O 6: Oxides and Insulator Surfaces: Structure, Epitaxy and Growth

Time: Monday 10:30–12:45 Location: H8

O 6.1 Mon 10:30 H8

Characterizing Approximants of Oxide Quasicrystals with a Novel Geometric Approach — •Martin Haller, Sebastian Schenk, Stefan Förster, and and Wolf Widdra — Martin-Luther-Universität Halle-Wittenberg, 06120 Halle, Germany

Oxide quasicrystals (OQCs) are aperiodic 2D oxide films exhibiting dodecagonal symmetry, which are grown on hexagonal metal substrates. This dodecagonal symmetry arises from a square-triangle-rhombus tiling, derived from Ba, Sr, or Eu hosted within a Ti-O network [1]. Approximants are periodic structures composed of the same tiling elements, thus exhibiting a close structural relationship to the OQC. Variations in stoichiometry lead to the emergence of different approximant structures, ranging from simple tilings with a triangle:square:rhombus frequency ratio of 4:2:0 to more complex configurations such as the 60:22:8 approximant [2]. In this presentation, we will introduce newly discovered approximant phases identified in the Sr-Ti-O/Pd(111) and Eu-Ti-O/Pd(111) systems through STM and LEED. Specifically, we will discuss two hexagonal approximants with tiling frequency ratios of 20:3:6 and 8:0:3, as well as an oblique 10:3:2 approximant. Additionally, we will apply a novel geometric approach for characterizing the tilings derived from STM data [3]. This innovative method provides a measure in a 4D hyperspace for classifying the relationship of approximants to the parent OQC.

[1] Schenk et al., Nature Communications, 13, 7542 (2022)
[2] Wührl et al., Phys. Rev. B, 107, 195414 (2023)
[3] Imperor-Clerc et al., Phys. Rev. B, 110, 144106 (2024)

O 6.2 Mon 10:45 H8

Chromium Oxide Thin Films on Pt(111): An STM and DFT Excursion through the Phase Diagram — •Ghada Missaoui[1], Piotr Igor Wemhoff[1], Claudine Noguera[2], Jacek Goniakowski[2], and Niklas Nilius[1] — [1]Carl von Ossietzky University, Institute of Physics, D-26111 Oldenburg, Germany — [2]CNRS-Sorbonne University, UMR 7588, INSP, F-75005 Paris, France

Formation of chromium oxide thin films on Pt(111) was investigated by electron diffraction and low-temperature scanning tunneling microscopy. Depending on the nominal Cr coverage and the oxygen-chemical potential used for preparation, two oxide phases were identified. A $(\sqrt{3}\times\sqrt{3})\mathrm{R}30^\circ$ phase emerges at sub-monolayer Cr exposure and O-rich oxidation conditions, while a (2x2) phase develops at higher coverage and after a vacuum-annealing step. For both phases, the atomic nature of cationic and anionic sub-lattices and the chemical composition were determined in detail. Guided by this experimental input, a global structure optimization was performed by genetic algorithms and key configurations were refined by density functional theory calculations afterwards. For the $(\sqrt{3}\times\sqrt{3})\mathrm{R}30^\circ$ phase, good agreement was revealed for a Cr_3O_6 trilayer, comprising a mixture of Cr^{3+} and Cr^{4+} ions in the central cationic plane. The (2x2) phase matches well a Cr_6O_{11} film, in which an O-Cr-O trilayer is capped by a Cr_2O_3 honeycomb plane. The identified configurations not only reproduce structure and symmetry deduced from experiment but also have the most favorable energetics at the employed oxygen chemical potential.

O 6.3 Mon 11:00 H8

Ferroelectric perovskite oxides: from bulk to surface polarization — •Dominik Wrana[1], Llorenç Albons[2], Marta Macyk[1], Andrzej Jasicki[1], Aji Alexander[2], Jesus Redondo[2], Igor Sokolovic[3], Pavel Kocan[2], Konrad Szajna[1], Martin Setvin[2], and Franciszek Krok[1] — [1]Institute of Physics, Jagiellonian University, Krakow, Poland — [2]Department of Surface and Plasma Science, Charles University, Prague, Czechia — [3]Institute of Applied Physics, TU Wien, Vienna, Austria

In leveraging the spontaneous polarization of ferroelectrics for photo-, pyro-, and piezocatalysis, it is essential to develop a comprehensive model of ferroelectricity's impact on perovskite surfaces.

Here we investigate oxide perovskites, which are known to exhibit record-high efficiencies toward water spitting. Careful analysis of ferroelectricity exhibited on surfaces of single crystals of as-cleaved ferroelectric $BaTiO_3$(001) and $KNbO_3$(001) compared to quantum paraelectric $KTaO_3$(001) reveals phenomena at both single-atom and macroscales. Polarization optical and scanning electron (SEM) microscopy data provides the spatial information of 90° ferroelectric domains, which typically have a width of 5-20 μm and length of up to hundreds of um. Actual domain structure and their directionality are provided by piezoresponse force microscopy (PFM) imaging, which also provides the correlation of surface reactivity with polarization.

qPlus ncAFM is used to demonstrate a reversible ferroelectric polarization of (1x1) surfaces at the nanoscale, by application of different tip-sample bias voltages.

O 6.4 Mon 11:15 H8

The influence of strain-induced ferroelectricity on the fracture of oxide perovskites — •Christian Ritterhoff and Bernd Meyer — Interdisciplinary Center for Molecular Materials and Computer Chemistry Center, FAU Erlangen-Nürnberg

The cleaving of bulk crystals using mechanical force is a common procedure to obtain well-defined surfaces under UHV conditions. While this method avoids chemical changes in the surface composition due to etching and annealing procedures, the strain necessary for cleavage can induce ferroelectric phase transitions during the fracture process whose influence is still visible on the as-cleaved surface, as shown, for example, by Sokolović *et al.* [1] for mechanically cleaved $SrTiO_3$.

Here, we present density-functional theory calculations to discuss the influence of increasing strain on the magnitude of possible ferroelectric distortions and the development of a spontaneous polarization for three prototype perovskite oxides: cubic $SrTiO_3$, ferroelectric $BaTiO_3$, and polar $KTaO_3$. First, we estimate the critical strain for mechanical cleavage in fracture Mode 1 and Mode 2. Subsequently, we calculate the polarization of the material at the point of fracture and discuss the implication on surface charges and the formation of surface defects.

[1] I. Sokolović, M. Schmid, U. Diebold, M. Setvín, Phys. Rev. Mater. **3** (2019) 034407

O 6.5 Mon 11:30 H8

Segregation Effects in 2D Mixed Oxide Nano-Islands: Edge Structure and Composition in Mixed V-Fe Oxide Monolayers — Ying Wang[1], Piotr Igor Wemhoff[1], Ghada Missaoui[1], •Niklas Nilius[1], Jacek Goniakowski[2], and Claudine Noguera[2] — [1]Carl von Ossietzky University, Institute of Physics, D-26111 Oldenburg, Germany — [2]CNRS-Sorbonne University, UMR 7588, INSP, F-75005 Paris, France

Low-coordinated atoms residing at the edges of oxide nanostructures play an important role in heterogenous catalysis. Their local configuration is however hardly available, especially for ternary materials with variable stoichiometry. In this study, low-temperature STM is employed to analyze the edge configurations of V-Fe-O honeycomb islands grown on Pt(111) as a function of film composition. The islands are delimited by zigzag and armchair edges, the latter with a tendency to reconstruct into sequences of four, five, six and seven-membered rings. STM spectroscopy is used to identify the chemical nature of the edge atoms. The thermodynamic forces for V or Fe segregation to the edges, both oxygen and cation terminated, are analyzed by DFT calculations. In an oxidizing environment, formation of vanadyl-terminated (VO-) edges is energetically favorable, while Fe atoms segregate towards the edges at O-poor conditions. The observed behavior is explained by the higher oxygen affinity of V versus Fe edge cations, and reflected in the higher stability of terminal vanadyl compared to ferryl groups. Our findings indicate a new pathway to tailor the chemical composition and catalytic reactivity of oxide edges via cationic mixing.

O 6.6 Mon 11:45 H8

Mapping the Energy-Angle-Landscape in lab-based X-ray photoelectron spectroscopy for Depth Profiling of Oxide Layers — •Martin Wortmann[1,4], Beatrice Bednarz[2], Olga Kuschel[2,3], Klaus Viertel[4], Negin Beryani Nezafat[5], Jan Schmalhorst[1], Gabi Schierning[5], Joachim Wollschläger[3], Andreas Hütten[1], and Timo Kuschel[1,2] — [1]Bielefeld University, Bielefeld, Germany — [2]Johannes Gutenberg University Mainz, Mainz, Germany — [3]University of Osnabrück, Osnabrück, Germany — [4]Bielefeld University of Applied Sciences, Bielefeld, Germany — [5]University of Duisburg-Essen, Duisburg, Germany

Many metals are reactive to atmospheric oxygen, forming stable nanometer-thin oxide layers by spontaneous self-passivation. Such native oxide layers are commonly analyzed by X-ray photoelectron spectroscopy (XPS). We previously introduced a method to calculate depth profiles from single fixed-angle spectra by fitting all emission peaks instead of just one, thus resembling energy-resolved XPS without the need for a synchrotron [1]. Here, we combine this approach with angular-dependent measurements, fitting the measured intensity ratios of oxide and metal as a function of energy (i.e. inelastic mean free path) and angle. This method not only improves the accuracy of earlier models and peak fittings but also paves the way for a more holistic understanding of the XPS spectrum. [1] Wortmann et al., Small Methods 8(3), 2300944 (2024)

O 6.7 Mon 12:00 H8

The polar spinel $MgAl_2O_4$ (001) surface is stabilized by an aluminum-rich reconstruction — •David Kugler[1], Andrea Conti[1], Johanna I. Hütner[1], Soumyajit Rajak[2], Matthias Meier[1], Nan Jiang[2], Florian Mittendorfer[1], Michael Schmid[1], Ulrike Diebold[1], Gareth S. Parkinson[1], and Jan Balajka[1] — [1]Institute of Applied Physics, TU Wien, Vienna, Austria — [2]Department of Chemistry, University of Illinois Chicago, USA

The atomic-scale surface structure of spinel oxides is key to understanding their catalytic properties. Magnesium aluminate ($MgAl_2O_4$, spinel), which gave this class of materials its name, is a wide-gap insulator and poses considerable challenges for experimental surface structure determination. Noncontact atomic force microscopy (nc-AFM) with a qPlus sensor and a well-defined tip apex allowed us to directly resolve the surface structure with atomic resolution and chemical sensitivity. The $MgAl_2O_4$(001) surface adopts a c(2 × 4) reconstruction accompanied by an increase of the Al/Mg ratio, as detected by x-ray photoelectron spectroscopy (XPS). The reconstructed surface is enriched in aluminum and contains ordered pairs of octahedrally coordinated magnesium atoms replacing their tetrahedral bulk sites. This charge redistribution within the reconstructed surface layer stabilizes the otherwise polar $MgAl_2O_4$(001) termination. The proposed surface reconstruction is similar to those observed on other spinel oxides, such as Fe_3O_4(001) and Mn_3O_4(001), suggesting a universal mechanism for compensating the polarity of spinel (001) surfaces.

O 6.8 Mon 12:15 H8

Elucidating the Growth Mechanism of 2D GaS on Sapphire in a Multitechnique Approach — •Stefan R. Kachel[1,2], Robin Günkel[2], Leonard Neuhaus[1], Oliver Massmeyer[2], Lukas Erlemeier[1], Kassandra Zoltner[1], Florian Münster[1], Carsten von Hänisch[1], Kerstin Volz[2], and J. Michael Gottfried[1] — [1]Department of Chemistry, Philipps-Universität Marburg, Germany — [2]Material Sciences Center and Department of Physics, Philipps-Universität Marburg, Germany

The utilization of 2D layers of GaS with its ultraviolet bandgap holds promise for applications in solar-blind photodiodes and LEDs. However, the growth of these 2D layers remains a significant challenge, driving considerable interest in understanding the growth mechanism underlying the metal-organic chemical vapor deposition (MOCVD) process. This study investigates the growth of 2D GaS using conventional precursors as well as a newly synthesized single-source precursor (SSP) on sapphire in a multitechnique approach. Scanning transmission electron microscopy (STEM) reveals that the formation of a closed Ga layer on the sapphire surface is a prerequisite for GaS growth. This finding is supported by temperature-programmed desorption (TPD) experiments showing intact desorption of the S-precursor, while the Ga-precursor decomposes partially even at low temperatures, leaving Ga residues on the surface, as confirmed by X-ray photoelectron spectroscopy (XPS). The new SSP enables the deposition of thin mixed layers of Ga and S on sapphire. Refining such single-source precursors could provide a pathway toward efficient growth of 2D GaS.

O 6.9 Mon 12:30 H8

Surface Reconstructions Govern Ice Nucleation on Silver Iodide – A Noncontact-AFM Investigation — •Johanna I. Hütner[1], Andrea Conti[1], David Kugler[1], Franziska Sabath[3], Florian Mittendorfer[1], Michael Schmid[1], Angelika Kühnle[2], Ulrike Diebold[1], and Jan Balajka[1] — [1]Institute of Applied Physics, TU Wien, Vienna, 1040, Austria — [2]Department of Chemistry, Bielefeld University, Bielefeld, 33615, Germany — [3]Max Planck Institute for Polymer Research, Mainz, 55128, Germany

Silver iodide (AgI) is used as a cloud seeding material due to its ability to nucleate ice efficiently, which is explained by the good lattice match between AgI and hexagonal ice. However, AgI consists of stacked planes of positively charged Ag^+ alternating with negatively charged I^-. Cleaving a AgI crystal along the (0001) plane thus exposes Ag^+ and I^- terminated surfaces. Both terminations are polar and inherently unstable.

We present atomically resolved noncontact atomic force microscopy (NC-AFM) images that show how AgI(0001) surfaces compensate for this non-zero electric dipole perpendicular to the surface. Both Ag and I terminated surfaces form reconstructions, whose structure affects their ice nucleating abilities. NC-AFM images of UHV-cleaved surfaces exposed to water vapor reveal that ice forms an epitaxial layer only on the Ag terminated surface, whereas on the I termination ice forms three-dimensional clusters.

These atomic-level observations could enhance our understanding of ice formation processes in the atmosphere.