chains of 2nd neighbor Fe and finally ordered (2x2) V/Fe islands separated by domain boundaries. The observed phase behavior can be traced back to attractive Fe-V and repulsive Fe-Fe pair interactions, which have been identified by DFT calculations and enable perfect reproduction of the experimental patterns by means of Monte-Carlo simulations. In contrast, a V/Fe self-organization scheme becomes active on Ru(0001) that only allows for one unique cation arrangement in the honeycomb oxide. DFT finds a layer of interfacial oxygen between Ru(0001) and the oxide film to be responsible for this rigid structural composition.

O 68.4 Wed 18:00 P2/EG

Atomic View on the (111) Surface of a Cu₂O Single Crystal: Reconstruction, Electronic Properties and Band Bending Effects — ALEXANDER GLOYSTEIN, JACK CREED, and ●NIKLAS NILIUS — Carl von Ossietzky University, Institute of Physics, D-26111 Oldenburg, Germany

The nature of the (sqrt(3)xsqrt(3))R30° reconstruction of the Cu₂O(111) surface has been heavily debated for almost 30 years. This work demonstrates that the nano-pyramidal reconstruction model that was recently developed for Cu₂O(111) thin films is valid also for bulk samples. Well-prepared crystals develop a robust (sqrt(3)xsqrt(3))R30° superstructure in electron diffraction, while atomically resolved STM images display extended arrays of trifold symmetric protrusions with 10.5 Å periodicity. Both findings are in perfect agreement with the nano-pyramidal model, in which Cu₄O units attach to every third Cu-O six-ring of a Cu-depleted (111) surface. STM conductance spectra reveal the p-type character of the oxide with the valence-band top pinned to the Fermi level. From band-bending effects in the tip electric field, an induced carrier concentration of 6x10¹⁷ cm⁻³ is determined for the (sqrt(3)xsqrt(3))R30° phase, increasing to 4x10¹⁸ cm⁻³ on the few (1x1) patches covered with a Cu-poor minority phase. This difference reflects the close interplay between atomic structure, electronic properties and local screening response for a given surface termination.

O 68.5 Wed 18:00 P2/EG

The Surface Chemistry of Hydrated Lime - Wave Optics tested on a Model System — ●NILS SCHEWE¹, THOMAS MAYERHÖFER², HICHAM IDRIS¹, and CHRISTOPH WÖLL¹ — ¹Institute of Functional Interfaces (IFG), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, Eggenstein-Leopoldshafen, 76344, Germany — ²Institut für Physikalische Chemie, Friedrich-Schiller-Universität Jena, Jena, 07745, Germany

We report on the results of a combined experimental and theoretical study of the interaction of sulfur dioxide with a calcium hydroxide single crystal surface. Our investigation of this model system for flue gas desulfurization and concrete corrosion was carried out on the Ca(OH)₂(001) surface under ultra-high-vacuum conditions. Combining polarization resolved UHV infrared reflection absorption spectroscopy (IR-RAS) with calculations based on wave optical considerations, we were able to demonstrate the adsorption behavior and mode of SO₂ on this surface. We show, that the preferred angle of adsorption is 23° below 65 K. Heating does not lead to reaction, but fully desorbs the formed adsorbate after crystallization between 80 - 100 K. Additionally, we were able to obtain the first low energy electron diffraction (LEED) pattern of an alkaline earth metal hydroxide by using UHV exfoliation for cleaning.