

O 10: Oxides I: Growth and Characterization

Time: Monday 10:30–13:45

Location: WIL B321

O 10.1 Mon 10:30 WIL B321

Growth, reconstruction and electronic band structure of ultrathin cuprous oxide Films on Ru(0001) — ●NICOLAS BRAUD¹, JAN INGO FLEGE², ENRIQUE G. MICHEL³, PAOLO MORAS⁴, and JENS FALTA¹ — ¹Institute of Solid State Physics, University of Bremen, Germany — ²Applied Physics and Semiconductor Spectroscopy, BTU Cottbus-Senftenberg, Germany — ³Departamento de Física de la Materia Condensada, Universidad Autónoma de Madrid, Spain — ⁴Istituto di Struttura della Materia, Consiglio Nazionale delle Ricerche, Italy

Cuprous oxide Cu₂O is a p-type direct semiconductor and is expected to play an important role in optoelectronics, solar technologies and in photoelectrochemistry due to its band gap of 2.17 eV and an optical gap of 2.62 eV which fit in the solar spectrum.

Here we present angle resolved photoelectron spectroscopy investigations of thin two dimensional cuprous oxide films. All the samples were characterized along the ΓM and the ΓK direction in a photon range between 75 and 125 eV.

Depending on the oxide thickness we observe three different phases by LEED and LEEM. After the oxidation of Cu/Ru(0001) in low oxygen partial pressure of 3×10^{-6} mbar at 400°, the surface exhibits a rectangular ($3 \times 2\sqrt{3}$) reconstruction. Increasing the oxygen partial pressure up to 3×10^{-5} mbar leads to a $(2\sqrt{7} \times 2\sqrt{7})R19.1^\circ$ reconstructed hexagonal Cu₂O(111)-like film. An oxygen pressure of 3×10^{-6} mbar leads to a (2×2) reconstruction. For these phases we also observed differences in the electronic band structure.

O 10.2 Mon 10:45 WIL B321

Epitaxial growth of wurtzite CoO(0001) on Au(111) and conversion into rocksalt CoO(001) — ●MAXIMILIAN AMMON¹, LUTZ HAMMER¹, SARA BAUMANN¹, ANDREAS RAABGRUND¹, TILMAN KISSLINGER¹, JOSEF REDINGER², and M. ALEXANDER SCHNEIDER¹ — ¹Lehrstuhl für Festkörperphysik, Universität Erlangen-Nürnberg — ²Institut für Angewandte Physik & CMS, TU Wien

Wurtzite (w-)CoO is a semiconducting [1] and antiferromagnetic [2] material. We establish the preparation parameters for the epitaxial growth of closed w-CoO films on Au(111) of several nanometer thickness. A LEED-IV analysis ($R_p = 0.112$) proves the structure to be w-CoO ($a = 3.26 \text{ \AA}$, $c = 5.22 \text{ \AA}$) with small relaxations in the 1. surface layer only. DFT calculations based on hybrid functionals or LDAU schemes reproduce all measured geometrical parameters very well.

We used STS and DFT to study the electronic properties of these w-CoO films. Films with a thickness of 15 bilayers (BL) ≈ 4 nm exhibit a bandgap of 1.8 ± 0.2 eV around E_F as measured by STS that is comparable to the optical bandgap quoted in literature [1]. We observe a reduction of the bandgap with decreased film thickness.

Annealing of w-CoO(0001) films to 600°C induces a phase transition to closed rocksalt (rs-)CoO(001) films. Experiments with ultrathin films (≤ 4 BL) show that this conversion results in films of homogeneous thickness corresponding to three cubic lattice constants of rs-CoO (≈ 1.2 nm).

[1] Wang et al., Chem. Commun. **54**, 13949 (2018)[2] Roca et al., Small **14**, 1703963 (2018)

O 10.3 Mon 11:00 WIL B321

Structural and electronic properties of single-layer CoO₂ — ●ANN-JULIE HOLT¹, MARCO BIANCHI¹, JONATHAN FERNANDEZ², YU ZHANG³, DAVIDE CURCIO¹, PAOLO LACOVIG⁴, SAHAR PAKDEL¹, NICOLA LANATA¹, JEPPE LAURITSEN², SILVANO LIZZIT⁴, PHILIP HOFMANN¹, and CHARLOTTE SANDERS³ — ¹Department of Physics and Astronomy, Aarhus University, Aarhus, Denmark — ²Department of Chemistry, Interdisciplinary Nanoscience Center (iNANO), Aarhus University, Aarhus, Denmark — ³Central Laser Facility, Oxfordshire, UK — ⁴Elettra - Sincrotrone Trieste S.C.p.A., Trieste, Italy.

Single-layer transition metal dichalcogenes are among the most actively investigated material systems of the past several years and increased attention is now being directed to the oxygen-based members of this family. In particular, CoO₂ is predicted to manifest intrinsic two-dimensional ferromagnetism and is a potential corrosion-resistant catalyst in the oxygen evolution reaction.

Here, we present an experimental study of single-layer CoO₂, obtained from a newly developed synthesis method for epitaxially fab-

ricating stable, rotationally aligned single-layer CoO₂ on Au(111) (e.g., [1]). The material structure is studied through scanning tunneling microscopy, low energy electron diffraction, and X-ray photoelectron diffraction. The electronic dispersion is characterised by the use of angle-resolved photoelectron spectroscopy, revealing a metallic behaviour. A structural model of the material is established, and the electronic structure is related to density functional theory calculations. [1] *ACS Nano* **9** (2015) 2445

O 10.4 Mon 11:15 WIL B321

Strongly strained VO₂ thin film growth — ●SIMON FISCHER¹, JAN INGO FLEGE², MICHAEL FOERSTER³, LUCIA ABALLE³, ANDREA LOCATELLI⁴, TEVFIK ONUR MENTES⁴, JENS FALTA¹, and JON-OLAF KRISPONEIT¹ — ¹Institute of Solid State Physics, University of Bremen, Germany — ²Applied Physics and Semiconductor Spectroscopy, BTU Cottbus, Germany — ³ALBA Synchrotron Light Facility, Barcelona, Spain — ⁴Elettra Sincrotrone Trieste, Italy

The semiconductor-metal transition temperature of VO₂ strongly shifts as a result of strain applied along the rutile *c* axis, making it relevant for various switching applications such as smart coatings and sensors. In the past this has been demonstrated, for instance, through the application of epitaxial strain on TiO₂ substrates.

We extend this tailoring approach by utilizing the much larger lattice mismatch of 8.78% occurring in the VO₂/RuO₂ system for orientations where the *c* axis lies in-plane. Depositing vanadium oxide by atomic oxygen-supported reactive MBE on an oxidized Ru(0001) template, we have grown VO₂ thin films on single domain RuO₂ islands with varying orientation. Locally resolved electron spectroscopy was used to ascertain the correct stoichiometry of the grown VO₂ films on all template island types. Low energy electron diffraction reveals the VO₂ films to grow indeed fully strained on RuO₂(110) but fully relaxed on RuO₂(100).

Hence, the presented template allows simultaneous access to a remarkable strain window ranging from bulk-like structures to massively strained regions.

O 10.5 Mon 11:30 WIL B321

Growth and Characterization of Calcium-Molybdate Thin Films on Mo(001) — MAIKE LOCKHORN¹, SERGIO TOSONI², GIANFRANCO PACCHIONI², and ●NIKLAS NILIUS¹ — ¹Institute of Physics, Carl von Ossietzky University Oldenburg, Germany — ²Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca, Italy

Ca-Mo mixed oxide films were grown on a Mo(001) surface and characterized by various surface science techniques and DFT. Several highly crystalline phases were observed with rising annealing temperature, before the mixed oxide decays to binary MoOx. The stoichiometry of the low-temperature phase was determined to CaMo₃O₆, and resembles a CaMo₅O₈ bulk structure. A corresponding DFT model consists of alternating flat-lying and upright-standing Mo octahedrons, separated by Ca²⁺ ion rows. As the Ca and O content decreases upon heating, the central Mo units grow in size and the film evolves through distinct (3x3), (4x4) and (6x6) reconstructions. This leads also to an increasing metallicity of the film, as probed with STM conductance spectroscopy. Our work presents an easy approach towards crystalline ternary oxide films that exploits the inter-diffusion of substrate atoms into a suitable binary oxide.

O 10.6 Mon 11:45 WIL B321

Detecting Tiny Cation Nonstoichiometry in Complex Oxide Films — ●MICHELE RIVA, GIADA FRANCESCHI, MICHAEL SCHMID, and ULRIKE DIEBOLD — IAP, TU Wien, Austria

The rise of semiconductor-based electronics has gone hand in hand with the technological advancements allowing to reproducibly prepare materials with exceptionally small concentration of defects. A similar control of defects and composition is the key to making all-oxide electronics a reality, allowing to fully exploit the multitude of functionalities of these materials. Precise tuning of the oxide composition, however, requires the development of reliable tools to detect cation nonstoichiometry with extreme sensitivity: We develop an unconventional method based on STM that pushes down this detection limit by at least one order of magnitude [1].

We take advantage of the well-controlled surface reconstructions of

SrTiO₃(110), and use the established relation between those reconstructions and the surface composition to assess the cation excess deposited in PLD-grown SrTiO₃(110) films. We demonstrate that a < 0.1% change in cation non-stoichiometry is detectable by our approach, and show that, for thin films that accommodate all the non-stoichiometry at the surface, our method has no fundamental detection limit.

[1] Phys. Rev. Mater. **3**, 043802 (2019)

O 10.7 Mon 12:00 WIL B321

Non-stoichiometry segregation in perovskite oxides and its role for film growth — ●GIADA FRANCESCHI, MICHAEL SCHMID, ULRIKE DIEBOLD, and MICHELE RIVA — TU Wien, Institute of Applied Physics, Wiedner Hauptstrasse 8-10/E134, 1040, Vienna, Austria

Achieving atomically flat and stoichiometric films of complex multi-component oxides is crucial for integrating these materials in emerging technologies. While pulsed laser deposition (PLD) can in principle produce these high-quality films, growth experiments often result in rough surfaces and nonstoichiometric compositions. To understand the cause, we follow the growth at an atomic level from its early stages as a function of the growth conditions, using atomically resolved STM. We investigate the growth of SrTiO₃(110) and La_{0.8}Sr_{0.2}MnO₃(110) films. Both accumulate small non-stoichiometries introduced during growth at the surface. As a result, their surface structure evolves along phase diagrams of surface structure vs. composition.[1] This can produce dramatic effects on the surface morphology: If two surface reconstructions with different sticking properties develop and coexist during growth, pits can form, degrading the surface morphology.[2] Moreover, if the introduced non-stoichiometry is too large to be accommodated by the surface via a change in its structure, ill-defined oxide clusters nucleate and grow, eventually dominating the surface morphology. We show our approach to grow films with thickness of tens of nanometers showing atomically flat surfaces, and with stoichiometry control within 0.1%.[1] [1] PRMater. **3**, 043802 (2019) [2] PRRResearch **1**, 033059 (2019)

O 10.8 Mon 12:15 WIL B321

Fundamental asymmetry in the electronic reconstruction of polar LaMnO₃/LaAlO₃ vs. LaAlO₃/LaMnO₃ thin films on SrTiO₃(001) — ●BENJAMIN GEISLER and ROSSITZA PENTCHEVA — Fakultät für Physik, Universität Duisburg-Essen, 47057 Duisburg

Interface polarity plays a key role in oxide heterostructures. Here we explore its effect on the electronic reconstruction in polar LaMnO₃/LaAlO₃ and LaAlO₃/LaMnO₃ thin films on SrTiO₃(001) and show that the materials sequence fundamentally impacts the mechanism. [1] First-principles calculations including a Coulomb repulsion term reveal that for (LaMnO₃)_n/(LaAlO₃)₂/SrTiO₃(001), the electronic reconstruction is triggered already at $n = 2$, and we observe the formation of a two-dimensional electron gas (2DEG) at the SrTiO₃(001) interface with enhanced Ti 3d occupation compared to the (LaAlO₃)₄/SrTiO₃(001) case. Interestingly, in the reversed (LaAlO₃)_m/(LaMnO₃)₃/SrTiO₃(001) system, charge transfer from the surface sets in at $m = 3$, but compensation occurs in the manganate and no 2DEG is formed at the SrTiO₃(001) interface. For lower $m = 2$, no charge transfer is observed at all, highlighting the pivotal role of the materials sequence and thickness. These findings suggest more general design principles of the electronic reconstruction in polar oxide thin films on a nonpolar substrate.

Funding by the DFG within TRR 80 (G3) is acknowledged.

[1] B. Geisler, P. Reith, H. Hilgenkamp, and R. Pentcheva, in preparation

O 10.9 Mon 12:30 WIL B321

Temperature-dependent SXR D from a two-dimensional oxide quasicrystal — ●SEBASTIAN SCHENK¹, STEFAN FÖRSTER¹, MARC DE BOISSIEU², and WOLF WIDDRA^{1,3} — ¹Institute of Physics, Martin-Luther-Universität Halle-Wittenberg, 06120 Halle, Germany — ²Universite Grenoble Alpes, CNRS, SIMaP, 38402 St Martin d Heres, France — ³Max-Planck-Institut für Mikrostrukturphysik, 06120 Halle, Germany

Two-dimensional oxide quasicrystals (OQC) are mono-atomically high ternary oxide layers with 12-fold rotation symmetry forming spontaneous on Pt(111) [1,2]. Here we report on studies of the structural dynamics of the prototypical example of the BaTiO₃-derived OQC using surface X-ray diffraction (SXR D) at the SIXS beamline, Soleil. In contrast to periodic systems, temperature-induced changes in the diffraction pattern of OQCs occur not only due to the excitation of phonons (Debye-Waller factor) but also due to additional excitations,

called phasons [3]. Both will cause a redistribution of intensity from the Bragg peaks to the diffuse background and will be discussed for temperature-dependent SXR D data in the range from 300 to 1300K. In this way, a separation of frozen-in phason flips and dynamically excited phasons is possible. In addition, changes of the shape of the most intense [1110] diffraction peaks are explained by frozen-in phason flips.

[1] S. Förster et al., Nature **502**, 215 (2013)

[2] S. Förster et al., Phys. Status Solidi B, doi: 10.1002/pssb.201900624, (2019)

[3] M. de Boissieu et. al., PRL **95**, 105503 (2005)

O 10.10 Mon 12:45 WIL B321

Oxide quasicrystal formation on Pd(111) — ●FRIEDERIKE WÜHRL¹, OLIVER KRAHN¹, STEFAN FÖRSTER¹, and WOLF WIDDRA^{1,2} — ¹Institute of Physics, Martin-Luther-Universität Halle-Wittenberg, 06120 Halle(Saale), Germany — ²Max-Planck-Institut für Mikrostrukturphysik, 06120 Halle(Saale), Germany

The discovery of a quasicrystalline phase in ultrathin films of BaTiO₃ (BTO) on Pt(111) opened a new field of research on ternary oxides on metal substrates. Its observation was the first example for spontaneous formation of an aperiodic dodecagonal structure at the interface to a periodic crystal. So far oxide quasicrystals (OQC) have been found only on the surface of Pt(111) [1]. Here we report on the first OQC on an alternative substrate, namely Pd(111). Pd(111) has a 1% reduced lattice parameter as compared to Pt(111). LEED and STM data show several long-range-ordered wetting layer structures between 3D BaTiO₃(111) islands after heating the film under UHV conditions. The diffraction spots of the BTO-islands show a Moiré pattern. The wetting layer structures finally converge at a temperature of 960 K to 1000 K into two domains of dodecagonal OQC's, which are rotated by $\pm 5^\circ$ against the high symmetry directions of the substrate. This dodecagonal structure coexist with another wetting layer structure. Surprisingly, the characteristic length of the newly discovered BTO-derived OQC is reduced according to the smaller lattice parameter.

[1] S. Förster et al., Phys. Status Solidi B, doi: 10.1002/pssb.201900624, (2019)

O 10.11 Mon 13:00 WIL B321

Large-Scale Quasicrystal Approximants in the SrTiO₃/Pt(111) System — ●OLIVER KRAHN¹, SEBASTIAN SCHENK¹, STEFAN FÖRSTER¹, and WOLF WIDDRA^{1,2} — ¹Institute of Physics, Martin-Luther-Universität Halle-Wittenberg, 06120 Halle, Germany — ²Max-Planck-Institut für Mikrostrukturphysik, 06120 Halle, Germany

The recent discovery of two-dimensional oxide quasicrystals (OQC) draws attention to aperiodic structure formation from perovskite materials on Pt(111) [1,2]. On the atomic level, the OQC generates an aperiodic self-similar tiling consisting of triangles, squares and rhombes with Ti atoms at the vertices and equal edge lengths. Periodically repeated patches of a quasicrystal are known as approximants.

In this talk, we present low-temperature scanning tunneling microscopy and spectroscopy data of the largest unit cell approximant known so far in 2D systems. Its unit cell is commensurate with a superstructure matrix of $\begin{pmatrix} 16 & 0 \\ 9 & 18 \end{pmatrix}$ with respect to Pt(111) and covers an area of $44.3 \text{ \AA} \times 43.2 \text{ \AA}$. The cell contains 48 Ti atoms that occupy the vertices of 48 triangles, 18 squares and 6 rhombes. These tiling elements are furthermore decorated with 48 Sr and 120 O atoms assuming a stoichiometry of 1:1:2.5 as determined for a related small unit cell approximant [3]. This adds up to a 2D unit cell containing 216 atoms.

[1] S. Förster et al., Nature **502** (2013)

[2] S. Förster, O. Krahn et al., Phys. Status Solidi B, doi: 10.1002/pssb.201900624 (2019)

[3] S. Förster et al., Phys. Rev. Lett. **117** (2016)

O 10.12 Mon 13:15 WIL B321

Bulk and Interface Characteristics of Ni_xCu_{1-x}O_y - An Alternative Inorganic Hole Transport Material Systems with Widely Tunable Optoelectronic Properties — ●LUCAS BODENSTEIN-DRESLER¹, ADI KAMA², JOHANNES FRISCH¹, CLAUDIA HARTMANN¹, ANAT ITZHAK², REGAN WILKS¹, GARY HODES², DAVID CAHEN^{2,3}, and MARCUS BÄR^{1,4,5} — ¹Helmholtz-Zentrum Berlin für Materialien und Energie GmbH — ²Bar-Ilan University — ³Weizmann Institute of Science — ⁴Friedrich-Alexander-Universität Erlangen-Nürnberg — ⁵Helmholtz-Institute Erlangen-Nürnberg for Renewable Energy

Halide perovskite (HaP) solar cells have reached efficiencies of over 25% being now primarily limited by the interfaces between the HaPs

absorber and the charge carrier transport layers (TL). Especially organic TL employed in standard HaP solar cells, like PEDOT:PSS or Spiro-OMeTAD, are potentially sources of degradation. Alternative inorganic ternary metal oxide (MO) hole TLs (HTL) promise better stability. Furthermore, their optoelectronic properties can be tuned, allowing for deliberate HaPs/HTL interface tailoring. One possible HTL MO is $\text{Ni}_x\text{Cu}_{1-x}\text{O}_y$, which we studied as a combinatorial NiO - Cu_2O 72 x 72 m² material library produced by pulsed laser deposition by photoelectron spectroscopy (XPS) to reveal composition-dependent chemical/electronic surface characteristics. In our presentation, the XPS analysis will be correlated to complementary crystal structure and optical bulk properties, to arrive at a complete picture of the $\text{Ni}_x\text{Cu}_{1-x}\text{O}_y$ system and allow first steps towards the tailoring of such.

O 10.13 Mon 13:30 WIL B321

Surface diffusion of precursors in area-selective Atomic Layer Deposition — •DANIEL ANDERS¹, PHILIP KLEMENT¹, JÖRG SCHÖRMANN¹, CHRISTIAN HEILIGER², and SANGAM CHATTERJEE¹ — ¹Institute of Experimental Physics I and Center for Materials Re-

search, Justus Liebig University Giessen, Germany — ²Institute of Theoretical Physics, Justus Liebig University Giessen, Germany

Bottom-up nanofabrication by area-selective Atomic Layer Deposition (ALD) is expected to become a key technology in the fabrication of sub 5-nm semiconductor-devices. ALD eliminates conventional top-down alignment errors by limiting the deposition to specific areas. Surface diffusion of precursors becomes important as precursors may adsorb to no-growth areas and diffuse towards growth areas leading to previously unconsidered phenomena.

Here we show the impact of precursor surface diffusion in area-selective ALD of TiO₂ on SiO₂. We find strongly increased growth rates on substrates with patterned poly(methyl methacrylate) masks and a non-uniform topography. We apply a kinetic Monte-Carlo simulation model for the growth process based on different diffusion coefficients on different surfaces. The numerical results agree excellently with the experimental observations and allow us to deduce the different diffusion lengths. This work facilitates the understanding of surface diffusion processes in area-selective deposition, and enables the control of area-selective deposition on small scales.