

O 92: Oxide and Insulator Surfaces II: Structure, Epitaxy and Growth

Time: Friday 10:30–13:00

Location: CHE 91

O 92.1 Fri 10:30 CHE 91

Growth of ultrathin silica films on Pt(111) and Rh(111): Influence of intermixing with the support — ●FLORIAN KRAUSHOFER¹, MATTHIAS KRINNINGER¹, NILS REFVIK², FRIEDRICH ESCH¹, and BARBARA LECHNER¹ — ¹TU Munich, Germany — ²University of Alberta, Canada

Silica is a widely used catalyst support material for clusters and nanoparticles. Understanding the relationship between these clusters and the support is challenging, however, because SiO₂ is insulating, and in most applications not crystalline, which limits the use of diffraction-based experimental techniques. Several previous studies have investigated ultrathin, quasi-2D silica films on a variety of metal supports [1], which can then be measured by scanning tunneling microscopy (STM). Previous work on Pt(111) did not result in closed films, which was attributed to lattice mismatch [2]. We show that closed films can in fact be grown on Pt(111) when silica is deposited in excess, likely due to formation of a platinum silicide layer with a slightly expanded lattice constant at the interface. We also report results of film growth on Rh(111), which is a near-perfect match to the lattice constant of freestanding SiO₂ films as calculated by theory. However, no high-quality films were achieved, which we attribute to a different balance of the formation energies for silicide and oxide.

[1] C. Büchner, M. Heyde, Two-dimensional silica opens new perspectives, *Prog. Surf. Sci.*, 92 (2017) 341-374.

[2] X. Yu, B. Yang, J. A. Boscoboinik, S. Shaikhutdinov, and H.-J. Freund, *Appl. Phys. Lett.* 100 (2012), 151608.

O 92.2 Fri 10:45 CHE 91

Growth of single-phase honeycomb Ti₂O₃ on Pd(111) — ●RAJESH CHIRALA, STEFAN FÖRSTER, and WOLF WIDDRA — Institute of Physics, Martin-Luther-Universität Halle-Wittenberg, 06120 Halle, Germany

Transition metal oxides are known to form honeycomb (HC) structures when grown on metal substrates. The oxide-substrate interaction strength defines the substrate-dependent HC lattice parameter. On Au(111), the Ti₂O₃ HC forms a (2×2) superstructure corresponding to lattice parameter of 5.77 Å [1]. On the contrary, Pt(111) has HC relaxing to a lattice parameter of 5.95 Å [2].

Here we study the growth of a Ti₂O₃ HC structure on Pd(111) from the initial stages up to monolayer coverages. The HC is grown by consecutive steps of room-temperature Ti deposition and annealing at 875 K in 7×10⁻⁹ mbar of O₂. Whilst the smallest HC patches grow with a lattice parameter of 5.8 Å with a rotation of 26° against the <112> direction of Pd(111), they relax to a lattice parameter of 5.95 Å at higher coverage. Due to this relaxation, the HC lattice coincides with the Pd(111) at a rotation of 30°. The implications of this HC structure as template for the growth of dodecagonal oxide quasicrystal will be discussed [3].

[1] F. Sedona et al., *J. Phys. Chem. B* **109**, 24411 (2005)

[2] C. Wu et al., *J. Phys. Chem. C* **115**, 8643 (2011)

[3] S. Schenk et al., *Nat. Commun.*, accepted (2022)

O 92.3 Fri 11:00 CHE 91

Magnetite homoepitaxy observed by X-ray intensity growth oscillations — ●STEFFEN TOBER^{1,2,3}, MARCUS CREUTZBURG¹, BJÖRN ARNDT¹, SIMON CHUNG¹, LEON JACOBSE¹, ARNO JEROMIN¹, VEDRAN VONK¹, and ANDREAS STIERLE^{1,2} — ¹Deutsches Elektronen-Synchrotron DESY, Centre for X-ray and Nanoscience, Hamburg — ²Universität Hamburg, Fachbereich Physik — ³Jülich Centre for Neutron Science (JCNS) and Peter Grünberg Institut (PGI), JARA-FIT, Forschungszentrum Jülich

Processes on the magnetite (Fe_{3-δ}O₄) (001) surface like oxidative re-growth, (partial) lifting of the subsurface cation vacancy reconstruction and the element-specific incorporation of adatoms demonstrate the sensitive relation of oxygen pressure, cation transport and structure in the near-surface region of Fe_{3-δ}O₄ influencing the performance of catalysts and devices [1,2,3]. We exemplarily studied the homoepitaxial growth of Fe_{3-δ}O₄ (001) surface in dependence of the O₂ pressure and iron flux. X-ray intensity growth oscillations proved ordered growth of Fe_{3-δ}O₄ for all probed conditions while atomic force microscopy revealed newly formed micrometre-sized surface structures exceeding the

amount of deposited material [4]. Our results indicate the presence of multiple parallel processes during reactive Fe_{3-δ}O₄ homoepitaxy suggesting similar processes to occur also in other applications of Fe_{3-δ}O₄. [1] Nie et al., *J. Am. Chem. Soc.* 135, 10091 (2013), [2] Arndt, B. et al. *PCCP* 22, 8336 (2020), [3] Mirabella et al., *Electrochimica Acta*, 389, 138638 (2021), [4] van der Vegt et al., *Phys. Rev. Lett.* 68, 3335 (1992)

O 92.4 Fri 11:15 CHE 91

The dependence of structure on thickness of NiO(100) films on Ag(100) studied by IV-LEED — ●JAN LACHNITT¹, SHUVANKAR DAS², KRISHNAKUMAR S. R. MENON², SUMAN MANDAL³, and JAN I. FLEGE¹ — ¹Applied Physics and Semiconductor Spectroscopy, Brandenburg University of Technology Cottbus-Senftenberg, Cottbus, Germany — ²Surface Physics & Material Science Division, Saha Institute of Nuclear Physics, Kolkata, India — ³Department of Physics, Sabang Sajanikanta Mahavidyalaya, Paschim Medinipur, India

Ultrathin NiO films have prospective applications especially in heterogeneous catalysis, microelectronics, and spintronics and are thus an object of active research. The Ag(100) surface is the usual support for these films, as its cubic lattice parameter is only 2.2 % smaller than that of NiO, which enables pseudomorphic growth at very low thicknesses. We have studied the NiO(100) surface for three thicknesses of the oxide: 2 ML on Ag(100), 20 ML on the same substrate, and a bulk single crystal. We have used intensity-voltage low-energy electron diffraction (IV-LEED) in combination with X-ray photoelectron spectroscopy (XPS) and density-functional theory (DFT) calculations. We focus on differences among the three thicknesses, mainly in terms of lattice parameters and surface defects, and our study deepens existing knowledge of the growth of ultrathin NiO films. The IV-LEED calculations have been carried out using the AQUALEED package, which will also be briefly presented.

O 92.5 Fri 11:30 CHE 91

LEED I(V) with ViPErLEED: Overview and Applications — ●ALEXANDER M. IMRE¹, FLORIAN KRAUSHOFER^{1,2}, FLORIAN DOERR¹, TILMAN KISSLINGER³, MICHAEL SCHMID¹, ULRIKE DIEBOLD¹, LUTZ HAMMER³, and MICHELE RIVA¹ — ¹TU Wien, Vienna, Austria — ²TU Munich, Munich, Germany — ³FAU Erlangen-Nürnberg, Erlangen, Germany

LEED *I(V)* is an extension to qualitative Low Energy Electron Diffraction (LEED) pattern analysis in which diffraction intensities are quantitatively studied as a function of incident electron energy. This yields structural information about the surface that can be difficult to obtain otherwise. Regrettably, LEED *I(V)* has been underutilized by the surface science community over the last decades.

Our group has developed the Vienna Package for TensErLEED (ViPErLEED); a suite of hardware and software aiming to drastically reduce the barrier of entry for the technique. The three core parts of ViPErLEED are: (1) electronics that enable upgrading existing LEED setups for LEED *I(V)*, (2) a spot tracker for easy *I(V)* curve extraction, and (3) a Python package for LEED *I(V)* analysis based on the TensErLEED package.

We present a quick overview of ViPErLEED and give insight into current developments. We then show LEED *I(V)* results obtained and analyzed using ViPErLEED for the α-Fe₂O₃(012)-(1×1) and (2×1) surfaces. While a bulk-truncation is confirmed for α-Fe₂O₃(012)-(1×1), current structural models cannot explain the (2×1) termination.

O 92.6 Fri 11:45 CHE 91

Reduction by H₂ exposure at room temperature of ceria ultrathin films grown by atomic layer deposition — ●CARLOS MORALES, YULIA 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) exhibits a high potential for integration as a scalable process in microelectronics, allowing well-controlled layer-by-layer deposition and conformal growth on 3D structures. Yet, the ALD technique is also well known to lead to amorphous and defective,

non-stoichiometric films, potentially resulting in modified materials properties that, in the case of ultra-thin deposits, can also be affected by film/substrate interaction. Interestingly, initial in situ X-ray photoemission spectroscopy (XPS) measurements of ceria ALD-deposits on Al₂O₃/Si, sapphire, and SiO₂ substrates confirm a Ce³⁺/Ce⁴⁺ mixture dependent on the substrate interaction, deposit thickness, and morphology. Using near-ambient pressure XPS, we have significantly reduced ultrathin (< 10 nm) ceria films grown by ALD by exposing them to different O₂/H₂ partial pressures at moderate temperatures (< 525K). Notably, the total amount of reduction to Ce³⁺ is found to depend on the deposit thickness and initial ceria/substrate interaction. Furthermore, the intrinsic defects related to the ALD method seem to play a critical role in the reversible reduction at room temperature.

O 92.7 Fri 12:00 CHE 91

Role of orientation and oxyhydroxide formation on the OER activity of LaNiO₃ surfaces — ●ACHIM FÜNGERLINGS¹, MARCUS WOHLGEMUTH², MARCEL RISCH³, FELIX GUNKEL², CHRISTOPH BÄUMER^{2,4}, and ROSSITZA PENTCHEVA¹ — ¹Department of Physics and Center for Nanointegration Duisburg-Essen (CENIDE), University of Duisburg-Essen, Duisburg, Germany — ²Peter Gruenberg Institute and JARA-FIT, Forschungszentrum JuelichGmbH, Juelich, Germany — ³Nachwuchsgruppe Gestaltung des Sauerstoffentwicklungsmechanismus, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany — ⁴MESA+ Institute for Nanotechnology, Faculty of Science and Technology, University of Twente, Enschede, Netherlands

We present a combined experimental and theoretical study of the influence of surface orientation and transformation on the OER activity of Ni-terminated (001), (110) and (111) oriented LaNiO₃ films, epitaxially grown on SrTiO₃ substrates via pulsed laser deposition and characterized by AFM and XRD, as well as Hall measurements of the electrical conductivity. Cyclic voltammetry shows the lowest overpotential for (111) and the highest for (001), and gives indication for the formation of a surface oxyhydroxide(-like) skin layer, supported by EXAFS measurements. Based on density functional theory calculations with an on site Hubbard U , we explored different models for the transformed surfaces and find a strong sensitivity of the OER activity on interlayer H concentration and number of oxyhydroxide layers with distinct behavior of the two surface orientations.

O 92.8 Fri 12:15 CHE 91

Electron-phonon coupling for the 2D electron gas at EuO/KTaO₃(001) studied by HREELS — ●HANNES HERRMANN, ANNE OELSCHÄGER, and WOLF WIDDRA — Martin-Luther-Universität Halle-Wittenberg, Institute of Physics, 06120 Halle, Germany

Recent studies at the KTaO₃(111) surface revealed a 2D electron gas (2DEG) with much higher charge carrier density than in SrTiO₃-based heterostructures [1]. Similar 2DEGs with lower charge carrier densities could be obtained on the (011) and (001) surfaces [2].

In this work, we study surface plasmon polaritons (SPP) and their coupling to a 2DEG with high-resolution electron energy loss spectroscopy (HREELS). By evaporating Eu on top of KTaO₃(001), a 2DEG is initiated resulting in a pronounced asymmetric SPP line

shape and extreme broadening compared to the phonons of the clean surface. The line shape will be analysed in terms of a strong coupling of the SPP with the 2DEG. The response can be described by a two-layer model with a 2D Drude-like response with frequency-dependent electronic mobility on top of a bulk-like KTaO₃.

[1] A. F. Santander-Syro, C. Bareille, F. Fortuna and M. J. Rozenberg, Phys.Rev. B 86, 121107 (2012)

[2] P. D. C. King, R. H. He, T. Eknapakul and W. Meevasana, Phys. Rev. Lett. 108.117602 (2012)

O 92.9 Fri 12:30 CHE 91

2D electron gas and interdiffusion processes at the EuO/SrTiO₃(001) interface — ●ANNE OELSCHLÄGER, HANNES HERRMANN, STEFAN FÖRSTER, and WOLF WIDDRA — Martin-Luther-Universität Halle-Wittenberg, Institute of Physics, 06120 Halle, Germany

The deposition of metallic europium (Eu) on SrTiO₃(001) (STO) creates a two-dimensional electron gas (2DEG) and concomitant Ti³⁺-O₂-vacancy complexes [1]. Here we study this interface by HREELS, XPS and LEED. The phonon spectra are dominated by the dipole-active surface phonon polaritons of STO. They show a prominent broadening in the presence of the 2DEG due to strong electron-phonon coupling.

Upon annealing to 1020 K, the Ti³⁺ related photoemission lines as well as the phonon broadening vanish. We assign these changes to diffusion of oxygen from the bulk to the EuO/STO interface. Finally, the intensity ratio of Sr3*p* and Ti2*p* core levels indicates a diffusion of Ti to the europium oxide (EuO) layer, i.e. formation of EuTiO₃.

[1] P. Lömker et al. Phys. Rev. Mater. 1, 062001(R), 2017

O 92.10 Fri 12:45 CHE 91

Surface Structures of La_{0.8}Sr_{0.2}MnO₃(001): from Commensurate to Quasicrystal Phases — ●ERIK RHEINFRANK¹, MICHAEL BRUNTHALER¹, GIADA FRANCESCHI¹, PETER MATVIJA², MICHAEL SCHMID¹, ULRIKE DIEBOLD¹, and MICHELE RIVA¹ — ¹Institute of Applied Physics, TU Wien, Austria — ²Faculty of Mathematics and Physics, Department of Surface and Plasma Science, Charles University, Prague, Czech Republic

Lanthanum-strontium manganite (La_{0.8}Sr_{0.2}MnO₃, 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(001) thin films on Nb-doped SrTiO₃ (STO) substrates via pulsed laser deposition (PLD). The as-grown films have a B-site (Mn) rich surface that can be transformed into an A-site (La/Sr) rich structure by Ar⁺ sputtering and subsequent annealing. The B-site rich surface is recovered by depositing Mn from a MnO target. In low-energy electron diffraction (LEED), the Mn-rich surface shows a 4-fold symmetric structure that is best explained by a set of four basis vectors. This is reminiscent of quasicrystals. Scanning tunneling microscopy reveals a non-periodic structure with a Fourier transform consistent with the LEED pattern.