

O 89: Oxides and Insulator Surfaces II

Time: Thursday 15:00–18:30

Location: H4

O 89.1 Thu 15:00 H4

Iron-Silicate films on Ru(0001) — ●GINA PESCHEL, HAGEN W. KLEMM, ALEXANDER B. FUHRICH, MAURICIO PRIETO, DIETRICH MENZEL, THOMAS SCHMIDT, and HANS-JOACHIM FREUND — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Deutschland

Zeolites offer strong catalytic activity and are already widely used in industry as desiccant, detergent or as molecular sieves. Iron-silicate could be seen as a model system, offering the possibility to understand structure and reactivity correlations and functionalize these materials even more. Our investigation addresses the growth and structure of ultrathin iron-silicate films on a Ru(0001) substrate with the methods of LEEM, LEED, XPS and XPEEM.

Our studies reveal the formation of co-existing structural domains. XPEEM results indicate that one kind of domain contains iron and silicon while the other domain type contains only silicon. The overall LEED pattern consists of a $(\sqrt{3} \times \sqrt{3}) R30^\circ$ pattern with Moiré spots, superimposed with a (2×2) structure, which could be assigned to the individual domains, respectively. Including additional XPS results we suggest a model for the iron-silicate consisting of a silica layer bound to a complete FeO layer on the Ru-support.

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AFM investigation on CaF₂(111) with atomically characterized tips — ●ALEXANDER LIEBIG, DANIEL MEUER, ANGELO PERONIO, and FRANZ JOSEF GIESSIBL — Universität Regensburg, Germany

Contrast formation in atomic force microscopy (AFM) images of ionic systems is often dominated by the electrostatic interaction between the ions of the sample and the tip apex. Thus, the chemical identity of the latter determines the contrast pattern, as e.g. shown for NaCl bilayers on the Cu(111) surface by Gross et al. [1]. To optimize atomic contrast in AFM experiments, the tip is usually poked slightly into the surface, ending up with picking up a cluster of sample atoms by the tip. The tip termination is thus uncharacterized, hindering the discrimination of the different species of atoms in the AFM images. In this work, the CaF₂(111) surface is studied by AFM measurements. In contrast to ionic crystals of the rock salt structure, the surface ions of CaF₂(111) are all charged negatively [2] and the contrast of the image allows to determine the tip polarity [2,3]. Similar to previous experiments on Cu₂N [4], we use tips that are characterized at the atomic level using COFI [5], where an adsorbed CO molecule is used to image the tip apex. Our goal is to characterize the imaging mechanisms and the electrostatics of our different tips on the CaF₂(111) surface.

References: [1]: L. Gross et al., Phys. Rev. B 90, 155455 (2014). [2]: A. Foster et al., Phys. Rev. Lett. 86, 2373 (2001). [3]: F. J. Giessibl, M. Reichling, Nanotechnology 16, 118 (2005). [4]: M. Schneiderbauer et al., Phys. Rev. Lett. 112, 166102 (2014). [5]: J. Welker et al., ACS Nano 7, 7377 (2013).

O 89.3 Thu 15:30 H4

(100)-oriented CeO₂ Nanoislands: Structure and Polarity Compensation — ●NIKLAS NILIUS¹, YI PAN², HANS-JOACHIM FREUND², CLAUDINE NOGUERA³, and JACEK GONIAKOWSKI³ — ¹Carl von Ossietzky Universität Oldenburg, Institut für Physik, D-26111 Oldenburg, Germany — ²FHI-Berlin, Fradayweg 14-16, D-14195 — ³CNRS-Sorbonne Universités, UPMC Univ. Paris 06, UMR 7588, INSP, F-75005 Paris, France

Compact CeO₂(111) films grown on Ru(0001) can be transformed into well-shaped nanoparticles by annealing them in an oxygen-poor environment. With increasing temperature, the particles undergo a shape evolution that finally leads to crystallites exposing wide (100) facets. The atomic structure of the (100) termination has been determined with a combination of high-resolution scanning tunneling microscopy and density functional theory. Two surface reconstructions are identified, composed either of CeO₄ nano-pyramids in a (2×2) arrangement or oxygen adatoms forming a $c(2 \times 2)$ super-structure. Both terminations enable full compensation of the polar dipole intrinsic to CeO₂(100), but also reflect a gradual reduction of the oxide that proceeds from the surface. Our study provides insights into the rarely explored (100) termination of ceria, which represents a good model system for structurally open and polar oxide surfaces.

O 89.4 Thu 15:45 H4

Thin Silica films on Ru(0001) — ●HAGEN WILLIAM KLEMM, GINA PESCHEL, ALEXANDER BENEDIKT FUHRICH, MAURICIO PRIETO, DIETRICH MENZEL, THOMAS SCHMIDT, and HANS-JOACHIM FREUND — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4, 14195 Berlin, Germany

Ultrathin SiO₂ and metal doped silicate layers on Ru(0001) offer various possibilities as model systems for understanding the relationship between structure and reactivity of very complex material systems like Zeolites. With the aberration corrected spectro-microscope SMART at the synchrotron light source BESSY-II in Berlin, allowing high-resolution XPEEM, μ XPS, valence band mapping, μ -LEED and LEEM, preparation conditions and their influence on the Silica layers were studied *in situ* at the mesoscopic scale. The deposited amount of Silicon and the oxidation conditions strongly influence the crystallographic and electronic structure of these Silica films. SiO₂ bilayer films are of special interest, because they are only Van de Waals like bound to the Ru(0001) substrate and therefore lift off the support. Under special preparation conditions an oxidation front, followed by an oxygen intercalation could be observed.

Invited Talk

O 89.5 Thu 16:00 H4

The growth and decay of oxide quasicrystals — ●STEFAN FÖRSTER¹, JAN INGO FLEGE², EVA MARIA ZOLLNER¹, FLORIAN SCHUMANN¹, KLAUS MEINEL¹, JENS FALTA², and WOLF WIDDRA^{1,3} — ¹Institute of Physics, Martin-Luther-Universität Halle-Wittenberg, Halle, Germany — ²Institute of Solid State Physics, University of Bremen, Bremen, Germany — ³Max Planck Institute of Microstructure Physics, Halle, Germany

Two-dimensional materials have recently pioneered a new field of materials science. Their peculiar properties are often related to their lower dimensional periodic structure. A new member in this class of materials are two-dimensional oxide quasicrystals (OQC)[1]. Here I will present the first in-situ high-temperature characterization of the BaTiO₃-derived OQC. This OQC develops in a 2D wetting layer spreading from 3D BaTiO₃ islands on Pt(111) and exhibits a sharp twelfold diffraction pattern [1]. The structure formation process includes the growth of an amorphous wetting layer which can either develop further into the OQC or into long-range ordered periodic structures, the so-called approximants. Insights into this process are derived from combining the findings of scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED) measurement with in-situ low-energy electron microscopy (LEEM) studies. Besides the details of the quasicrystalline growth process, the in-situ LEEM and μ -LEED studies reveal also the high-temperature stability of this new phase.

[1] S. Förster, K. Meinel, R. Hammer, M. Trautmann, and W. Widdra, Nature 502, 215 (2013).

O 89.6 Thu 16:30 H4

Another 2-dimensional oxide quasicrystal: Strontium titanate on Pt(111) — ●SEBASTIAN SCHENK¹, RENÉ HAMMER¹, FLORIAN SCHUMANN¹, STEFAN FÖRSTER¹, KLAUS MEINEL¹, and WOLF WIDDRA^{1,2} — ¹Institute of Physics, Martin-Luther-Universität Halle-Wittenberg, 06120 Halle, Germany — ²Max-Planck-Institut für Mikrostrukturphysik, 06120 Halle, Germany

Recently the formation of a BaTiO₃-derived 2-dimensional oxide quasicrystal (OQC) with 12-fold diffraction symmetry has been discovered on Pt(111) substrates [1]. Following an analogous preparation procedure, we show that SrTiO₃ on Pt(111) develops an OQC as well. First, a closed SrTiO₃ film on Pt(111) has been prepared using MBE. The stoichiometry and structure of the film has been analyzed by means of AES and SPA-LEED. Annealing the film in an O₂ atmosphere yields the formation of 3-dimensional SrTiO₃ islands with bare Pt(111) in between. Annealing in UHV causes a rewetting on the Pt(111) via surface diffusion of SrTiO₃ from the islands. SPA-LEED and STM reveal that at temperatures around 700°C an OQC is formed in the rewetting layer. The SrTiO₃ derived OQC is composed by quadratic, triangular, and rhombic elements of equal side length of about 0.6 nm. They form an aperiodic structure, which displays a well-ordered 12-fold diffraction pattern. Our results suggest that OQC formation is a general process of oxide perovskites on suitable substrates.

[1] S. Förster, K. Meinel, R. Hammer, M. Trautmann, and W. Widdra, Nature 502 (2013) 215.

O 89.7 Thu 16:45 H4

Software-based analysis of aperiodic structures of quasicrystals — ●BERIT SCHRECK¹, STEFAN FÖRSTER¹, RENÉ HAMMER¹, KLAUS MEINEL¹, and WOLF WIDDRA^{1,2} — ¹Institute of Physics, Martin-Luther-Universität Halle-Wittenberg, Halle, Germany — ²Max-Planck-Institut für Mikrostrukturphysik, Halle, Germany

The discovery of a novel class of oxide quasicrystals (OQC) leads to a new field in surface and material science research. BaTiO₃ develops a 2D structure of twelve-fold rotational symmetry when prepared as thin film on Pt(111) [1]. In order to determine the atomic structure and the statistics of the tiling, a software based approach for the drift correction and the extraction of atomic coordinates from atomically resolved STM images has been developed. The OQC structure is composed by an aperiodic arrangement of triangular, quadratic, and rhombic building blocks, comparable to the Stampfli-Gähler-Tiling [2]. Angles, edge lengths, and frequency of occurrence of the OQC tiling elements have been extracted and will be compared with the theoretical model.

[1] Förster, S. et al., Nature 502, 215 (2013). [2] Gähler, F. in Quasicrystalline Materials, Ch. Janot and J.M. Dubois (eds.), World Scientific (1988).

O 89.8 Thu 17:00 H4

Transition metal-oxide hybrid chain structures on Ir(100) - a general trend? — ●PASCAL FERSTL¹, FLORIAN MITTENDORFER², CHRISTOPHER SOBEL¹, MATTHIAS GUBO¹, KLAUS HEINZ¹, JOSEF REDINGER², M.ALEXANDER SCHNEIDER¹, and LUTZ HAMMER¹ — ¹Lehrstuhl für Festkörperphysik, Universität Erlangen-Nürnberg — ²Institut für Angewandte Physik & CMS, TU Wien

We show that the oxidation of a 1/3 monolayer of different transition metals (Mn, Co, Fe and Ni) on the Ir(100) surface leads to the formation of a surface oxide of nearly the same crystallographic structure. All of the metals (Me) form quasi-one-dimensional chains of MeO₂ stoichiometry and grow exclusively with threefold lateral spacing on the plain Ir(100) terraces forming an almost defect-free 3×1 superstructure. This allows for a quantitative determination of the crystallographic structure of the chains by means of full dynamical LEED-IV analyses which resulted in Pendry R-factor values around 0.11 for all investigated systems. The best fit structures were independently confirmed by DFT calculations. The MeO₂ stripes only bind via the oxygen atoms to the substrate, while the central mono-atomic metal wire is decoupled from its Ir neighbours. The only notable difference between the various metal-oxide hybrid structures is the buckling of the Me atom with respect to the first Ir layer that varies between 1.1 and 0.7 Å.

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Growth and morphological characterization of thin vanadium dioxide films — ●MIRCO SCHULZ, JON-OLAF KRISPONEIT, JAN INGO FLEGE, and JENS FALTA — Universität Bremen, Bremen, Germany

Vanadium dioxide exhibits a metal-insulator transition near room temperature, comprising a rich phenomenology that is still not fully understood. Close to the transition, the system responds sensitively to uniaxial substrate-induced stress, resulting in a wide variation of the transition temperature. In this contribution, thin VO₂ films were grown on TiO₂(001) and TiO₂(110) substrates by molecular beam epitaxy. Two different growth methods were used: first, vanadium evaporation under O₂ ambient and, second, cyclic vanadium deposition and post-annealing in O₂, following an approach by J. W. Tashman et al. [1]. For both methods the prevalence of the V⁴⁺ oxidation state was confirmed by x-ray photoelectron spectroscopy. The surface structure was analyzed with low energy electron diffraction, indicating an epitaxial growth on the substrate and good crystallinity of the films. While scanning tunneling microscopy revealed continuous films of VO₂ on both substrates, we found faceting in the case of (110) substrate orientation, but terraces on (001) substrates.

[1] J. W. Tashman et al., Appl. Phys. Lett. **104**, 063104 (2014).

O 89.10 Thu 17:30 H4

SMSI effect of a non-reducible oxide: ZrO₂/metal inverse model catalysts — ●MICHAEL SCHMID, PETER LACKNER, JOONG-IL J. CHOI, and ULRIKE DIEBOLD — Institut f. Angewandte Physik, TU Wien, Vienna, Austria

Many oxide-supported metal catalysts exhibit the so-called SMSI (strong metal-support interaction) effect, where the metal gets overgrown by an ultrathin oxide layer under reducing conditions [1,2]. This effect is usually limited to reducible oxides, and the ultrathin oxide is

substoichiometric. We have deposited few-layer ZrO₂ films on Pt and Rh(111) surfaces and find dewetting upon annealing to high temperatures in oxygen, i.e., between the oxide islands the bare metal surface gets uncovered. Annealing in ultrahigh vacuum instead leads to a structure akin to Stranski-Krastanov growth, i.e., oxide islands with the metal in between covered by an ultrathin oxide, as in SMSI systems. We identify this ultrathin oxide as an essentially stoichiometric ZrO₂ trilayer [3], thus the reason for the SMSI effect observed must be different from the usual variation of oxide stoichiometry. We propose a new mechanism for the SMSI effect, which is alloying between Zr and the metal, modifying the metal-oxide bonding.

[1] Tauster, Fung, Baker, Horsley, Science 211, 1121 (1981).

[2] Dulub, Hebenstreit, Diebold, Phys. Rev. Lett. **84**, 3646 (2000).

[3] Antlanger et al., Phys. Rev. B **86**, 035451 (2012).

O 89.11 Thu 17:45 H4

Thermal Reduction of Au(111)-Supported Cuprous Oxide Films — ●HANNA FEDDERWITZ¹, CLAUDINE NOGUERA², JACEK GONIAKOWSKI², and NIKLAS NILIUS¹ — ¹Carl von Ossietzky Universität Oldenburg, Institut für Physik, D-26111 Oldenburg, Germany — ²CNRS-Sorbonne Universités, UPMC Univ. Paris 06, UMR 7588, INSP, F-75005 Paris, France

Thin Cu₂O films with stoichiometric (111)-termination and a band gap of 2.0 eV are prepared by reactive Cu deposition on Au(111) surfaces. Annealing to temperatures above 700 K, both in vacuum and 5 × 10⁻⁶ mbar of oxygen, results in a gradual reduction of the oxide, as monitored by XPS and STM. The reduction process starts off with the appearance of single Cu atoms and small clusters at distinct sites of the Cu₂O(111) lattice. At higher temperature, metallic Cu patches develop at the surface, clearly distinguishable from the oxide domains via their deviating atomic and electronic structure. Simultaneously, bare Au(111) regions emerge, which coexist with the Cu and Cu₂O domains and continuously increase in size at higher temperature. Additional insight into the Cu₂O to Cu transition comes from characteristic changes of the Cu LVV Auger lines, as probed with XPS. The observed reduction behavior of thin-film Cu₂O is rationalized with the help of stability diagrams derived from DFT*based ab-initio thermodynamics.

O 89.12 Thu 18:00 H4

ALD growth of Al₂O₃ on Stepped Surface of HOPG and Ag-HOPG — ●ZIED ROUISSI¹, KARSTEN HENKEL¹, MASSIMO TALLARIDA², and DIETER SCHMEISSER¹ — ¹Brandenburg University of Technology Cottbus-Senftenberg — ²ALBA Synchrotron, 08290 Cerdanyola del Vallès, Barcelona, Spain

Atomic Layer Deposition (ALD) is an excellent deposition technique to grow thin film with high homogeneity coverage on ideal surfaces. Here we are interested in the growth properties on non-ideal (stepped, inert) surfaces. Using STM we studied the growth of Al₂O₃ by ALD on stepped surface of HOPG and silver covered HOPG (Ag-HOPG). The HOPG sample was cleaved to and then cleaned by N₂ in vacuum. We obtain regular steps with terrace widths of 50nm * 500nm. Ag was deposited by thermal deposition on the HOPG. The Al₂O₃ growth at RT was studied after the first, third, and fifth cycle. Silver evaporation leads to step decoration with island of 1nm-7nm. On the terraces we find the formation of 2D domain of Ag chains. The features caused by the individual ALD cycles of Al₂O₃ depend on the terrace widths of the HOPG substrate. For small terraces (*100nm) we obtain a growth of 2D domains (20nm-25nm) on the edge steps and in the middle of the terrace. For large terraces (*100nm) we find agglomeration of the precursors on individual nucleation sites. Here 3D islands are formed with a height of up to 5nm in the fifth ALD cycle.

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HfO₂ grow by ALD on Si(111)-H terminated stepped surface — ●ZIED ROUISSI¹, MASSIMO TALLARIDA², and DIETER SCHMEISSER¹ — ¹Applied Physics and Sensors, K.-Wachsmann-Allee 17, D-03046 Cottbus, Germany — ²ALBA Synchrotron, 08290 Cerdanyola del Vallès, Barcelona, Spain

We studied by STM the growth of HfO₂ on Si (111)-H stepped surface (miscut by 0.5°). The steps are aligned in the [11-2] direction. In order to obtain well defined steps and terraces we prepare the sample by chemical etching in 40% NH₄F. In our in-situ study we investigate the ALD growth of HfO₂ by TDMAH and H₂O [1-2]. We follow for the first four ALD cycles the distribution of the nucleation sites. We also study the influence of the substrate temperature by comparing the growth within the ALD window at 300K and 580K. We observed that at RT

the as-grown HfO_2 forms stripes which are oriented normal to the step orientations. Further growth starts from the step edges and proceeds towards the terraces. Defects created by the etching processes act as nucleation sites for 3D islands. Based on our STM data we are able to correlate the structural changes on that inert and stepped Si(111)-H surface during ALD with experimental [3] and theoretical [4] results

obtained for planar Si(100) surfaces.

- [1] M. Tallarida et al., *Semicond. Sci. Technol.* 27, 074010 (2012)
- [2] K. Kolanek et al., *Thin Solid Films* 518, 4688 (2010)
- [3] K. Kolanek et al., *J. Vac. Sci. Technol. A* 31, 01A104 (2013)
- [4] L. Riikka et al., *J. Appl. Phys.* 96, 7686 (2004)