

O 27: Metal Oxide Surfaces I: Structure, Epitaxy and Growth

Time: Tuesday 10:30–13:00

Location: H16

O 27.1 Tue 10:30 H16

Surface characterization of single-crystalline $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ films — ●MICHELE RIVA, GIADA FRANCESCHI, MICHAEL SCHMID, and ULRIKE DIEBOLD — Institute of Applied Physics, TU Wien, Wiedner Hauptstrasse 8-10/E134, 1040, Vienna, Austria

Solid oxide fuel cells are eco-friendly devices that produce energy from chemical reactions. A widespread material for the cathode of such devices is Sr-doped lanthanum manganite ($\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$, or LSMO). Although the reactions that occur at the LSMO surface during the device operation highly affect its overall efficiency, little to nothing is known about the atomic details of its surface, and how these details affect the ongoing chemical reactions. The scarcity of such investigations is mainly due to the lack of available single crystals. We overcome this limitation by growing high-quality LSMO films by PLD. We characterize the films with a plethora of surface science techniques (STM, LEED, XPS, LEIS), and with *ex-situ* XRD, RBS, TEM, and SMOKE.

Our efforts point to the establishment of a model system for the LSMO surface, while investigating the effect of different growth and preparation conditions. Different growth parameters result in different surface compositions and surface structures, related to each other through a composition phase diagram: Deposition of controlled amounts of MnO, La_2O_3 , and SrO allows to move between the different structures in a continuous and reversible way.

O 27.2 Tue 10:45 H16

The surface phase diagram of strontium-lanthanum manganite in STM — ●GIADA FRANCESCHI, MICHELE RIVA, MICHAEL SCHMID, and ULRIKE DIEBOLD — Institute of Applied Physics, TU Wien, Wiedner Hauptstrasse 8-10/E134, 1040, Vienna, Austria

Solid oxide fuel cells are energy conversion devices that produce clean electricity by electrochemically oxidizing a fuel. This reaction follows the incorporation of oxygen in the device via a cathode surface; the rate of this reaction is limiting the device efficiency. In most commercial applications, the cathode material is Sr-doped lanthanum manganite ($\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$, or LSMO). Recent studies have demonstrated that the surface atomic details of a related complex oxide, SrTiO_3 , are key to the oxygen incorporation [1]. To enable similar investigations on the technologically-relevant LSMO, a model for its surface structures needs to be established. To this end, we have combined pulsed laser deposition with surface techniques (most prominently STM), to grow epitaxial crystalline LSMO(110) films (10-100 nm-thick) on SrTiO_3 (110). We observe a plethora of composition-related surface reconstructions that compensate for the bulk polarity. We will show our current understanding of these surface structures, along with some considerations about their stability under different oxygen chemical potentials.

[1] Riva, *et al.*, Nat. Comm., 9, 3710 (2018)

O 27.3 Tue 11:00 H16

Atomically-resolved AFM study of the bulk-terminated SrTiO_3 (001) 1x1 surface — ●IGOR SOKOLOVIĆ, MICHAEL SCHMID, ULRIKE DIEBOLD, and MARTIN SETVIN — Institute of Applied Physics, TU Wien, Wiedner Hauptstraße 8-10, 1040 Vienna, Austria

Working with bulk-terminated perovskite surfaces is challenging since the surface preparation techniques suitable for preparation of binary oxide surfaces lead to a plethora of surface reconstructions. We successfully cleaved the prototypical cubic perovskite oxide, SrTiO_3 (STO), by utilizing strain-induced ferroelectricity, and possibly found a way to cleave other cubic perovskites with no preferable planes of cleavage. The bulk-terminated (1x1) STO (001) surface was investigated by non-contact atomic force microscopy (ncAFM) which reveals that the as-cleaved surface consists of two distinct terminations: terraces with a metallic TiO_2 and a semiconducting SrO termination, both being up to micrometers in size. During the cleaving Sr atoms are pulled out of the top SrO layer and remain on the opposite TiO_2 surface in the form of adatoms; the concentration of these Sr adatoms is the same as the concentration of Sr vacancies on the SrO surface. These charged point defects serve as a polarity compensation mechanism for stabilizing the strain-induced polarity along the [001] direction in the crystal. Annealing the surface gradually alters the (1x1) termination and turns the surface amorphous.

O 27.4 Tue 11:15 H16

Plasma assisted cleaning and homoepitaxial growth of $\beta\text{-Ga}_2\text{O}_3$ — ●NICOLAS BRAUD, FELIX FESKE, THOMAS SCHMIDT, and JENS FALTA — Institute of Solid State Physics, University of Bremen, Germany

$\beta\text{-Ga}_2\text{O}_3$ is expected to play an important role in power electronics due to its high breakdown field and high Baliga figure of merit. In addition, gallium oxide has a wide band gap of 4.9 eV, which enables exciting applications as transparent conducting oxide (TCO).

In this work, annealing in molecular as well as in atomic oxygen have been compared to a sputter-cleaning approach. Optimum results regarding hydroxide and carbon removal, surface morphology and structure has been achieved with plasma assisted cleaning at up to 700 °C, as revealed by x-ray photoelectron spectroscopy, low-energy electron diffraction, and microscopy.

We also present structural and morphological investigations of the initial homoepitaxial growth by molecular beam epitaxy of $\beta\text{-Ga}_2\text{O}_3$ on two different surface orientations: (100-) and (010)- $\beta\text{-Ga}_2\text{O}_3$.

Invited Talk

O 27.5 Tue 11:30 H16

Cationic mixing in metal-supported oxide ultra-thin films: interplay of intrinsic and substrate-induced effects — ●JACEK GONIAKOWSKI and CLAUDINE NOGUERA — Institut des Nanosciences de Paris, CNRS and Sorbonne Université, Paris, France

Ternary and mixed oxides represent promising materials for many applications because combining cations of different sizes and electronegativities can be used to tune the structural and electronic properties of the resulting oxide alloys. At the nano-scale, these properties are additionally impacted by an interplay of intrinsic (size and dimensionality) and substrate-induced effects. However, despite rapid advances in the fabrication, the characterization, and the control of supported oxide ultra-thin films, a unified conceptual picture of the factors which drive their mixing characteristics at the nano-scale has not yet emerged.

In this context, considering the technological importance of transition metal oxides and in particular of M_2O_3 sesquioxides, we will consider a series of Au-supported $\text{MM}'\text{O}_3$ honeycomb monolayers ($\text{M}, \text{M}' = \text{Ti}, \text{V}, \text{Cr}, \text{and Fe}$) and we will analyse the microscopic mechanisms responsible for the cationic mixing, with the help of first principle calculations. Moreover, we will highlight the nano-oxide nature of such supported monolayers, which distinguishes them from the corresponding unsupported films and bulk materials.

O 27.6 Tue 12:00 H16

identification of two-dimensional FeO_2 termination of hematite $\alpha\text{-Fe}_2\text{O}_3$ (0001) surface — ●JESÚS REDONDO^{1,2}, PETR LAZR³, PAVEL PROCHÁZKA⁴, STANISLAV PRŮŠA⁴, JAN LACHNITT², BENJAMÍN MALLADA¹, ALEŠ CAHLÍK¹, JAN BERGER¹, BŘETISLAV ŠMÍD², PAVEL JELÍNEK¹, JAN ČECHAL⁴, and MARTIN ŠVEC¹ — ¹Institute of Physics, Czech Academy of Sciences, Prague — ²Faculty of Mathematics and Physics, Charles University, Prague — ³RCPTM, Olomouc — ⁴CEITEC, Brno

Iron oxides are among the most abundant compounds on Earth and have consequently been studied and used extensively in industrial processes. Despite these efforts, concrete understanding of some of their surface phase structures has remained elusive, in particular the oxidized $\alpha\text{-Fe}_2\text{O}_3$ (0001) hematite surface. We detail an optimized recipe to produce this phase over the entire hematite surface and study the geometrical parameters and composition of its complex structure by means of atomically resolved microscopy, electron diffraction and surface-sensitive spectroscopies. We conclude that the oxidized $\alpha\text{-Fe}_2\text{O}_3$ (0001) surface is terminated by a two-dimensional iron oxide with structure, lattice parameters, and orientation different from the bulk substrate. Using total-energy density functional theory for simulation of a large-scale atomic model, we identify the structure of the surface layer as antiferromagnetic, conductive $1T\text{-FeO}_2$ attached on half-metal terminated bulk. The model succeeds in reproducing the characteristic modulations observed in the atomically resolved images and electron diffraction patterns.

O 27.7 Tue 12:15 H16

Surface structure of Ti-doped Hematite $\alpha\text{-Fe}_2\text{O}_3$ films grown by pulsed laser deposition — ●FLORIAN KRAUSHOFER, GIADA FRANCESCHI, ZDENEK JAKUB, MAGDALENA BICHLER, MICHELE RIVA,

MICHAEL SCHMID, ULRIKE DIEBOLD, PETER BLAHA, and GARETH S. PARKINSON — TU Wien, Vienna, Austria

Hematite (α -Fe₂O₃) is a promising material for technological applications due to its abundance, low cost, and chemical stability. Its 2.2 eV bandgap makes it potentially ideal as a photoanode for photoelectrochemical water splitting, but performance is hampered by slow reaction kinetics and the need for a significant overpotential.

One widespread strategy for improving the electrocatalytic behavior of hematite anodes is to dope them slightly with titanium. However, the resulting performance usually scales with the doping level in a non-trivial way, suggesting multiple competing effects, such as independent modification of bulk conductivity and surface reactivity. How the hematite surface is modified by the presence of titanium has not been explored in depth.

Here we present an atomic-scale scanning tunneling microscopy (STM) study of Ti-doped hematite films, grown homoepitaxially on undoped hematite single crystals by pulsed laser deposition. We show that on hematite (1 $\bar{1}$ 02), titanium substitutes iron in the surface layer to form areas of an ilmenite-type FeTiO₃ termination even at low bulk doping levels, suggesting preferential agglomeration in the surface. For comparison, titanium was also deposited directly on an undoped hematite sample, which yields the same surface modification after annealing.

O 27.8 Tue 12:30 H16

In-situ growth study of Fe₃O₄/NiO bilayer and NiFe₂O₄ films using surface sensitive high energy x-ray diffraction

— •MARTIN HOPPE^{1,2}, TOBIAS POHLMANN^{1,2}, FLORIAN BERTRAM², JANNIS THIEN¹, KEVIN RUWISCH¹, and JOACHIM WOLLSCHLÄGER¹ — ¹University of Osnabrück, Osnabrück, Germany — ²DESY, Hamburg, Germany

The (inverse-) spinel structure of ferrites displays a large variety of electronic and magnetic properties¹, making some of them interesting for potential applications in spintronics. The performance of such ferrites as thin film devices, however, is strongly coupled to the structure and interface of these materials, which are determined by the growth conditions.

With the help of surface sensitive High Energy X-Ray Diffraction

(HEXRD) it was possible to record several crystal truncation rods and film reflections simultaneously on a large area Detector and achieve a good time resolution within the few seconds range, which has also been shown with CO oxidation on Pd(100) by Gustafson, et al.².

In this study, we investigated the growth of Fe₃O₄/NiO bilayers and NiFe₂O₄ on both MgO(001) and SrTiO₃(001) substrates. By recording simultaneously several CTRs we could follow the evolution the Laue fringes time dependent. By tracing the film peak position as a function of time strain parameters could be extracted as function of film thickness.

[1] K. Kuepper et al., Phys. Rev. B **94.2** (2016), 024401

[2] J. Gustafson et al., Science **343** (2014), 6172 758 – 761

O 27.9 Tue 12:45 H16

Iron cation diffusion in the near-surface region of Fe₃O₄ (001) — •STEFFEN TOBER^{1,2}, MARCUS CREUTZBURG^{1,2}, BJÖRN ARNDT^{1,2}, KONSTANTIN KRAUSERT^{1,2}, STEFAN MATTAUCH³, SABINE PÜTTER³, AMIR S. MOHD³, ALEXANDROS KOUTSIUBAS³, LUKAS VOLGGER⁴, HERBERT HUTTER⁴, HESHMAT NOEI¹, VEDRAN VONK¹, DIETER LOTT⁵, and ANDREAS STIERLE^{1,2} — ¹Deutsches Elektronen-synchrotron Hamburg — ²Universität Hamburg, Fachbereich Physik — ³Jülich Centre for Neutron Science — ⁴Technische Universität Wien, CTA — ⁵Helmholtz Zentrum Geesthacht

Magnetite is a versatile catalyst, used for example in the water-gas-shift-reaction or the Fischer-Tropsch synthesis. Its excellent catalytic properties are closely linked to the defect structure in the near surface region. Scanning tunnelling microscopy (STM) and low energy electron diffraction (LEED) studies of the ($\sqrt{2} \times \sqrt{2}$)R45° reconstructed (001) surface suggested a subsurface cation vacancy stabilisation mechanism, also confirmed by surface x-ray diffraction (SXRD) [1,2].

We present the results for the homoepitaxial growth of ⁵⁷Fe₃O₄ on magnetite (001) substrates by reactive molecular beam epitaxy (MBE). Using ⁵⁷Fe as a marker, the interdiffusion of iron ions across the film-substrate interface was followed by combining neutron reflectometry [3] and time of flight secondary ion mass spectroscopy (TOF-SIMS).

[1] Bliem, R. et al. Science. 346, 1215 (2014)

[2] Arndt, B. et al. Surf. Sci. 653, 76 (2016)

[3] Schmidt et al., Adv. Eng. Mat. 11, 446 (2009)