Surface Science Division
Room D136 - Session SS+2D+AS+HC-TuM

Oxide and Chalcogenide Surfaces and Interfaces

Moderators: Rachael Farber, University of Kansas, **Gareth Parkinson**, TU Wien

8:00am **SS+2D+AS+HC-TuM-1 ViPErLEED: LEED-*I*(*V*) Made Easy*, Alexander Michael Imre*[1]**, TU Wien, Austria*; F. Kraushofer,* TU Munich, Germany*; T. Kißlinger, L. Hammer,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany*; M. Schmid, U. Diebold, M. Riva,* TU Wien, Austria

Most surface science laboratories are equipped with a low-energy electron diffraction (LEED) setup. LEED patterns provide quick, qualitative insight into surface structure and ordering. However, the diffracted electron beams contain a large amount of additional structural information which is often ignored. By studying the diffraction intensities as a function of incident electron energy [LEED-*I*(*V*)], it is possible to quantitatively compare experimentally observed surfaces with structural models.

Despite the clear need for such a direct experiment-to-theory comparison, LEED-*I*(*V*) is only routinely used by few specialized groups. A main obstacle for widespread adoption is that existing solutions for LEED-*I*(*V*) analysis and simulation are time-consuming and hard to use for scientists who are not already experts in the field.

To resolve this issue, we have developed the Vienna Package for Erlangen LEED (ViPErLEED) – a package of three independent but complementary tools for easy LEED-*I*(*V*) acquisition and analysis. All parts of ViPErLEED will be released as open source at the time of publishing:

1. **Electronics:** We provide schematics and control software for electronics, which allows users to easily and cheaply upgrade most existing LEED setups for acquiring high-quality LEED-*I*(*V*) data. These ViPErLEED electronics are based on an Arduino microcontroller and can be home-built from off-the-shelf components. The associated control software synchronizes with the camera and automates the experiment.
2. **Spot-tracker:** ViPErLEED provides a plugin for the public-domain image processing program ImageJ, for spot tracking and extraction of LEED-I(V) spectra from series of raw diffraction images. The automatically extracted I(V) curves can be used for further analysis or as a fingerprint of the surface surface. The plugin package also provides user-friendly options for examination, selection and smoothing of the *I*(*V*) data.
3. **Simulation software:** For structure analysis, we introduce a Python package for calculation of LEED-*I*(*V*) spectra and structure optimization. This software is based on the established TensErLEED package and extends its functionality while still making it easy for new users to get started with the technique. It uses standard file formats for the surface structure, provides automated symmetry detection, and requires just a handful of parameters for running a structure determination.

8:20am **SS+2D+AS+HC-TuM-2 Quasicrystal-like Ordering of the $La_{0.8}Sr_{0.2}MnO_3$(001) Surface*, Erik Rheinfrank*,** *G. Franceschi, L. Lezuo, M. Schmid, U. Diebold, M. Riva,* TU Wien, Austria

Lanthanum-strontium manganite ($La_{0.8}Sr_{0.2}MnO_3$, LSMO) is a perovskite oxide used as a cathode material in solid oxide fuel cells, which convert chemical energy to electrical energy. To gain deeper insights into the reaction mechanisms, it is important to understand the structure of the surface at the atomic scale. To this end, we grow atomically flat single-crystalline LSMO thin films on Nb-doped $SrTiO_3$ (STO) substrates via pulsed laser deposition (PLD). Previously, this has been achieved for the (110) orientation.[1,2. Here, we use a similar approach on the (001) surface that is commonly used for oxide-based electronics and spintronics. The as-grown films have a MnO_x terminated surface that shows a 4-fold symmetric structure in low-energy electron diffraction (LEED), best explained by a set of four basis vectors reminiscent of quasicrystals. Scanning tunnelling microscopy (STM) and Q+ non-contact atomic force microscopy (nc-AFM) reveal an aperiodic arrangement of tiles with rotation angles of ±26.6° and 90±26.6°, and a Fourier transform consistent with the LEED pattern. As for quasicrystals, the surface has a sharp diffraction pattern despite the lack of translational symmetry.

[1] Franceschi *et al.*, J. Mater. Chem. A, 2020, **8**, 22947-22961

[2] Franceschi *et al.*, Phys. Rev. Materials, 2021, **5**, L092401

8:40am **SS+2D+AS+HC-TuM-3 AVS Graduate Research Awardee Talk: The Selective Blocking of Potentially Catalytically-Active Sites on Surface-Supported Iron Oxide Catalysts*, Dairong Liu*[2,3]***, N. Jiang,* University of Illinois - Chicago

The extensive research on ultrathin ferrous oxide (FeO) islands and films over the last few decades has significantly contributed to the understanding of their structural and catalytic properties.One important aspect that has been investigated is the surface properties of ultrathin FeO islands, particularly the role played by the edges of these islands in catalytic reactions, such as CO oxidation. So far, two different types of edge, Fe-terminated edge and O-terminated edge, have been identified in the well-growth FeO island. However, despite this significant progress, the local chemical properties of these two types of edges, including their metal affinity, have remained largely unexplored. Here, we used scanning tunneling microscopy (STM) to study the interaction of Pd and Pt with FeO grown on Au(111). Different Fe affinities for Pd and Pt are demonstrated by the preferential growth of Pd on the Fe-terminated edge and Pt on the O-terminated edge of FeO nanoislands, resulting in selectively blocked FeO edges. In addition to revealing the different metal affinities of FeO edges, our results provide new insights into the edge reactivity of FeO/Au(111) and suggest an approach for controlling the selectivity of FeO catalysts. By comparing the behavior of different edges in the catalysis reaction, the catalytic activity of these edges can be studied solely, thereby sheds light into the future modification of ferrous-based catalysts.

9:00am **SS+2D+AS+HC-TuM-4 Unraveling Surface Structures of Ga-Promoted Transition Metal Catalysts in CO_2 Hydrogenation*, Si Woo Lee,*** *S. Shaikhutdinov, B. Roldan Cuenya,* Fritz Haber Institute of the Max Planck Society, Germany

Gallium-containing alloys with transition metals (TM) have recently been reported to be reactive in the selective hydrogenation of CO_2 for methanol synthesis. However, a full understanding of the Ga-promoted catalysts is still missing due to the lack of information about the *surface* structures formed under reaction conditions. In this respect, studies using surface-sensitive techniques applied to well-defined model systems can provide key information to elucidate the reaction mechanism and provide the basis for the rational design of Ga-promoted catalysts.

In this work, we employed *in-situ* Near Ambient Pressure Scanning Tunneling Microscopy (NAP-STM) and X-ray Photoelectron Spectroscopy (NAP-XPS), which make it possible to study surfaces in the reaction conditions, for monitoring the structural and chemical evolution of the Ga-covered Cu surfaces in the CO_2 hydrogenation reaction. NAP-STM images recorded in the reaction mixture revealed temperature- and pressure-dependent de-alloying of the initially formed, well-ordered $(\sqrt{3}\times\sqrt{3})R30°$-Cu(111) surface alloy and the formation of Ga-oxide islands embedded into the Cu(111) surface, exposing GaO_x/Cu(111) interfacial sites. Notably, in our atomically-resolved STM image of Ga-oxide/Cu(111), it is clearly observed that Ga-oxide grows into an ultrathin oxide layer form with $(4\sqrt{3}\times4\sqrt{3})R30°$ superstructure. From NAP-XPS studies on Ga/Cu(111) in the presence of CO_2 and H_2, the formation of formate was observed, and this reaction intermediate was eventually transformed into methoxy at elevated temperatures, representing the final surface-bound intermediate for methanol synthesis. In contrast to Ga-containing Cu catalyst, on the other hand, there was no reaction intermediate at high temperature on the Ga-free Cu(111) surface, demonstrating that further reactions do not occur anymore from chemisorbed $CO_2^{\delta-}$ on Cu surface alone. Therefore, the GaO_x/Cu interface formed under reaction conditions may expose catalytically active sites never considered for this reaction before. We believe that our experimental results shed light on the complex surface structure of Ga-containing catalytic systems, which is only possible to obtain using state-of-the-art experimental techniques under reaction conditions. Only by establishing the atomic structure of the Ga-oxide layer(s) and its interface to the transition metal under working conditions can one bring insight into the reaction mechanism of this methanol synthesis catalyst.

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[1] **SSD Morton S. Traum Award Finalist**

[2] **AVS Graduate Research Awardee**

[3] **SSD Morton S. Traum Award Finalist**

9:20am **SS+2D+AS+HC-TuM-5 Ultrathin Metal Oxide, Nitride and Sulfide Films: Bringing the Well-Known Compounds to a Unit-Cell Thickness***, **Mikołaj Lewandowski,*** NanoBioMedical Centre, Adam Mickiewicz University in Poznań, Poland **INVITED**

Bringing the well-known materials from bulk size to a unit-cell thickness may significantly influence their structure and physicochemical properties. As an example, ultrathin (< 1-nanometer-thick) films of metal/non-metal compounds, such as metal oxides, nitrides or sulfides epitaxially grown on single-crystal supports, are characterized by unique electronic, catalytic and magnetic properties not observed for their bulk counterparts. Such films also exhibit superior structural flexibility, undergoing phase transitions upon exposure to external factors (such as reactive gases or high temperatures) [1,2]. All this makes them promising candidates for applications in various technological fields, including nanoelectronics, spintronics and heterogeneous catalysis.

Within the lecture, I will address the growth, structure and properties of ultrathin metal oxide, nitride and sulfide films, with compounds of iron as exemplary cases. The scanning tunneling microscopy and spectroscopy (STM/STS), low energy electron diffraction (LEED), X-ray photoelectron spectroscopy (XPS), low energy electron microscopy (LEEM) and density functional theory (DFT) results – obtained by my group and our collaborators – provide universal guidelines for designing ultrathin films with desired structure and properties [1–3].

[1] Y. Wang, G. Carraro, H. Dawczak-Dębicki, K. Synoradzki, L. Savio, M. Lewandowski, Applied Surface Science 528 (2020) 146032.

[2] N. Michalak, T. Ossowski, Z. Miłosz, M. J. Prieto, Y. Wang, M. Werwiński, V. Babacic, F. Genuzio, L. Vattuone, A. Kiejna, Th. Schmidt, M. Lewandowski, Advanced Materials Interfaces 9 (2022) 2200222.

[3] P. Wojciechowski, W. Andrzejewska, M.V. Dobrotvorska, Y. Wang, Z. Miłosz, T. Ossowski, M. Lewandowski, submitted (2023).

The author acknowledges financial support from the National Science Centre of Poland (through SONATA 3 2012/05/D/ST3/02855, PRELUDIUM 11 2016/21/N/ST4/00302 and M-ERA.NET 2 2020/02/Y/ST5/00086 projects), as well as the Foundation for Polish Science (First TEAM/2016-2/14 (POIR.04.04.00-00-28CE/16-00) project co-financed by the European Union under the European Regional Development Fund).

11:00am **SS+2D+AS+HC-TuM-10 Optimized Infrared Reflection Absorption Spectroscopy for Metal Oxides: Overcoming Challenges of Low Reflectivity and Sub-Monolayer Coverage***, **Jiri Pavelec**, D. Rath, M. Schmid, U. Diebold, G. Parkinson,* Vienna University of Technology, Austria

Infrared reflection absorption spectroscopy (IRAS) is a wide-spread technique in heterogenous catalysis, and it is an ideal tool for the comparison of real and model catalysts [1]. Most surface science groups perform IRAS studies either directly on metal single crystals, or on (ultra-)thin metal oxide films grown on such samples [2]. Achieving high-quality data from metal-oxide single crystal surfaces is difficult because their low reflectivity necessitates averaging many individual measurements with long acquisition times [3]. The goal of this work was to develop an IRAS setup for studying the adsorption of molecules on model “single-atom” catalysts. Here, the low reflectivity of oxide support is exacerbated by the sub-monolayer coverage of adsorbates on single adatoms. In the contribution, I will present the novel IRAS system we have developed to overcome these two challenges.

The main improvements over commonly-used setups are a high numerical aperture, an optimized optical path, control of the incidence angle range, and high mechanical stability. The high numerical aperture of the optical system leads to an increase in the amount of light reflected from a small single crystal sample. This is achieved by placing both the illumination and collector mirrors inside the UHV chamber close to the sample. To minimize the loss of signal, optimization of the optical path was performed using a ray tracing program. The other limit is the small area on the sample that is covered with adsorbates: in our setup, a molecular beam delivers adsorbates with a spot diameter of 3.5 mm [4]. Infrared light is reflected only from this area.

The reflectivity and absorbance of non-metallic samples varies strongly with incidence angle, and can even change a sign, leading to cancellation. The optimum angle ranges are different for every material. As our setup has a large range of incident angles, we can use this to our advantage: Using two adjustable aperture plates, we can vary the minimum and maximum incidence angle from 49° to 85° to maximize the signal for each single crystal sample. Angle control also allows us to optimize the signal for both p-polarized and s-polarized light independently.

We successfully executed and compared D_2O and CO absorbance measurements on a rutile $TiO_2(110)$ surface, and our results agree with the established literature [3]. By properly selecting the incidence angle range, we achieved a signal-to-noise ratio of ~16 for 1 ML CO adsorbed on TiO_2 with only 150 seconds of measurement time.

[1] F. Zaera, Chem. Soc. Rev., 43, 2014
[2] J. Libuda et al., J. Chem. Phys., 114, 10, 2001
[3] N. G. Petrik et al., The Journal of Physical Chemistry C, 126 (51), 2022
[4] J. Pavelec et al., J. Chem. Phys., 146, 2017

11:20am **SS+2D+AS+HC-TuM-11 VO Cluster-Stabilized H_2O Adsorption on a TiO_2 (110) Surface at Room Temperature***, **Xiao Tong**,* Brookhaven National Laboratory

We probe the adsorption of molecular H_2O on a TiO_2 (110)-(1 × 1) surface decorated with isolated VO clusters using ultrahigh-vacuum scanning tunneling microscopy (UHV-STM) and temperature-programmed desorption (TPD). Our STM images show that preadsorbed VO clusters on the TiO_2 (110)-(1 × 1) surface induce the adsorption of H_2O molecules at room temperature (RT). The adsorbed H_2O molecules form strings of beads of H_2O dimers bound to the 5-fold coordinated Ti atom (5c-Ti) rows and are anchored by VO. This RT adsorption is completely reversible and is unique to the VO-decorated TiO_2 surface. TPD spectra reveal two new desorption states for VO stabilized H_2O at 395 and 445 K, which is in sharp contrast to the desorption of water due to recombination of hydroxyl groups at 490 K from clean TiO_2(110)-(1 × 1) surfaces. Density functional theory (DFT) calculations show that the binding energy of molecular H_2O to the VO clusters on the TiO_2 (110)-(1 × 1) surface is higher than binding to the bare surface by 0.42 eV, and the resulting H_2O-VO-TiO_2 (110) complex provides the anchor point for adsorption of the string of beads of H_2O dimers.

11:40am **SS+2D+AS+HC-TuM-12 Synthesis and Multimodal Characterization of Thin-Film Oxides***, **Dario Stacchiola**,* Brookhaven National Laboratory

Thin films of metal oxides exhibit a variety of unique physical and chemical properties leading to broad applications in optics, microelectronics, optoelectronics, superconducting circuits, gas sensors, thermal catalysis, electrocatalysis, and solar energy harvesting. Many metal oxides can form stoichiometric and non-stoichiometric alloys and compounds with each other, commonly known as complex metal oxides. Alloy and compound formation, including growth and process conditions, offer great flexibility for manipulating the lattice, atomic scale structure motifs, and electronic structure to realize desired properties. In order to exploit this potential, knowledge about fundamental processes and atomic level structural information is required. We present here the synthesis and multimodal characterization of mixed-oxide films based on silica and titania, from single layers to complex metal oxides.

1. “Deciphering phase evolution in complex metal oxide thin films via high-throughput materials synthesis and characterization”, Nanotechnology 34, 125701 (2023)

2. “Resolving the evolution of atomic layer deposited thin film growth by continuous in situ X-ray absorption spectroscopy”, Chem. Mat. 33, 1740-1751 (2021)

3. “First-Principles Study of Interface Structures and Charge Rearrangement at the Aluminosilicate / Ru(0001) Heterojunction” J. Phys. Chem. C 123, 7731–7739 (2019)

12:00pm **SS+2D+AS+HC-TuM-13 Atomic Structure of Reconstructed Al_2O_3(0001) Surface***, J. Hütner, A. Conti,* TU Wien, Austria*; D. Kugler,* CEITEC, Czechia*; F. Mittendorfer, U. Diebold, M. Schmid, **Jan Balajka**,* TU Wien, Austria

Corundum α-Al_2O_3 is an important ceramic widely used in electronics, optical applications, or as catalyst support. Despite its importance, the atomic structure of the most stable (0001) termination has not been conclusively determined. Detailed studies of Al_2O_3 surfaces have been stymied by its insulating nature, preventing the use of many surface science methods.

Structural models based on surface X-ray diffraction (SXRD) [1], and atomic force microscopy (AFM) [2], concluded the $(\sqrt{31} \times \sqrt{31})\mathrm{R}\pm 9^\circ$-reconstructed Al_2O_3(0001) surface formed upon high-temperature annealing is terminated by one or two layers of metallic Al strained to lattice-match the oxide substrate.

We imaged the reconstructed Al_2O_3(0001) surface with noncontact AFM (nc-AFM) using specifically functionalized tips for chemically-sensitive contrast. In particular, CuO_x terminated tips [3], enabled us to directly identify oxygen and aluminum atoms in the topmost layer.

With the aid of *ab-initio* calculations, we propose a structural model of the $(\sqrt{31} \times \sqrt{31})R\pm9°$-reconstructed $Al_2O_3(0001)$ surface consistent with atomically resolved nc-AFM images and area-averaging spectroscopic data. Unlike prior models, the surface does not contain a metallic Al layer but consists of oxygen and aluminum atoms arranged in similar structural units as reported in thin AlO_x films [4,5].

[1] G. Renaud, et al., *Phys. Rev. Lett*. **73**, 13 (1994)

[2] J. V. Lauritsen, et al., *Phys. Rev. Lett.***103**, 076103 (2009)

[3] B. Shulze Lammers, et al., *Nanoscale***13**, 13617 (2021)

[4] G. Kresse, et al., *Science***308**, 1440 (2005)

[5] M. Schmid, et al., *Phys. Rev. Lett.***99**, 196104 (2007)

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