O 55: Oxide and insulator surfaces: Structure, epitaxy and growth II

Time: Wednesday 10:30–12:30 Location: HSZ/0204

O 55.1 Wed 10:30 HSZ/0204

Modulated structures in complex 2D oxides — •Muriel Wegner, Loi V. Tran, Oliver Krahn, Stefan Förster, and Wolf Widdra — Martin-Luther-Universität Halle-Wittenberg, Germany

Crystalline materials are typically characterized by a set of lattice vectors that reflect the materials dimensionality. In surface science we are used to two vectors spanning the lattice. However, systematic lattice modifications, which can be displacive in nature or connected to a different periodicity in a given materials property like magnetism, can call for the need of additional modulation vectors for a proper interpretation of the diffraction pattern. Such modulated structures are rarely discussed in surface science. Here we present the structure of a Ba-Ti-O monolayer film grown on Pd(111) and Pt(111). On Pd(111) this structure is commensurate and fully determined by two lattice vectors. In contrast, on Pt(111) four vectors are needed, two describing the average structure and two additional modulation vectors. This Ba-Ti-O structure is a complex network of Ti-O rings, in which 53% of the rings are decorated with Ba atoms. On Pd(111) it forms a rhombic structure with a periodicity of 23.2 Å and an inner angle of 129.7°. On Pt(111) it grows with the identical lattice parameters. However as a consequence of the modified substrate spacing, the domain size is restricted by systematic inclusions of defects, which cause a modulation period of about 100 Å.

O 55.2 Wed 10:45 HSZ/0204

How coordination preferences dictate the mixing behavior of 2D oxide films: Fe/Cr spinel-type oxides on Pt(111) — Ghada Missaoui[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

Fe/Cr mixed oxide films, prepared by reactive co-deposition of both elements on Pt(111), are analyzed by STM and DFT calculations. The mixed oxide grows into bi- (h=0.5 nm) and tri-stack films (h=0.7 nm) terminated either by open (2x2) (bi-stacks) or dense (1x1) atomic patterns (bi- and tri-stacks). The former is identified as Cr6O11 phase composed of an interfacial O-Cr-O trilayer and a Cr2O3 honeycomb plane. The latter develops upon substituting Fe into the surface plane, where it forms a hexagonally dense-packed Fe-O bi-layer. Two polymorphs with different mixing enthalpy occur as a function of mixing ratio. At high Fe content, X6O9-type bi-stacks prevail (X = Fe,Cr) with Cr preferentially accumulating in octahedral sites at the interface and Fe filling tetrahedral sites at the surface. At low Fe content, the Cr interface stack reconstructs to stabilize more oxygen, while the surface stack remains Fe-dominated. The resulting film has X6O11 stoichiometry and deviates from the X6O9 structure not only by the oxygen content but also by its workfunction and surface buckling, in agreement with STM data. The observed cationic stacking, with alternating Fe and Cr planes resembles the bulk ilmenite structure (FeCrO3).

Invited Talk O 55.3 Wed 11:00 HSZ/0204

Cationic Mixing in Ultrathin Oxide Films: How substrate and oxygen conditions control nanoalloying. — •Jacek Goniakowski — Institut des NanoSciences de Paris, CNRS & Sorbonne Université, Paris, France

While alloying is a powerful strategy for tuning material properties, the fundamental physics and chemistry of cation mixing in metal-supported ultrathin oxide films, including those relevant to inverse catalysts, remain poorly understood, and only a few doped or mixed phases have been characterized at the atomic scale. Here, density functional theory, combined with recent surface science experiments, is used to elucidate how oxygen conditions and substrate properties govern the formation of mixed two-dimensional oxide phases through a subtle interplay of structural and electronic effects.

The study shows that, although bulk V-Fe-O mixed oxides are rare, reduced V-Fe-O monolayers on Pt(111) are stable across a wide range of cation compositions. However, oxidation of the film strongly narrows the accessible compositional window. Likewise, substrate passivation (e.g., oxidized Ru(0001)) restricts the range of stable compositions. For somewhat thicker films, exemplified by V-Cr-O bistacks, the presence of crystallographically distinct cation sites further promotes mixing, enabling the stabilization of spinel-like V-Cr phases with no direct bulk counterparts. Our results highlight key effects governing compositionally complex supported ultrathin oxide films and suggest pathways to explore novel mixed phases.

O 55.4 Wed 11:30 HSZ/0204

Surface reconstruction of the polar spinel $MgAl_2O_4$(001) surface — David Kugler[1], Andrea Conti[1], Johanna I. Hütner-Reisch[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 governs the surface chemistry of materials. Magnesium aluminate ($MgAl_2O_4$) spinel, a wide-gap insulator, poses considerable challenges for experimental surface characterization. Using noncontact atomic force microscopy (nc-AFM), we resolve the atomic structure of the $MgAl_2O_4$(001) surface. The surface adopts a c(2×4) reconstruction accompanied by altered surface stoichiometry. The reconstructed surface is enriched in aluminum and contains ordered pairs of octahedrally coordinated Mg atoms that, in bulk, occupy tetrahedral sites. This cation redistribution stabilizes the otherwise polar $MgAl_2O_4$(001) termination. The resulting structure closely resembles reconstructions observed on other spinel oxides, suggesting a common mechanism for polarity compensation across the spinel group.

O 55.5 Wed 11:45 HSZ/0204

Size Matters: Size-dependent non-equilibrium dynamics of fluxional subnanoclusters — •Patricia Poths[1], King Chun Lai[2], Christoph Scheurer[1], Sebastian Matera[1], and Karsten Reuter[1] — [1]Fritz-Haber-Institut der Max-Planck Gesselschaft, Berlin — [2]Max Planck Computing and Data Facility, Garching

Sub-nanoclusters are known to be fluxional, thermally populating multiple structural isomers, and to have size-dependent catalytic behavior. Due to computational limitations, only quasi-static equilibrium properties could be addressed by first-principles methods so far. Here, we investigate the kinetic evolution underlying isomer fluxionality by coupling machine-learned interatomic potentials (MLIPs) with our recently introduced automatic process explorer (APE) [1]. With this methodology, we construct comprehensive isomerization networks of Pdn (n=3-11) clusters deposited on the MgO(100) surface, and evaluate the corresponding state-to-state dynamics. Using methods from Markov State Modeling, we find that the intrinsic timescales for equilibration can vary by several orders of magnitude based on cluster size. Furthermore, intrinsic timescales for each cluster isomer can vary by multiple orders of magnitude, indicating the existence of metastable sets with quasi-liquid behavior, i.e. rapid conversion between isomers within the set but only slow transition to isomers outside. These simulations reveal that the prevalent quasi-static picture is of limited use for nonequilibrium problems like catalysis, but also that relaxation dynamics should be observable on experimental timescales.

[1] K.C. Lai et al., Phys. Rev. Lett. 134, 096201 (2025).

O 55.6 Wed 12:00 HSZ/0204

Structural and electronic evolution of noble metal-deposited CeO2 catalysts: from model to powder systems — •Zairan Yu, Shuang Chen, Wangtao Li, Alexei Nefedov, Christof Wöll, and Yuemin Wang — Institute of Functional Interfaces (IFG), Karlsruhe Institute of Technology (KIT), 76344 Eggenstein-Leopoldshafen, Germany

The interaction between noble metals and oxide supports is crucial in heterogeneous catalysis, governing key reactions such as CO oxidation and the water-gas shift. Pt- and Pd-ceria systems show particularly strong electronic and structural metal-support interactions among these reactions. Despite extensive investigation, the atomic-scale structure and reactivity of these interfaces remain incompletely understood. Here, we combine polarization-resolved IRRAS on single-crystal surfaces and in situ UHV-FTIR transmission studies on ceria nanoparticles, using CO as a probe to elucidate surface structural dynamics and active sites. For Pt/CeO2(111), IRRAS and DFT results reveal that isolated Pt single atoms are not stabilized on the surface, but instead migrate into subsurface interstitial sites at low coverages,

giving rise to a characteristic blue-shifted CO band at 2169 cm-1. In the Pd/CeO2/γ-Al2O3 system, highly dispersed Pd cations embedded in the ceria matrix with nearby interfacial oxygen vacancies are identified, correlating with superior catalytic performance in STD reactions. This work was funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation)-Project-ID 426888090-SFB 1441.

O 55.7 Wed 12:15 HSZ/0204

Titanium intermixing into cuprous oxide thin films: An STM and XPS study — •Bo-Yi Zhong and Niklas Nilius — Carl-von-Ossietzky University, Institute of Physics, D-26111 Oldenburg, Germany

According to DFT calculations, gap size and p-type conductivity of binary Cu2O can be tuned over wide ranges by doping the material with transition metal ions. To test this assumption, we have prepared Cu/Ti mixtures and exposed them to different oxidation conditions. Mixing is only revealed at low temperature and gives rise to amorphous oxide films without diffraction pattern. Annealing in oxygen triggers a gradual phase separation, with TiOx moving to the surface and CuOx remaining at the interface to the Pt(111) support. The phase separation produces a distinct intensity behavior of the Ti 2p and Cu 2p XPS peaks as a function of temperature. Morphologically, the Ti ions get embedded into the surface reconstruction of Cu2O(111) at low Ti content, as observed in atomically resolved STM images. With rising Ti level, the surface Ti-O forms large crystallites exposing distinct stripe-patterns on their surface, suggesting a TiO2(110)-type morphology. Moreover, STM spectroscopy finds a gap state at 1.5 eV in Ti-poor preparations, compatible with the empty-state resonance of the Ti impurities. At higher Ti content, the gap state broadens and evolves to the TiO2 conduction band. The electronic response of the phase-separated system, with Cu2O at the interface and TiO2 at the surface, resembles the one of a pn-junction.