O 31: Oxide and Insulator Surfaces: Structure, Epitaxy and Growth I

Time: Tuesday 10:30–13:00 Location: WIL C107

O 31.1 Tue 10:30 WIL C107

Ultra-thin Germania films on Ru(0001) and Pt(111) studied by Spectromicroscopy — •Alexander Fuhrich[1], Thomas Schmidt[1], Dietrich Menzel[1,2], and Hans-Joachim Freund[1] — [1]Department of Chemical Physics, Fritz-Haber-Institute of the Max-Planck Society, Berlin, Germany — [2]Physik-Department E20, Technische Universität München, Garching, Germany

We studied the growth and structures of ultra-thin GeO$_2$ films supported on Ru(0001) and Pt(111). Germania is an analogue of Silica and has similar structures. Germanium growths epitaxially on both substrates which allows to determine the thickness of the ultra-thin Germania films. We studied the growth of Germanium in-situ and in real-time by LEEM and LEED. Germanium oxidizes partially already at room temperature on 3O-(2x2)-Ru(0001) and forms small domains. An alternative preparation recipe, where Ge is deposited on the pure (1x1)-Ru(0001) surface at elevated temperatures (540K) and subsequent oxidized in 10^{-6} mbar O$_2$ at 630K, yield in larger domain size. The morphology and structure of the oxide film will be discussed in dependence of the preparation parameters and the supporting substrate.

O 31.2 Tue 10:45 WIL C107

Ultra-thin films of iron-silicate — •Gina Peschel[1], Alexander Fuhrich[1], Hagen W. Klemm[1], Mauricio Prieto[1], Dietrich Menzel[1,2], Thomas Schmidt[1], and Hans-Joachim Freund[1] — [1]Department of Chemical Physics, Fritz-Haber-Institute of the Max-Planck Society, Berlin, Germany — [2]Physik-Department E20, Technische Universität München, Garching, Germany

Silicates belong to the most widely existing minerals in nature and are thus extensively used in our society. Consisting only of Si and O the system is known as silica. However, some silicon atoms can be substituted by iron in order to prepare a model system for zeolite structures, known for their very high catalytic properties. Preparing ultra-thin films offers the possibility to understand the correlation between structure and reactivity and functionalize these materials even more. This study addresses the growth and structure of ultra-thin iron-silicate films on Ru(0001) using the methods of LEEM, LEED, XPS and XPEEM.

Our studies reveal that on Ru(0001) the formation of iron-silicate is energetically favoured compared to a phase separation of pure iron-oxide and silica domains. XPS results fit well to a model with a silica layer bound to a layer of FeO on top of the Ru(0001) support. Silica orders in form of a ($\sqrt{3}$ x $\sqrt{3}$) R30° regarding the FeO layer, as could be seen in the LEED pattern. Thus silica is well ordered on top of FeO and arranged regarding the Fe atoms.

O 31.3 Tue 11:00 WIL C107

Structure of ultra-thin ZnO films supported on Ag(111) characterized by IR spectroscopy — •Xiaojuan Yu, Alexei Nefedov, Yuemin Wang, and Christof Wöll — Institute of Functional Interfaces, Karlsruhe Institute of Technology, 76344, Eggenstein-Leopoldshafen, Germany.

The importance of thin oxide layers on the surface of metals under reaction conditions has already been pointed out in many contexts. The particular interest in ZnO films has recently been reinforced due to the observations of interlayer structural relaxations resulting in depolarized graphitic structures. Here, we report a thorough study of CO absorption on a Zn/Ag alloy single-crystal substrate (Ag/Zn ratio 9:1) subjected to different oxidation procedures using primarily infrared reflection absorption spectroscopy (IRRAS) in conjunction with XPS, LEED and DFT calculations. The evolution of ZnO thin films on Ag(111) is monitored by IRRAS using CO as a probe molecule. The results show a typical CO band at 2160 cm-1 that shifts to 2178 cm-1 with decreasing the coverage. This frequency is slightly lower than those observed for wurtzite ZnO bulk but significantly different from ZnO thin films formed on Cu(111). In the later case, a huge red shift around 70 cm-1 relative to wurtzite ZnO was detected due to strong interactions between ZnO and the supporting metal. Based on the DFT calculations, we propose that the Zn and O atoms are arranged in planar sheets like in the hexagonal boron-nitride prototype structure, in accord to previous results.

O 31.4 Tue 11:15 WIL C107

Well-ordered ultrathin oxides on magnetic substrates: tuning the magnetic properties through atomic scale control of the interface chemistry. — •andrea picone — Dipartimento di Fisica, Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy

In the last 20 years, a large body of knowledge has been gained on the preparation and characterization of ultra-thin oxide films on noble and quasi noble metals [1,2]. Oxide/metal inverse model catalysts have been successfully exploited for the study of complex chemical processes occurring on solid surfaces. Despite their extreme importance in the field of spintronics, comparatively much less work has been devoted to the atomic scale investigation of epitaxial oxide films deposited on top of ferromagnetic substrates [3]. Whenever an oxide film is grown on the surface of a ferromagnetic metal, a remarkable structural and chemical modification of the substrate occur. Taking into account these alterations is extremely important, since the magnetic order of the atoms is directly affected by their local chemical environment. By considering the Fe(001) surface as paradigmatic example of ferromagnetic substrate and highly reactive metal, I will show how the chemical composition of the oxide/Fe(001) layered systems can be finely tuned, and how their magnetic properties depend on the interface chemistry.

[1] S. Surnev, A. Fortunelli, F.P. Netzer Chem. Rev. 113, 4314 (2013).

[2] HJ Freund, G. Pacchioni Chem. Soc. Rev. 37, 2224 (2008).

[3] A. Picone et al. Surf. Sci. Rep. 71, 32 (2016).

O 31.5 Tue 11:30 WIL C107

Probing the surface structure of thin TiO$_x$ films on Pt$_3$Ti(111) by IRRAS and XPS — •Ludger Schöttner[1], Marco Moors[2], Fabian Bebensee[1], Xiaojuan Yu[1], Alexei Nefedov[1], Yuemin Wang[1], and Christof Wöll[1] — [1]Institute of Functional Interfaces, Karlsruhe Institute of Technology, 76344 Eggenstein-Leopoldshafen, Germany — [2]Peter Grünberg Institute, Forschungszentrum Jülich, Wilhelm-Johnen-Straße, 52425 Jülich, Germany

A fundamental understanding of bimetallic catalysts is of great interest because of their important applications in clean energy production. Here we present a thorough study of the structure evolution of TiO$_x$ thin films on Pt$_3$Ti(111) monitored by IRRAS with CO as probing molecule in conjunction with XPS and LEED analysis. The results demonstrate consistently the formation of different oxide phases on Pt$_3$Ti(111) including z'-TiO$_x$, w'-TiO$_x$, z-TiO$_x$ and rect-TiO$_2$, which vary depending on the substrate temperature and the amount of dosed O$_2$. The pure Pt$_3$Ti(111) surface is terminated by Pt atoms as confirmed by the IR band at 2087 cm^{-1} for Pt-bonded on-top CO. During oxidation at elevated temperatures, TiO$_x$ thin film growth was resolved by the observation of an additional CO band at 2100 cm^{-1} in the initial state. For the z'-TiO$_x$ structure, no any CO vibrations are detected, revealing the formation of a closed oxide layer with oxygen termination. The thickness of various TiO$_x$ thin films is estimated by a quantitative XPS analysis. The structure evolution of TiO$_x$ thin films will be discussed in detail based on the elaborate IR and XPS results.

O 31.6 Tue 11:45 WIL C107

Surface Faceting and Reconstruction of Ceria Nanoparticles — •Chengwu Yang[1], Xiaojuan Yu[1], Stefan Heissler[1], Alexei Nefedov[1], Sara Colussi[2], Jordi Llorca[3], Alessandro Trovarelli[2], Yuemin Wang[1], and Christof Wöll[1] — [1]Institute of Functional Interfaces (IFG), Karlsruhe Institute of Technology, 76344 Eggenstein-Leopoldshafen, Germany. — [2]Dipartimento Politecnico, Università di Udine, via cotonificio 108 - 33100 Udine, Italy. — [3]Institut de Tècniques Energètiques and Centre for Research in Nanoengineering, Universitat Politècnica de Catalunya, 808028 Barcelona, Spain.

The surface atomic arrangement of metal oxides strongly determines their physical and chemical properties, and the ability to control and optimize structural parameters is of crucial importance for many applications, in particular in heterogeneous catalysis and photocatalysis. While for macroscopic single crystals such structure determinations can be carried out using established methods, for nanoparticles (NPs) this is a challenging task. Here, we report the results of an IR spectroscopic study where CO is used as a probe molecule to determine the structure of surfaces exposed by rod-shaped ceria NPs. After calibrating the CO stretch frequencies using results obtained for different ceria single crystal surfaces we find that the rod-shaped NPs actually restructure and expose {111} nanofacets. This finding has important consequences for understanding the controversial surface chemistry of these catalytically highly active ceria NPs and paves the way for a predictive, rational design of catalytic materials at nanoscale.

O 31.7 Tue 12:00 WIL C107

Surface lattice vibrations of BaO(001) thin film on Pt(001) — •Veronica Goian[1], Florian Schumann[1], and Wolf Widdra[1,2] — [1]Institute of Physics, Martin-Luther-Universität Halle-Wittenberg, 06120 Halle, Germany — [2]Max-Planck-Institut für Mikrostrukturphysik, 06120 Halle, Germany

In this work, we report the growth of c(2x2) ordered BaO(001) thin films on Pt(001). The thicknesses of the thin films vary from 36 monolayers down to 3 monolayers. The stoichiometry and long range order are analyzed by AES and LEED. According to LEED, BaO thick films start to order near 1075 K. The surface vibrational properties were measured near the surface Brillouin zone center using high-resolution electron energy loss spectroscopy (HREELS). The Fuchs-Kliewer phonon for thick films appears at 390 cm^{-1} and becomes stronger at higher UHV annealing temperatures. A quantitative comparison of the experimental data with the calculated loss function based on dielectric theory reveals an excellent agreement between bulk and BaO thin film phonon properties. Temperature and thickness dependence of HREELS spectra will be discussed.

O 31.8 Tue 12:15 WIL C107

Ordered structures in reduced SrTiO$_3$ on Pd(111) — •Bettina Leibundgut[1], Stefan Förster[1], and Wolf Widdra[1,2] — [1]Institute of Physics, Martin-Luther-Universität Halle-Wittenberg, Halle, Germany — [2]Max Planck Institute of Microstructure Physics, Halle, Germany

Ultrathin perovskite films exhibit extraordinary complex structures on Pt(111) in the two-dimensional limit. Upon reduction by UHV annealing, two-dimensional oxide quasicrystal or closely related periodic approximant structures have been reported for BaTiO$_3$ and SrTiO$_3$ on Pt(111) [1-3]. Here we report on the formation of similarly complex structures from SrTiO$_3$ on Pd(111). The films are grown by reactive molecular beam epitaxy from a Nb-doped SrTiO$_3$ single crystal and a Ti rod. For Ti rich growth conditions, a phase separation in TiO$_x$ and SrO occurs upon annealing at 950 K. This is deduced from SPALEED observation of the rectangular phase of reduced TiO$_x$ on Pd(111), which is well-known for Pt(111) [4]. When approaching stoichiometric SrTiO$_3$ films, several large unit cell superstructures are observed, that will be discussed with respect to aperiodic structures.
[1] S. Förster K. Meinel, R. Hammer, M. Trautmann, W. Widdra, Nature 502, 215 (2013) [2] S. Förster et al., Phys. Rev. Lett. 117, 095501 (2016) [3] S. Schenk et al., submitted to J. Phys: Condens. Matter [4] F. Sedona et al., J. Phys. Chem. B 7, 697 (2005).

O 31.9 Tue 12:30 WIL C107

DFT study of the stability of thin zirconia films and meta-stable bulk phases — •Jakub Planer, Wernfried Mayr-Schmölzer, Florian Mittendorfer, and Josef Redinger — Institute of Applied Physics and Center for Computational Materials Science, TU Vienna, Wiedner Hauptstrasse 8-10/134, 1040 Vienna, Austria

Zirconium dioxide (ZrO$_2$) has been intensively studied due to its huge potential in various applications. Bulk ZrO$_2$ and thin films can be used as an electrolyte in solid-oxide fuel cells, an oxygen gas sensor or as a catalyst for methanol synthesis. We used the Vienna Ab-Initio Simulation Package (VASP) to perform DFT calculations comparing the performance of GGA, vdW-DF, hybrid and RPA approaches to investigate the structural stability of the cubic, tetragonal and monoclinic zirconia bulk phases and derived slab configurations. All functionals reproduce the experimentally found order of stability (monoclinic, tetragonal, cubic) and we present two new meta-stable phases. The first one, called meta-monoclinic, is depending on the functional 10-60 meV/f.u. ZrO$_2$ more stable than the tetragonal phase, but still 50-70 meV less stable than the monoclinic ground state. The second one is structurally similar to anatase titania and is calculated to be 20 meV/f.u. above the monoclinic ground state for GGA and 200 meV/f.u. for vdW-DF functionals. We also present GGA calculations of the stability of thin zirconia films derived from the different bulk phases. We will discuss the dependence of the surface energy and the film stability upon layer thickness.

O 31.10 Tue 12:45 WIL C107

Strain and ordering effects of ultrathin epitaxial ferrite films on SrTiO$_3$(001) — •Jari Rodewald, Tabea Nordmann, Jannis Thien, and Joachim Wollschläger — Fachbereich Physik, Universität Osnabrück, Barbarastraße 7, 49076 Osnabrück

Ultrathin epitaxial ferrite films as NiFe$_2$O$_4$ or CoFe$_2$O$_4$ are in the focus of spintronics since both materials are semiconducting and ferrimagnetic. Thus, they are well-suited to be used as spin filters due to spin dependent tunneling barrier. Here, the homogeneity of the films is essential to form tunneling barriers. Furthermore, the cation ordering on the different sublattices of the inverse spinel structure determines the magnetic properties of the ferrite films which is crucial for the performance as a spin filter. Therefore, the formation of ferrite films has to be carefully controlled if high quality devices are aimed for.

Hence, in this work ultrathin ferrite films of different thicknesses are prepared via reactive molecular beam epitaxy (RMBE) on SrTiO$_3$(001). In order to investigate structural strain and ordering effects in the films, grazing incidence x-ray diffraction (GIXRD) experiments are performed. The chemical composition and structural ordering at the surface are investigated by x-ray photoelectron spectroscopy (XPS) and low energy electron diffraction (LEED), respectively. Magnetic properties are characterized via vibrating sample magnetometry (VSM).