

O 37: Metal Oxide Surfaces II: Structure, Epitaxy and Growth

Time: Tuesday 14:00–16:45

Location: H16

O 37.1 Tue 14:00 H16

Growth and phase transitions of wurtzite CoO films on Au(111) — ●MAXIMILIAN AMMON¹, SARA BAUMANN¹, TILMAN KISSLINGER¹, LUTZ HAMMER¹, JOSEF REDINGER², and M. ALEXANDER SCHNEIDER¹ — ¹Lehrstuhl für Festkörperphysik, Universität Erlangen-Nürnberg, D-91058, Germany — ²Institut für Angewandte Physik & CMS, TU Wien

The metastable wurtzite polymorph of CoO shows interesting properties, but has so far only be found as nanoparticles and islands on Au(111) [1,2]. Here we establish the wurtzite polymorph on Au(111) by a LEED-I(V) analysis, STM and DFT calculations.

Cobalt oxide films with a thickness of ~ 3 nm are grown reactively on Au(111) at $T = 280$ K in UHV. STM identifies that films grown under oxygen poor conditions are closed with grain sizes around 20 nm. LEED-I(V) proves the structure to be oxygen-terminated wurtzite CoO ($R_P = 0.13$), the structural parameters are in agreement with DFT calculations. Oxygen rich conditions lead instead to spinel Co_3O_4 . Both polymorphs undergo distinctly different irreversible phase transitions upon annealing in UHV: wurtzite CoO is a precursor for rocksalt CoO(100) ($T \geq 600$ K), while spinel CoO converts above 800 K to rocksalt CoO(111). Films of a thickness $\lesssim 1$ nm grow only in the wurtzite phase as identified by the conversion to CoO(100) and the observed lattice constant of 0.326 nm.

[1] Risbud et al., Chem. Mater. 17, 834-838 (2004)

[2] Walton et al., ACS Nano 9, 2445-2453 (2015)

O 37.2 Tue 14:15 H16

Dopant-induced diffusion at metal-oxide interfaces studied for Fe- and Cr-doped MgO/Mo(001) films — STEFANIA BENEDETTI¹, SERGIO TOSONI², GIANFRANCO PACCHIONI², and ●NIKLAS NILIUS³ — ¹CNR, Istituto Nanoscienze, 41125 Modena, Italy — ²Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca, 20125 Milano, Italy — ³Institute of Physics, Carl von Ossietzky University, 26111 Oldenburg, Germany

X-ray photoelectron spectroscopy reveals spontaneous atom diffusion from a Mo(001) support into a MgO thin film doped with transition-metal ions. The amount of interfacial mixing depends on the nature of the dopants and is larger for Fe than for Cr impurities. DFT calculations find the reason for Mo diffusion in the ability of the dopants to change oxidation state. Cr exclusively occurs as $3+$ ion in MgO and charge mismatch with native ions is compensated for by Mg vacancies. Conversely, the Fe oxidation state depends on temperature, which enables Mo atoms from the support to move into Mg vacancies where they oxidize via electron transfer into the Fe dopants. The talk unravels a novel charge-compensation scheme in doped oxides that proceeds via chemical intermixing at a metal-oxide interface.

O 37.3 Tue 14:30 H16

High quality MgO-films grown at low temperatures on CoO(100) — ●ALEXANDRA SCHEWSKI, TILMAN KISSLINGER, LUTZ HAMMER, and ALEXANDER SCHNEIDER — Lehrstuhl für Festkörperphysik, Friedrich-Alexander-Universität Erlangen-Nürnberg

Interfaces between oxides have recently received great attention showing that new electronic properties [1] but also an influence on magnetic transition temperatures can be observed, e.g. for rocksalt CoO on Fe_3O_4 [2]. In all these cases it is important to prepare a high quality interface and ideally characterize its structure.

Here we report on the growth and characterization of the non-magnetic insulator MgO on the anti-ferromagnet CoO. As a substrate we used CoO(100) films on Ir(100) that grow perfectly with terrace sizes larger than 200 nm [3]. On top, we deposited Mg reactively in an oxygen atmosphere at different temperatures and subsequently annealed up to a maximum of 1270 K. Surprisingly, even low-temperature deposition at 90 K leads to well-ordered, closed films with a sharp (1×1) LEED-pattern. The LEED-I(V) analysis confirms pure MgO(100) overlayers. It is remarkable that the film quality does hardly improve by annealing up to 870 K. Annealing beyond this temperature leads to the recovery of the CoO(100) LEED-pattern due to a dewetting of the MgO on the surface. The formed micrometer sized MgO particles on CoO are readily identified by SEM.

[1] F. Hellmann et al. Rev. Mod. Phys., **89**, 025006 (2017).

[2] Y. Ijiri et al., Phys. Rev. Lett. **99**, 147201 (2007).

[3] K. Heinz, L. Hammer, J. Phys.-Condens. Mat. **25** 173001 (2013)

O 37.4 Tue 14:45 H16

EuO ultrathin films: Growth and strain engineering — ●PAUL ROSENBERGER¹, PATRICK LÖMKER², and MARTINA MÜLLER^{1,3} — ¹Peter Grünberg Institut (PGI-6), Forschungszentrum Jülich GmbH, Jülich — ²Deutsches Elektronen-Synchrotron (DESY), Hamburg — ³Expt. Physik I, TU Dortmund, Dortmund

It has been shown that the ferromagnetic insulator Europium monoxide (EuO) is a highly efficient spin filter and thus a very interesting material for spintronics. Furthermore, EuO is predicted to become ferroelectric, and thus multiferroic, under sufficiently large biaxial strain. Our goal is to synthesize ultrathin strained EuO films onto suitable substrates and to study their electronic and magnetic properties.

We grow EuO (ultra-)thin films ($d \lesssim 10$ ML) using MBE in an adsorption-limited growth mode, which is typically employed to synthesize stoichiometric films free from metallic Eu or its higher oxides. We use Ytria-stabilized zirconia, YSZ(001), as a model substrate due to a nearly perfect lattice match. However, we found that for MBE growth of EuO/YSZ thermodynamics has to be considered as oxygen supply from YSZ causes the formation of Eu_2O_3 or Eu_3O_4 . Based on an XPS study, we present a 4-step growth model of EuO/YSZ(001).

Moreover, we launched the synthesis of EuO ultrathin films on pseudocubic LaAlO_3 , LAO(001), which provides 4.2% tensile strain to EuO and is thus a candidate for tailoring a ferroelectric phase in EuO. We varied growth temperature and O_2 partial pressure in order to optimize the parameters for strained EuO/LAO and analyzed the resulting films using electron- and X-ray diffraction as well as magnetometry.

O 37.5 Tue 15:00 H16

Vanadium dioxide thin films on (100)- and (110)-oriented ruthenium dioxide islands — ●SIMON FISCHER¹, MICHAEL FOERSTER², LUCIA ABALLE², VEDRAN VONK³, JENS FALTA¹, JON-OLAF KRISPONEIT¹, and JAN INGO FLEGE⁴ — ¹Institute of Solid State Physics, University of Bremen, Germany — ²ALBA Synchrotron Light Facility, Barcelona, Spain — ³Deutsches Elektronen Synchrotron DESY, Hamburg, Germany — ⁴Applied Physics and Semiconductor Spectroscopy, BTU Cottbus, Germany

Bulk vanadium dioxide exhibits a metal-insulator transition at 68 °C. Because this change in resistivity is linked to a structural transition, the transition temperature can be tuned by epitaxial strain. Due to the high lattice mismatch of RuO_2 with VO_2 , this substrate promises a highly shifted transition temperature, which enables new types of switching devices, smart coatings, and sensors. It is prepared by oxidizing a $\text{Ru}(0001)$ crystal, providing micron-sized, (110)- as well as (100)-oriented RuO_2 islands simultaneously.

One of the challenges in preparing VO_2 is to reliably meet the desired stoichiometry. We investigated the vanadium oxidation state using local XAS and XPS measurements taken at a synchrotron-based XPEEM instrument, revealing that VO_2 stoichiometry is maintained throughout the entire film. This was found not only on $\text{RuO}_2(100)$ and $\text{RuO}_2(110)$, but also on the bare ruthenium substrate. The VO_2 film thickness was determined to 3.6 nm by ex situ XRR measurements.

Financial support from the DFG is acknowledged.

O 37.6 Tue 15:15 H16

Ab-initio studies of the (110) surface terminations of rutile VO_2 — ●JAKUB PLANER, FLORIAN MITTENDORFER, and JOSEF REDINGER — Vienna University of Technology, 1040 Vienna, Austria

Vanadium dioxide is a promising candidate for fast electronic or optical switching. These applications are based on a metal-insulator transition at 340 K, where the structure changes from a monoclinic to a rutile phase. Yet this transition is sensitive to the presence of strain or defects, such as oxygen vacancies. We present results for the bulk and surface properties of the VO_2 phases under varying oxygen partial pressure, and compare our results to recent experimental findings. The calculations were performed with the Vienna Ab initio Simulation Package (VASP). We find that standard GGA functionals (PBE) offer an appropriate description of the structural properties of the rutile phase and monoclinic phase, but more advanced functionals such as meta-GGA approaches (SCAN) have to be employed to capture surface energies well. The stability of various surface terminations for

the rutile (110) surfaces will be discussed in relation to experimental findings. For PBE we find a slightly oxidized tetrahedral termination under UHV conditions ($\mu = -1.88$ eV). Using PBE+U ($U = 2$ eV) a buckled (110) termination is obtained from simulated annealing calculations. At last, we will present the results of an enlarged search for relevant surface terminations applying a state-of-the-art meta-GGA SCAN(+U) functional together with a first-principles genetic algorithm as implemented in the USPEX package.

O 37.7 Tue 15:30 H16

Surface reconstructions on VO₂(110) — ●JON-OLAF KRISPONEIT¹, SIMON FISCHER¹, JAN INGO FLEGE^{1,2}, and JENS FALTA¹ — ¹Institute of Solid State Physics, University of Bremen, Germany — ²Applied Physics and Semiconductor Spectroscopy, BTU Cottbus, Germany

Vanadium dioxide features a pronounced metal-insulator transition at 340 K. For thin films, this transition is adjustable via substrate-induced strain, making VO₂ highly attractive for oxide electronic applications like switching devices and sensors. In addition, VO₂ is considered for smart coatings and as catalytic material. For such applicational efforts, a thorough understanding of the relevant surfaces is an important prerequisite.

Among the low-indexed surfaces orientations of VO₂, the (110) surface is energetically favorable. We have prepared VO₂(110) thin films by means of reactive molecular beam epitaxy on two different substrate types: TiO₂(110) single crystals as well as on RuO₂(110) islands grown on Ru(0001) crystals. The film stoichiometry was confirmed via XPS, while the surface structure was investigated by μ LEED. For both substrate types diffraction patterns of three distinct symmetries have been observed in dependence on temperature. The corresponding surface reconstructions will be discussed in terms of surface oxygen content.

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O 37.8 Tue 15:45 H16

Structural characteristics of oxide surfaces from quantum-mechanical calculations — ●MAOFENG DOU and MARIA FYTA — Institute of Computational Physics, Universität Stuttgart, Allmandring 3, 70569 Stuttgart, Germany

Oxide surfaces are studied here by means of quantum-mechanical calculations implementing the density functional theory. We investigate different surfaces made of ZnO, TiO₂, and SiO₂. These are analyzed with respect to their structure and morphology. Through our simulations, we also assess their stability with respect to the different crystallographic planes taken to cut the surface from the bulk crystal. Amorphous surfaces are also considered and the influence of density and surface roughness is assessed. Our results underline the characteristics in their electronic properties, such as the electronic density of states and their band structure. These are compared to their bulk counterparts and show distinct features. In the end, we will discuss the relevance of these oxide surfaces in accommodating an organic layer to form inorganic/organic hybrid materials.

O 37.9 Tue 16:00 H16

Probing copper oxidation by in-situ optical spectroscopy — ●BJÖRN MAACK and NIKLAS NILIUS — Institute of Physics, Carl von Ossietzky University, 26111 Oldenburg, Germany

The oxidation characteristic of metals stands in the focus of fundamental and applied research already for many decades. Standard rate-laws for oxidation, as predicted by Cabrera/Mott and Wagner, are typically

valid only at the onset of oxide formation and deviate from the experimental findings with increasing oxide thickness. Using optical transmission spectroscopy, we have followed the process of copper oxidation in-situ at well-defined pressure and temperature conditions. The data were analyzed with the transfer-matrix method, including plasmonic, percolation and interference effects. The derived time-dependence of oxide growth reveals an accelerated rate at intermediate film thicknesses, in contrast to classical theories. This behavior is understood, if the increase of the reactive metal-oxide interface is considered together with the diffusive transport of the reactive species.

O 37.10 Tue 16:15 H16

Reduction and reoxidation of (111) and (100) oriented cerium oxide islands on Cu(111) — ●LINUS PLEINES¹, FRANCESCA GENUZIO², TEVFIK ONUR MENTES², ANDREA LOCATELLI², JENS FALTA^{1,3}, and JAN INGO FLEGE⁴ — ¹Institute of Solid State Physics, University of Bremen, Germany — ²ELLETRA Synchrotron Light Source, Basovizza, Italy — ³MAPEX Center for Materials and Processes, Bremen, Germany — ⁴Applied Physics and Semiconductor Spectroscopy, Brandenburg University of Technology Cottbus-Senftenberg, Germany

The conversion of CO₂ to methanol is an important process of high industrial potential. It could help solving the greenhouse gas problem (CO₂) and further provide methanol which can be used as a synthetic fuel. In order to lower the activation energy barrier of the reactions a catalyst is necessary. We studied the interaction of H₂ and CO₂ with ultrathin cerium oxide islands on a Cu(111) substrate observed by low-energy electron microscopy (LEEM), x-ray absorption spectroscopy (XAS) and resonant photoelectron spectroscopy (RPES). From earlier studies the orientation of the CeO_x is known to be decisive for the catalytic activity. In our experiments CeO_x(100) is directly compared to CeO_x(111) via a side-by-side growth, so that the same conditions prevail during the experiment. At low temperatures no reduction of the CeO_x(111) and CeO_x(100) were observed. However, at a higher temperature the reduction was activated. Furthermore, we show that the exposure to CO₂ leads to the formation of partially reoxidized CeO_x and saturation below CeO₂ with progressive CO₂ exposure.

O 37.11 Tue 16:30 H16

Evidence of a nanosize regime in oxide/metal heteroepitaxy — ●CLAUDINE NOGUERA¹, JACEK GONIAKOWSKI¹, GREGORY CABAILH¹, JACQUES JUPILLE¹, RÉMI LAZZARI¹, JINGFENG LI¹, PIERRE LAGARDE², and NICOLAS TRCERA² — ¹CNRS, Sorbonne Université, Institut des NanoSciences de Paris, UMR 7588, 4 Place Jussieu, F-75005 Paris, France — ²Synchrotron SOLEIL, Orme des Merisiers, St-Aubin, BP48, F-91192 Gif sur Yvette, France

The growth mode of strained epitaxial films relies on the interaction strength, the lattice matching and the mechanical response of the system. The present work focuses on the basic physics of supported nano-islands by examining the characteristics of MgO/Ag(100) taken as a case study. By a combination of experiments and simulations, we highlight the existence of a small size regime in which, despite the largest adhesion and the smallest mismatch, the islands are the least distorted by the substrate. We assign this unexpected behaviour to the enhanced island stiffness which makes the cost of elastic distortion prohibitive compared to the associated gain of MgO-Ag interaction energy. The analysis provides a general framework to predict and/or understand nanoscale effects on interfacial pseudomorphy. These are likely to hold whatever the nature of the deposit and substrate under consideration. It may have far reaching consequences on many properties of supported nano-objects.