O 49: Oxide and Insulator Interfaces I

Time: Wednesday 10:30–13:00 Location: MA 144

O 49.1 Wed 10:30 MA 144

Structure of the Al_2O_3(0001) surface — Jan Balajka[1], Andrea Conti[1], Johanna Hütner[1], Florian Mittendorfer[1], Georg Kresse[2], •Michael Schmid[1], and Ulrike Diebold[1] — [1]Institute of Applied Physics, TU Wien, Austria — [2]Computational Materials Physics, Universität Wien, Austria

Corundum (α-Al_2O_3) is the thermodynamically stable form of aluminum oxide and used in many fields of technology. Nevertheless, the structures of its surfaces have not been determined yet. Our high-quality ncAFM images of the $\text{Al}_2\text{O}_3(0001)$-$(\sqrt{31}\times\sqrt{31})R\pm 9^\circ$ reconstruction, which forms after high-temperature annealing, rule out the aluminum termination proposed previously [1,2]. The surface is very similar to ultrathin alumina films, which have well-established structural models [3,4]. To determine the structure of the subsurface layers not directly imaged by ncAFM, we employed density functional theory calculations and machine-learned force fields to search the large configuration space, resulting in a lowest-energy structure that fits the experiment. DFT calculations also show that the standard model for the unreconstructed $\text{Al}_2\text{O}_3(0001)$-$(1\times1)$ surface cannot be thermodynamically stable at any conditions. We discuss reasons for the high stability of the reconstruction.

[1] Renaud et al. Phys. Rev. Lett. 73, 1825 (1994)
[2] Lauritsen et al. Phys. Rev. Lett. 103, 076103 (2009)
[3] Kresse et al. Science 308, 1440 (2005)
[4] Schmid et al. Phys. Rev. Lett. 99, 196104 (2007)

O 49.2 Wed 10:45 MA 144

Metal-oxide surfaces: Chemical selective nc-AFM imaging with O-terminated copper tips — •Philipp Wiesener[1], Johanna Hütner[2], Jan Balajka[2], Bertram Schulze Lammers[1], Harald Fuchs[1], Saeed Amirjalayer[1], and Harry Mönig[1] — [1]Physikalisches Institut, Universität Münster, Germany — [2]Institute of Applied Physics, TU Wien, Austria

Previously we investigated the performance of various atomically defined tip terminations on the Cu(110)O(2x1) surface with non-contact AFM [1]. A direct comparison of the imaging properties shows, that only for an oxygen terminated copper tip (CuOx-tip [2]) a chemical selective contrast between metal and oxygen atoms on the surface can be observed.

In this work we exhibit the generalized ability of CuOx-tips for an outstanding characterization of metal-oxide surfaces. By performing constant height measurements on a variety of copper-, iron-, titanium- and aluminum-oxide systems with increasing structural complexity the robustness of the chemical selectivity is demonstrated. For an additional contrast analysis we complement our site-selective microscopy with force spectroscopy measurements on the observerd metal and oxygen atoms and investigate predominant defects.

Supporting DFT calulations reveal that the chemical selectivity can be explained by purely electrostatic interactions, which are determined by the strongly electronegative tip termination.

[1] B. Schulze Lammers et. al., Nanoscale 13, 13617 (2021).
[2] H. Mönig et al., ACS Nano 10, 1201-1209 (2015).

O 49.3 Wed 11:00 MA 144

Observation of a dodecagonal europium oxide quasicrystal on Pd(111) — •Martin Haller, Sebastian Schenk, Stefan Förster, and Wolf Widdra — Martin-Luther-Universität Halle-Wittenberg, 06120 Halle, Germany

Oxide quasicrystals (OQCs) are 2D oxide films with dodecagonal symmetry grown on a hexagonal metal substrate. The dodecagonal symmetry results from a square-triangle-rhombus tiling of alkaline earth atoms, as Ba or Sr, in a Ti-O network [1]. Europium has a comparable ionic radius as Sr and the same 2+ oxidation state and is an interesting OQC substituent due to its half-filled 4f shell resulting in a strong magnetic moment. Here, we show that an OQC forms by Eu deposition onto a Ti-O network on Pd(111) and subsequent annealing. We analyze the Eu-Ti-O OQC and compare it with the prototypical Ba-Ti-O system based on LEED and STM data. From LEED, we deduce a reduction of the characteristic length scale and a close match with the theoretical diffraction pattern. In real space, the tiling frequencies are found to be 2.80:1:3.78 for squares:triangles:rhombi. Those are in good agreement to the ideal ratio of 2.73:1:0.37 [2]. Lastly, we analyze the datasets in hyperspace, where we observe the typical confinement of the projected points inside the dodecagonal acceptance domain.

[1] Schenk et al., Nature Communications, 13, 7542 (2022)
[2] Schenk et al., Acta Crystallographica A, 75, 307 (2019)

O 49.4 Wed 11:15 MA 144

Atomic layer deposition of cerium oxide monitored by operando ellipsometry and in-situ X-ray photoelectron spectroscopy — •Rudi Tschammer[1], Yuliia Kosto[1], Carlos Morales[1], Marcel Schmickler[2], Karsten Henkel[1], Anjana Devi[2], and Jan Ingo Flege[1] — [1]Applied Physics and Semiconductor Spectroscopy, BTU Cottbus-Senftenberg, Cottbus, Germany — [2]Inorganic Materials Chemistry, Ruhr University Bochum, Universitätsstraße 150, Bochum, Germany

Atomic layer deposition (ALD) has been used extensively to grow homogeneous films with excellent coverage and atomic-scale thickness control for a variety of applications. However, remaining challenges include the investigation of novel precursor-oxidant combinations for low-temperature deposition as well as unraveling the complex interplay between substrate and coating for ultrathin films. In this work, we present a detailed investigation of ultrathin cerium oxide films grown using the novel Ce(dpdmg)_3 precursor with H_2O and O_2. Following a surface science-based approach, we have combined operando spectroscopic ellipsometry and in-situ X-ray photoelectron spectroscopy to allow rapid process optimization and determination of the complex relation between oxide stoichiometry, film thickness and ALD growth parameters, revealing a distinct dependence of inital Ce^{3+} content on the film thickness and choice of oxidant. This offers the possibility of adjusting the oxide properties to application requirements e.g. in gas sensing by choosing a suitable precursor-oxidant combination.

O 49.5 Wed 11:30 MA 144

Bridging the Pressure and Materials Gap in Heterogeneous Catalysis: A Combined UHV, In Situ, and Operando Study Using Infrared Spectroscopy — •Lachlan Caulfield, Eric Sauter, and Christof Wöll — Karlsruher Institut für Technologie (KIT)/Campus Nord, Hermann-von-Helmholtz-Platz 1,Eggenstein-Leopoldshafen, 76433,Germany

In the last decades, ceria-based systems have seen an increase in popularity, due to its unique redox behavior and catalytic characteristics. Ceria powders are widely used in exhaust catalysts as three-way catalysts (TWC) well as many other catalytic cycles, due to the cheap and simple preparation methods. To gain a better understanding of the chemical and structural behavior of ceria nanoparticles and their interaction with gaseous molecules, an operando DRIFTs study was carried out in combination with in-situ FT-IR studies. By tuning the temperature of the sample under a constant flow of carbon monoxide the reactions on the surface could be monitored in real time, without changing the surface. Notably, increasing the temperature from liquid nitrogen temperature to room temperature and above, it is possible to observe very minor changes to the oxidation state of the ceria nanoparticles as the surface becomes increasingly reduced. Using operando DRIFTS in combination with carbon monoxide dually as a reducing agent and as a probe molecule, the chemical and structural changes of polycrystalline ceria and other metal oxides can easily be investigated.

O 49.6 Wed 11:45 MA 144

Atomic-scale Structure of K-Feldspar Microcline (001) — •Tobias Dickbreder[1], Franziska Sabath[1], Bernhard Reischl[2], Rasmus V. E. Nilsson[2], Adam S. Foster[3,4], Ralf Bechstein[1], and Angelika Kühnle[1] — [1]Physical Chemistry I, Bielefeld University, Germany — [2]Institute for Atmospheric and Earth System Research/Physics, Faculty of Science, University of Helsinki, Finland — [3]Department of Applied Physics, Aalto University, Finland — [4]Nano Life Science Institute (WPI-NanoLSI), Kanazawa University, Japan

Ice nucleation governs the aggregate state of water in clouds and, thus, understanding ice nucleation is essential for improving climate models. Most atmospheric ice nucleation is heterogeneous caused by ice nucleating particles (INP). Among the most important INP under mixedphase cloud conditions are feldspar minerals. The mechanism by which feldspar minerals facilitate ice nucleation, however, remains elusive. A prerequisite for unravelling this mechanism is a solid understanding of the surface structure of feldspar minerals. In this regard, it is especially crucial that experimental studies on the atomic-scale structure of feldspar minerals are sparse. Here, we present atomic force microscopy images of K-feldspar microcline (001) taken in ultrahigh vacuum. Our high-resolution AFM data reveal features consistent with a hydroxyl-terminated surface as predicted by density functional theory. This finding suggests that water in the residual gas readily reacts with the surface. These insights into the surface structure will contribute to understanding the excellent ice nucleating ability of feldspar minerals.

O 49.7 Wed 12:00 MA 144

Atomic-scale imaging of K-feldspar surfaces and their interaction with water — •Luca Lezuo[1], Andrea Conti[1], Rainer Abart[2], Florian Mittendorfer[1], Michael Schmid[1], Ulrike Diebold[1], and Giada Franceschi[1] — [1]Institute of Applied Physics, TU Wien, Wiedner Hauptstrasse 8-10/E134, 1040 Wien, Austria — [2]Department of Lithospheric Research, Universität Wien, 1090 Wien, Austria

K-Feldspars ($KAlSi_3O_8$) are common minerals in the Earth's crust and play a crucial role as ice nucleators in atmospheric processes. In particular, the well-ordered low-temperature polymorph microcline is a very effective ice nucleator.[1] Understanding their interaction with water is essential for various scientific fields, including atmospheric chemistry and climate science.

This study presents experimental atomic-scale imaging of the interaction between K-feldspar and water.[2] We cleaved the mineral in ultra-high vacuum and analyzed the surface using non-contact atomic force microscopy (AFM) and X-ray photoelectron spectroscopy. The surfaces are prone to hydroxylation, exposing arrays of silanol (Si-OH) and aluminol (Al-OH) groups. We studied the onset of ice nucleation by introducing H_2O vapor at low temperatures on such hydroxylated surfaces. Ab-initio calculations in tandem with AFM simulations employing the Probe Particle Model [3] helped us interpret our results.

[1] A. Kumar, et al., Atmos. Chem. Phys. 18, 7057 (2018)
[2] G. Franceschi, et al., submitted (2023)
[3] P. Hapala, et al., Phys. Rev. B 90, 085421 (2014)

O 49.8 Wed 12:15 MA 144

Unraveling the effects of substrate interaction on the chemical properties of atomic layer deposited ultra-thin ceria layers — •Carlos Morales, Yuliia Kosto, Rudi Tschammer, Karsten Henkel, and Jan Ingo Flege — Applied Physics and Semiconductor Spectroscopy, Brandenburg University of Technology Cottbus-Senftenberg, Konrad-Zuse-Strasse 1, D-03046 Cottbus, Germany

Atomic layer deposition (ALD) is well known to lead to amorphous and defective, non-stoichiometric films, potentially resulting in modified material properties that can also be affected by film/substrate interaction in the case of ultra-thin growths. For example, the formation, diffusion, and recovery of oxygen vacancies can be favored in disordered, reducible metal oxides compared to more ordered deposits, whereas interdiffusion processes can critically affect the film/substrate interface region. These effects have extensively been studied for thin thermal-ALD ceria films (below 15 nm) by combining in-situ and ex-situ characterization techniques in our lab and at synchrotron radiation facilities. While using alumina or silica substrates modifies the initial growth rate, Ce^{3+}/Ce^{4+} ratio, and ceria morphology, the formation of different species at the interface affects its reactivity. Interestingly, the experiments have shown high reducibility of ALD-ceria ultrathin films on silica for very low hydrogen concentrations, even at room temperature, whereas for alumina substrates the formation of aluminates at the interface prevents further oxidation. Moreover, the comparison with more ordered films indicates a key role of the defective structure of ALD films in Ce^{3+}/Ce^{4+} conversion.

O 49.9 Wed 12:30 MA 144

Dynamics of an Fe_3O_4(001) support for Pt$_n$ cluster catalysts under the fast STM — Sebastian Kaiser[1], Johanna Reich[2], Ueli Heiz[1], Barbara A.J. Lechner[2], and •Friedrich Esch[1] — [1]Chair of Physical Chemistry, TUM School of Natural Sciences and Catalysis Research Center, Technische Universität München, Lichtenbergstr. 4, 85748 Garching — [2]Functional Nanomaterials Group, TUM School of Natural Sciences and Catalysis Research Center, Technische Universität München, Lichtenbergstr. 4, 85748 Garching

Reducible oxides are valuable supports for cluster catalysts in oxidation reactions due to their capability to contribute lattice oxygen. Here, we present a study on the surface dynamics of Fe_3O_4 in the absence and in the presence of supported size-selected Pt_5 clusters [1, 2]. With our dedicated FAST add-on module [3], we drive our variable temperature scanning probe microscope at choice in a fast-imaging mode at movie rates of several images per second and in a particle-tracking mode that allows to follow diffusion paths with a time resolution down to 10 ms. This paves the way to unravel in situ a variety of surface dynamics at the atomic scale that remain hidden to static imaging: Hydrogen diffusion, subsurface Fe interstitial transport, hole growth upon catalytic surface reduction, and, finally, cluster diffusion in the Smoluchowski ripening regime, at the verge of encapsulation.
[1] S. Kaiser et al., ACS Catalysis 11, 9519 (2021).
[2] S. Kaiser et al., ACS Catalysis 13, 6203 (2023).
[3] C. Dri et al., Ultramicroscopy, 205, 49 (2019).

O 49.10 Wed 12:45 MA 144

Imaging surface structure and premelting of hexagonal ice with atomic resolution — •Jiani Hong, Ye Tian, Tiancheng Liang, Xinmeng Liu, Limei Xu, Enge Wang, and Ying Jiang — School of Physics, Peking University, Beijing, P. R. China

The ice surfaces are closely relevant to many physical and chemical properties of ice, such as melting, freezing, friction, gas uptake, and atmospheric reaction. Despite massive experimental and theoretical investigations, the exact atomic structure of the ice interface still remains elusive due to the vulnerable surface hydrogen-bonding network and the complicated premelting process. Here, we realize the first atomic-resolution imaging of basal surface structure of hexagonal water ice by using qPlus-based cryogenic atomic force microscopy with a CO-functionalized tip. We find that the crystalline ice-Ih surface is composed of mixed Ih- and Ic-stacking nanodomains, forming periodic superstructures. DFT reveals that such a reconstructed ice surface is stabilized over the ideal ice surface mainly by minimizing the electrostatic repulsion between dangling OH bonds at the surface. Moreover, we find that the ice surface gradually becomes disordered with increasing temperature in experiment, revealing the onset of the premelting process. The surface premelting occurs from the defective boundaries between the Ih and Ic domains and can be promoted by the formation of a planar local structure. Those results put an end to the long-standing debate on the ice surface structure and shed new light on the molecular origin of ice premelting, which may lead to a paradigm shift in the understanding of ice physics and chemistry.