

Wednesday Afternoon, October 22, 2008

Surface Science

Room: 208 - Session SS1-WeA

Structure of Oxide Surfaces and Oxide Heterostructures

Moderator: Ch. Wöll, Ruhr-University, Germany

1:40pm **SS1-WeA1 Tuning the Properties of Metals on Oxides: Au on MgO a Case Study**, *T. Risse*, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany **INVITED**

This contribution will focus on the recent efforts to characterize the properties of Au atoms and particles on well ordered MgO films and the ability to tune these properties by modifying the oxide film. The studies are embedded in the current endeavor to correlate the properties of oxide supported Au deposits with their catalytic activity. In this respect the charge state of Au particles has come under scrutiny, in particular after combined theoretical and experimental evidences suggested that nucleation of Au clusters at point defects of MgO leads to a charging of the particles which in turn was made responsible for the enhanced catalytic activity in low-temperature CO oxidation. More recently theoretical calculations predicted that not only defects sites might be able to induce charging of Au atoms and cluster, but the film thickness may serve a suitable parameter to control charging.^{1,2} In this contribution we present a combined low-temperature scanning tunneling microscopy/spectroscopy (STM/STS), infrared (IR), and electron paramagnetic resonance (EPR) spectroscopic investigation on the properties of gold atoms and clusters adsorbed on well ordered MgO films. These studies aim at providing experimental evidences for the presence of negatively charged Au atoms and particles on these oxide surfaces. First we will focus on the impact of color centers. To this end STM/STS and EPR spectroscopic results will be discussed which can be used to characterize these centers and prove the adsorption of Au particles on them. In combination with IR spectroscopy it is possible to show that color centers are indeed capable to donate charge onto Au particles. As a second part we want to discuss the question if the MgO film thickness is a suitable parameter to tune the charge state of Au deposits as predicted theoretically. Thereto low temperature STM experiments of Au atoms and clusters deposited on 3 ML and 8 ML thick MgO films will be discussed to find evidences for a charge transfer for 2-3 ML thick MgO films.

¹ G. Pacchioni, L. Giordano, M. Baistrocchi, Phys. Rev. Lett. 94, 226104 (2005).

² D. Ricci, A. Bongiorno, G. Pacchioni, and U. Landman, Phys. Rev. Lett. 97,036106 (2006).

2:20pm **SS1-WeA3 Shape Transitions of Anatase Islands during Epitaxial Strained Layer Growth**, *M.S.J. Marshall, M.R. Castell*, University of Oxford, UK

It is well established that misfit strain between epitaxial islands and their substrates significantly influences the shape evolution of the islands as they increase their volume during growth. We have studied the growth of anatase islands on SrTiO₃ surfaces. Extended annealing in UHV causes the surface region of single crystalline SrTiO₃(001) to become enriched with TiO₂. This results in the formation of epitaxial islands of anatase TiO₂ (001). These islands are studied using UHV scanning tunneling microscopy (STM) and UHV scanning electron microscopy (SEM), which reveals the changes in morphology during growth induced by misfit strain. Screw dislocations observed with STM on some of the islands enable the rapid growth of micron-sized square islands. Starting from a square island, two types of shape transitions are observed. In the first, above 1000°C, the square anatase islands elongate in length and narrow in width. This growth behavior follows the established Tersoff and Tromp model of strain relief in epitaxial islands.¹ In the second growth mode, below 1000°C, the islands relieve strain by the formation of trenches in the middle of each side of the square, thereby evolving into crosses. This shape arises because a lower annealing temperature imposes a kinetic constraint on the detachment of growth units necessary for island narrowing. While it might be expected that the growth of the notches would proceed to form four squares, each of optimal dimension, this does not occur. The shape transitions occur because the strain energy term in square islands increases more rapidly with volume than the surface and interface energy terms. In our system the islands are widely spaced, thus avoiding inter-island interactions, but there are still substantial differences between the theoretically predicted critical island size of a few 10s of nm edge length and our observed 1µm length. This can probably be explained because of partial strain relief due to dislocations in the anatase islands.

¹ J. Tersoff, and R. M. Tromp, Phys. Rev. Lett. 70, 2782 (1993).

2:40pm **SS1-WeA4 SEM Controlled STM Characterization of Cu/ZnO Nanoparticles**, *A. Birkner, V. Schott, Z. Wang, Ch. Wöll*, Ruhr-Universität Bochum, Germany

The investigation of Cu deposits on ZnO substrates is of significant importance for understanding methanol synthesis using Cu/ZnO/Al₂O₃ catalysts. The role of the Cu is still under debate. Whereas some authors propose that the active sites are on the surface of bare Cu particles, others suggest that under reaction condition the surface in fact is covered by a thin layer of ZnO. In order to resolve this issue we have investigated temperature induced morphology changes of Cu islands deposited on ZnO substrates. We have extended the STM investigations of Kroll and Köhler¹ by additionally employing scanning electron microscopy (SEM). Our combined SEM/STM instrument allows to investigate Cu nanoparticles directly after deposition and heating and after exposure to reactants at pressures up to 1 bar. With the help of the SEM the very same Cu particle can be addressed before and after gas-phase exposure. By additionally employing Auger spectroscopy we can determine the composition of the surfaces of the Cu particles. We will also present first STM measurements of Cu clusters deposited on ZnO powder particles.

¹ M. Kroll, U. Köhler, Surf. Sci. 601 (2007) 2182.

3:00pm **SS1-WeA5 Preparation of TiO₂ Nanocrystals by Oxidation of Ti-Au Surface Alloys**, *D.V. Potapenko, R.M. Osgood*, Columbia University

The formation of TiO₂ nanoparticles on a non-reactive, single-crystal noble metal substrate is useful for studies of nanocatalytic reactions. The formation of Ti-Au surface alloy on Au(111) surface and the growth of TiO₂ nanocrystals from the surface alloy have been studied with scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS) and Auger electron spectroscopy (AES). In our study, titanium was vapor deposited on Au(111) surface at 200 K. STM images show that Ti nucleates at the elbows of the surface herringbone reconstruction. At low Ti coverages (< 0.3 ML) extensive surface alloying occurs already at 400 K through island – substrate atomic exchange. Yet even at 900 K some amount of Ti stays near the surface. The exposure of the sample at 900 K to the flux of O₂ leads to oxidation of this sub-surface Ti and to growth of TiO₂ nanocrystals. At low initial Ti coverages (< 0.1 ML) the majority of the crystallites have triangular shape and at higher coverage, we observe hexagonal and ridge-like crystallite formation. The results of our experiments form an interesting comparison to recent studies of TiO₂ nanocrystals formed via reaction of vapor-deposited Ti on water multilayers on Au(111).

4:00pm **SS1-WeA8 Interface and Electronic Characterization of Thin Epitaxial Co₃O₄ Films**, *C.A.F. Vaz, H.-Q. Wang, C.H. Ahn, V.E. Henrich, M.Z. Baykara, T.C. Schwendemann, N. Pilet, B.J. Albers, U.D. Schwarz*, Yale University, *L.H. Zhang, Y. Zhu*, Brookhaven National Laboratory, *J. Wang, E.I. Altman*, Yale University

The oxides of the 3d transition metals form an important class of materials with properties that depend sensitively on the cationic oxidation state and the electronic environment. As a consequence, these compounds display a multiplicity of magnetic, electronic and catalytic behavior, which makes them interesting from both fundamental and practical perspectives. In this work, we study the interface and electronic structure of thin (~20-74 nm) Co₃O₄(110) epitaxial films grown by oxygen-assisted molecular beam epitaxy on MgAl₂O₄(110) single crystal substrates. Using several real and reciprocal space techniques, we show that the surface and bulk properties of [110]-oriented Co₃O₄ thin films depend sensitively on growth conditions and post-growth annealing. The as-grown film surfaces are found to be relatively disordered and exhibit an oblique low energy electron diffraction (LEED) pattern associated with the O-rich CoO₂ bulk termination of the (110) surface. Post-annealing is found to improve considerably the film characteristics; in particular, the film surface displays sharp rectangular LEED patterns, suggesting a surface stoichiometry of the alternative Co₃O₄ bulk termination of the (110) surface. Non-contact atomic force microscopy demonstrates the presence of wide terraces separated by atomic steps in the annealed films that are not present in the as-grown structures; the step height of ~2.7 Å corresponds to two atomic layers and confirms a single termination for the annealed films, consistent with the LEED results. Finally, magnetic susceptibility measurements show that antiferromagnetic order is present at low temperatures, with an ordering temperature close to 47 K for the as-grown films and of about 30 K for the annealed films. Such well characterized and high quality surfaces could be employed as templates for the growth of other materials or as a model system for the study of exchange bias.

4:20pm **SSI-WeA9 Surface Structure of ZnO(0001) Nanolayers on Pd(111)***, *G. Weirum*, Karl-Franzens University Graz, Austria, *R. Schennach*, *A. Winkler*, Graz University of Technology, Austria, *I. Bako*, Chemical Research Centre of the Hungarian Academy of Science, Hungary, *S. Surnev*, *F.P. Netzer*, Karl-Franzens University Graz, Austria

Zinc oxide has attracted a significant scientific and technological interest since it is widely used in catalysis, gas sensing, and in the fabrication of optoelectronic devices. When the wurtzite ZnO crystal is cleaved parallel to the basal plane (0001), two structurally and chemically different surfaces are created on each side of the crystal, which are Zn- and O-terminated. The structure stabilisation mechanism of these two polar surfaces has been extensively investigated,^{1,2,3,4} but consensus models have not evolved yet. When prepared in a nanolayer form (1-2 monolayers thick), ZnO has been shown to adopt a hexagonal boron-nitride structure, where the Zn and O atoms are arranged in a trigonal planar (i.e. non-polar) configuration.⁵ Here we have studied the surface structure by scanning tunnelling microscopy (STM) and low energy electron diffraction (LEED) of ZnO nanolayers grown on a Pd(111) surface as a function of the Zn coverage and the oxygen pressure. ZnO layers have been prepared either by reactive evaporation of Zn in oxygen atmosphere (5×10^{-8} – 5×10^{-6} mbar) onto the Pd substrate or by post-oxidation of Zn metal deposits, both methods yielding similar results. In the submonolayer coverage range two two-dimensional hexagonal ZnOx phases coexist on the Pd(111) surface: one of them exhibits an open honeycomb structure with a surface periodicity of ~ 11 Å, whereas the other one has a close-packed structure with a lattice constant of 3.3 Å, which is close to the bulk value of ZnO(0001) surfaces (3.25 Å). The latter phase becomes dominant at higher oxygen pressures and also at higher Zn coverages. The first ZnO monolayer on Pd(111) contains the hexagonal close-packed layer phase only and displays a (6x6) Moiré structure. At higher coverages the flat film morphology is maintained, but two different terminations are resolved in STM, which are found to show pronounced oxygen pressure dependence.

¹O. Dulub et al., Surf. Sci. 519, 201 (2002)

²O. Dulub et al, Phys. Rev. Lett. 90, 016102 (2003)

³B. Meyer and D. Marx, Phys. Rev. B67, 035403 (2003)

⁴F. Ostendorf et al., Phys. Rev. B77, 041405 (2008)

⁵C. Tusche et al., Phys. Rev. Lett. 99, 026102 (2007)

*Supported by the Austrian Science Funds (FWF) via the Project P19198-N02 and the National Research Network "Nanoscience on Surfaces".

4:40pm **SSI-WeA10 Growth of Au on Single Crystalline Anatase TiO₂(101) and (001): Probing Under-Coordinated Sites with Core Level Photoelectron Spectroscopy**, *L.E. Walle*, Norwegian University of Science and Technology, Norway, *S. Plogmaker*, Uppsala University, Sweden, *A. Borg*, Norwegian University of Science and Technology, Norway, *A. Sandell*, Uppsala University, Sweden

Gold has for a long time been regarded as an inert surface of little use as catalyst. However, in the last decade gold particles have begun to garner attention for their unique catalytic properties.¹ Supported gold particles on metal oxides have been shown to be effective catalysts for several processes, including CO oxidation at remarkably low temperatures, down to 200 K. Most intriguing is the strong size dependence, particles below 5 nm in size are far superior to larger particles in terms of catalytic activity.² The detailed mechanism behind the CO oxidation process on the Au/TiO₂ system is still largely an enigma. Many studies have suggested under-coordinated Au atoms and the Au-TiO₂ interface as reactive sites. A fundamental understanding of the growth mechanism of Au clusters on TiO₂ and the nature of the Au/TiO₂ bond is thus of great importance. Up till now most experimental studies of Au particles on single crystal TiO₂ have been done on the rutile phase, due to the good availability of rutile single crystals. On the other hand, the anatase TiO₂ polymorph seems to be the preferred phase when forming nanosized particles. In the last couple of years good quality anatase single crystals have become commercially available which has triggered an increased research interest. In this contribution we present a study of Au growth on single crystalline anatase TiO₂(101) and TiO₂(001) surfaces under UHV conditions using core level photoelectron spectroscopy. The data were obtained at the Swedish National Synchrotron Facility MAX II. A preliminary analysis gives that Au nucleates at steps on both surfaces. Regarding the (101) surface this is in agreement with a recent report by Gong et al.³ In addition, we have studied subsequent adsorption of CO at 120 K on the Au particles. Adsorption of CO induces a shift of the Au 4f core level by 1 eV, which is easily observed. The relative amount of Au atoms that can bond to CO varies with the amount of deposited Au. Since CO only bonds to under-coordinated Au atoms at 120 K the results thus give information regarding the geometrical properties of the Au particles.

¹ M. Haruta, Catal. Today 36, 153 (1997).

² M. Valden, X. Lai, and D. W. Goodman, Science 281, 1647 (1998).

³ X.-Q. Gong, A. Selloni, O. Dulub, P. Jacobson and U. Diebold, J. Am. Chem. Soc. 130, 370 (2008).

5:00pm **SSI-WeA11 Growth of CeOx Nanoparticles on TiO₂(110)**, *J.B. Park*, *D.J. Stacchiola*, *J. Graciani*, *S. Ma*, *A. Nambu*, Brookhaven National Laboratory, *J.F. Sanz*, Universidad de Sevilla, Spain, *J.A. Rodriguez*, *J. Hrbek*, Brookhaven National Laboratory

Catalysts containing nanoparticles of ceria supported on titania exhibit a high activity for the water-gas shift reaction and the CO oxidation. It has been suggested that this catalytic activity is related to the easy reversible change of the oxidation states of ceria (Ce³⁺ and Ce⁴⁺), but very little is known about the ceria-titania interactions and the growth mode of ceria on titania. In this work, the growth of CeOx on rutile TiO₂ (110) have been investigated by STM and PES in UHV. The deposition of CeOx changes the morphology of TiO₂ (110), creating several layers deep steps. At low coverages (less than 0.3ML of Ce), CeOx nanoclusters are preferentially nucleated on the in-plane oxygen atoms of TiO₂ (110) and exhibit diagonal arrays along the [001] direction by sharing bridging oxygens. At high coverages, extended rectangular islands of CeOx are observed. XPS studies show that the diagonal arrays of CeOx nanoclusters and their coverage-dependent morphological changes are associated with changes in the oxidation states of the CeOx nanoparticles. The DFT calculations provide the detailed atomic structures for CeOx on rutile TiO₂ (110).

This research was carried out at Brookhaven National Laboratory and supported by the US Department of Energy (Chemical Sciences Division, DE-AC02-98CH10886).

5:20pm **SSI-WeA12 Experimental Band Dispersions and Surface Morphology of the Wide Band Gap Oxide Semiconductor β -Ga₂O₃ With and Without Mn Doping**, *T.C. Lovejoy*, *J. Morales*, *E.N. Yitamben*, University of Washington, *N. Shamir*, Nuclear Research Center - Negev, Israel, *S. Zheng*, *S.C. Fain*, *F.S. Ohuchi*, *M.A. Olmstead*, University of Washington

Experimental studies of the wide band gap semiconductor β -Ga₂O₃ have been conducted on bulk single crystals using angle resolved photoemission (ARPES) and scanning tunneling microscopy (STM). This system exhibits interesting electronic and optical properties including electroluminescence and resistivity changes upon gas adsorption. In addition, the resistance can vary over many orders of magnitude with annealing and/or electric field treatment of the transparent crystal. Measured valence band dispersion relations are in qualitative agreement with previously reported theoretical calculations. The observed local surface structure is similar to that previously reported for thin films, but the larger scale morphology is characterized by rectangular pits or islands a single unit cell high with lateral sizes varying on the 10-100nm scale. Preliminary experiments with transition metal (Mn) doping reveal changes in electronic structure and surface morphology that may be relevant for application of Mn:Ga₂O₃ as a dilute magnetic oxide. Work supported by NSF grant DMR-0605601. TCL was supported by an IGERT Fellowship, NSF/NCI DGE 0504573; ENY was supported by an IBM Fellowship. Some experiments were performed at the Advanced Light Source, Berkeley, supported by DOE contract DE-AC02-05CH11231.

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