Tuesday Afternoon, November 8, 2016

Surface Science
Room 104E - Session SS+AS-TuA
Structure and Characterization of Oxides

Moderator: Robert Bartynski, Rutgers, the State University of New Jersey

2:20pm **SS+AS-TuA1 Phase Formation and Stability of Reactive Sputtered Zirconium Dioxide Thin Films**, ***Mohsin Raza***, *D. Cornil, J. Cornil,* University of Mons, Belgium*; S. Lucas,* University of Namur, Belgium*; A.L. Thomann, A. Caillard, M. El Mokh,* GREMI CNRS/Université d'Orléans, France*; J.F. Pierson, P. Boulet,* Université de Lorraine, France*; R. Snyders, S. Konstantinidis,* University of Mons, Belgium

As materials properties are greatly influenced by their phase constitution, therefore it's of high importance to understand and address the mechanisms driving their phase formation and stability. In this respect, zirconium oxide (ZrO_2) has been the focus of a special attention for the last couple of decades regarding the stabilization of its cubic (c) phase at room temperature.

In the present study, the role of the film chemistry i.e. of oxygen vacancies and of energy deposited during the film growth is investigated. To this purpose, 100 nm thick films of zirconium oxide are grown in the poisoned mode as well as in the transition zone with the help of voltage feedback control unit (Speedflo mini from Gencoa UK). During the film growth, to have a fast response from the feedback unit and thus a tight control over the film chemistry (i.e. O/Zr ratio), oxygen is injected just at the target surface. By systematically varying the working parameters, it is observed that for films grown at 200 mA, 10 mTorr in the poisoned mode, the XRD diffractograms only exhibits reflections from the low-temperature stable monoclinic (m) phase. To the contrary, while working inside the transition zone i.e. by growing sub-stoichiometric zirconium oxide thin films as demonstrated by careful elemental characterization, the film phase is dramatically modified and only the c reflections are observed. Theoretical calculations at the Density Functional Theory level are in remarkable agreement with the experimental data, hence highlighting that the incorporation of oxygen vacancies is the sole responsible mechanism for the stabilization of the c-phase. It is also observed that any deviation from the optimized working conditions i.e. change in discharge current or pressure leads to the change in film phase constitution. Thermal annealing analysis performed in air and N_2 shows the oxygen vacancy stabilized zirconia films are stable up-to 750 °C. Above 750 °C, the mechanical stress, generated in the film due to the mismatch of the thermal expansion coefficients of both the zirconia film and the substrate, apparently surpasses a critical value and leads to the appearance of m-phase.

In conclusion, c-phase of zirconia can be stabilized at room temperature (up to 750 °C) by solely incorporating oxygen vacancies in the zirconia lattice. However, increasing the energy flux during film growth or the mechanical stress may induce the transformation of the oxygen vacancy stabilized cubic phase of zirconia into the m-phase.

2:40pm **SS+AS-TuA2 W-oxide on Ag(100): a Flexible Decoupled 2-D Oxide Layer**, *T. Obermüller, S. Surnev,* ***Falko P. Netzer***, Karl-Franzens University, Austria

Two-dimensional (2-D) transition metal oxide layers have attracted significant interest during the past decade due to their novel emergent properties and high potential for nanotechnology applications [1,2]. For practical reasons 2-D oxide layers are usually supported on metal surfaces. This leads to a coupling of the oxide overlayer to the metal substrate, thus creating a hybrid system with properties largely determined by the oxide-metal interface. Here, we report the formation of a 2-D W-oxide layer on a Ag(100) surface, where the oxide appears to be essentially *decoupled* from the substrate. The W-oxide has been prepared by vapor phase deposition of $(WO_3)_3$ clusters at 500°C substrate temperature. The WO_x grows as a well-ordered incommensurate 2-D wetting layer in large domains with variable orientation with respect to the substrate. This gives rise to a variety of oxide domains with different azimuthal orientation, which can easily be recognized in the STM by their different Moiré patterns. The overlayer lattice can be imaged with atomic resolution in the STM and analyzed using the Moiré formula, from which the square overlayer lattice constant can be accurately evaluated to a = 3.72 Å; this is close to the respective WO_3 bulk lattice constant. AES and XPS spectra indicate an overlayer stoichiometry close to WO_3, but the W 4f binding energy suggests a lower oxidation state than W^{6+}. A structure model in terms of a 2-D WO_x sheet is discussed. It is conjectured that this WO_x sheet on Ag(100) behaves essentially like an isolated 2-D oxide layer.

[1] G. Pacchioni, *Two-dimensional oxides: multifunctional materials for advanced technologies.* Chem. Eur. J. 18(2012) 10144

[2] *Oxide materials at the two-dimensional limit.* F.P. Netzer, A. Fortunelli, Eds. (Springer Series in Materials Science, April 2016)

3:00pm **SS+AS-TuA3 Growth and Termination of a Rutile IrO2(100) Layer on Ir(111)**, ***Rahul Rai***, *T. Li, Z. Liang,* University of Florida, Gainesville*; M. Kim, A. Asthagiri,* Ohio State University*; J.F. Weaver,* University of Florida, Gainesville

Iridium oxide is an effective catalyst for promoting electrochemical water splitting and is a promising material for effecting other chemical transformations as well. In this talk, I will discuss our recent investigations of the growth and termination of a crystalline $IrO_2(100)$ film that develops during the oxidation of Ir(111) by gaseous O-atoms. We characterized the oxidation of Ir(111) using temperature programmed desorption (TPD), low energy electron diffraction (LEED), low energy ion scattering spectroscopy (LEISS) and density functional theory (DFT) calculations. We find that a well-ordered surface oxide with $(\sqrt{3} \times \sqrt{3})R30°$ periodicity relative to Ir(111) develops as the oxygen coverage increases to 1.4 ML (monolayer). Continued oxidation produces a rutile $IrO_2(100)$ layer that reaches a kinetic saturation, under the conditions employed, after the growth of about four atomic layers and decomposes during TPD to yield a sharp O_2 desorption peak at ~770 K. We assert that favorable lattice matching at the $IrO_2(100)$/Ir(111) interface is responsible for the preferential growth of the $IrO_2(100)$ facet during the initial oxidation of Ir(111), as LEED reveals the formation of a well-defined (6 × 1) coincidence structure. TPD experiments show that CO and H_2O probe molecules bind weakly on the $IrO_2(100)$ surface, and LEISS measurements reveal that the oxide surface is strongly enriched in O-atoms. These characteristics provide evidence that the rutile $IrO_2(100)$ layer is oxygen-terminated, and therefore lacks reactive Ir atoms that can strongly bind molecular adsorbates. Finally, I will discuss our DFT predictions of the stability of so-called on-top and bridging oxygen atoms on rutile IrO_2 and RuO_2 surfaces. The DFT results support the conclusion that $IrO_2(100)$ is oxygen-terminated at the growth temperatures that we employed (< 650 K), and further reveal that on-top oxygen atoms significantly destabilize bridging oxygen atoms on the rutile (100) surfaces; such destabilization is less pronounced on the (110) surfaces. This destabilization may explain our observation that the desorption of on-top oxygen atoms and complete decomposition of the $IrO_2(100)$ film occur over a similar range of temperatures during TPD. Our findings have implications for understanding the generation of rutile IrO_2 layers for model surface chemistry studies.

3:20pm **SS+AS-TuA4 Vibrational Spectroscopy of Iron Oxide Nanostructures and Thin Films Supported on Graphite**, ***Joel Langford***, *F. Rosner, J.Y. Kwon, J.C. Hemminger,* University of California Irvine

Iron oxide nanostructures supported on highly oriented pyrolytic graphite have been investigated with high resolution electron energy loss spectroscopy (HREELS) and Auger electron spectroscopy (AES). The average O:Fe ratio, as measured by AES, can be increased or decreased by annealing in an oxygen background of $1x10^{-7}$ Torr or *in vacuo*, respectively. Depending on annealing temperature, and oxygen exposure, the O:Fe ratio can range from near metallic to hematite (Fe_2O_3) stoichiometry. Regardless of stoichiometry, no iron oxide vibrational modes were observed in the specular HREELS spectra. Only the collective free charge carrier excitation of the graphite substrate was observed. The absence of iron oxide modes in specular HREELS is due to an electrostatic screening from the surface dipole generated by the collective graphite excitation. This screening effect is supported by calculations of the electron energy loss function for a thin iron oxide film supported on graphite. Off specular HREELS shows that the graphite phonon dispersion is unperturbed by the presence of iron oxide nanostructures. Thus, there is minimal interaction between the graphite substrate and the supported iron oxide nanostructures. HREELS spectra of water and carbon monoxide adsorbed on iron oxide nanostructures show hindered vibrational modes. The intensity of the hindered mode is high when compared to the intramolecular modes and the elastic peak. The intensity enhancement is due to a resonance effect between the hindered mode and a longitudinal phonon mode of the nanoparticle i.e. a substrate Fermi resonance. A more descriptive interpretation of this resonant enhancement and finite relaxation lifetime based off perturbation theory will be discussed.

4:20pm **SS+AS-TuA7 Electron Transfer Processes on Single Crsystalline Alkaline Earth Metal Oxide Films***, **Thomas Risse**,* Freie Universität Berlin, Germany **INVITED**

Charge transfer processes are central ingredients to understand the chemical and physical properties of matter in general and on surfaces in particular. These processes may be classified into transient charge transfer states as created e.g. after photo excitation and processes, which create metastable charge transfer products such as molecular radicals. The Presentation will be restrict to the discussion of spontaneous charge transfer processes and will among other techniques discuss results obtained by electron paramagnetic resonance (EPR) spectroscopy to characterize paramagnetic species.

We will focus on results obtained on single crystalline, epitaxial MgO(001) film and show how film thickness, defects as well as dopants in the film are involved in charge transfer processes both between intrinsic species within the MgO as well as adsorbates such as molecular oxygen or metal atoms.

5:00pm **SS+AS-TuA9 Tungsten Trioxide Monolayer on Pd(100)***, N. Doudin, M. Blatnik,* Karl-Franzens University, Austria*; D. Kuhness,* Karl-Franzens University, Germany*; A. Fortunelli,* CNR-ICCOM & IPCF Pisa, Italy*; F.P. Netzer, **Svetlozar Surnev**,* Karl-Franzens University, Austria

Tungsten trioxide (WO_3) is a key material in several applications including smart windows technology, photo-electrochemical water splitting, gas sensors and heterogeneous catalysis. In particular, tungsten oxides are important acid-base and redox catalysts, and they show excellent activity for many catalytic reactions, such as alcohol dehydrogenation, alkane hydrogenation and metathesis [1]. WO_3 has been produced in single crystal form or as supported thin films with the bulk crystal structure. Recently, the formation of an ordered two-dimensional (2D) tungsten oxide layer on Pt(111) has been reported, where W atoms show a mixture of 5+ and 6+ oxidation states [2].

Here we report on the preparation of a well-ordered 2D WO_3 layer on a Pd(100) surface and the characterization of its geometric, electronic and vibrational structure by a combination of STM, LEED, XPS, HREELS measurements, supported by DFT calculations. The WO_3 monolayer on Pd(100) surface and features a surface network consisting of small (~ 4 nm) square-shaped domains, separated by narrow (~ 0.3 nm) trenches (Fig. 1a). The latter are identified as anti-phase domain boundaries, as evidenced by atomically-resolved STM images (see inset of Fig. 1a) and the characteristic spot splitting in the LEED pattern (Fig. 1b). The STM image shows that each domain exhibits a square surface structure with a lattice constant of 0.39 nm, which corresponds to a c(2x2) superstructure. Another important feature is the presence of few dark depressions inside the domains, which we attribute to missing terminal O atoms (see model in Fig. 1d), in corroboration with HREELS results and high-resolution W 4f core-level spectra (Fig. 1c). The latter consist of three $4f_{7/2}$ - $4f_{5/2}$ doublet components, due to W atoms at different surface locations: within the defect-free areas (major component at 34.4 eV), with missing terminal oxygens (minor component at 33.3 eV), and at the domain boundaries (35.2 eV). The DFT derived structure model of the WO_3 monolayer is shown in Fig. 1d and consists of a layer of O atoms adsorbed in on-top Pd positions, followed by a c(2x2) layer of W atoms, which are connected at the top to terminal O atoms via strong W=O bonds, as suggested by the HREELS results. It can be viewed in a way as a 2D analogue of a cubic WO_3(001) crystal, featuring a similar lattice constant (0.39 nm vs. 0.38 nm) and polyhedral linkage, but with a modified W-O coordination sphere due to the contact with the Pd(100) surface.

[1] D. Gazzoli et al, J. Phys. Chem. B 101 (1997) 11129

[2] Z. Li, et al, J. Phys. Chem. C 115 (2011) 5773

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5:20pm **SS+AS-TuA10 Electron Energy Loss Study of Excess Electrons in Reducible TiO_2: Dual Behaviour or Coexistence of Trapped and Free States? Bulk or Surface Defects?***, **Remi Lazzari**, J. Li, J. Jupille,* Institut des NanoSciences de Paris, France

Stoichiometry defects play a tremendous role in the surface chemistry of titanium oxide [1,2]. Reduced rutile is indubitably a n-type semiconductor in terms of electrical transport but electron-based spectroscopies and scanning tunnelling microscopy show the existence of a defect-related gap state lying 0.8-1eV below the Fermi level [1,2]. Its nature *i.e.* surface oxygen vacancies [2,3] versus sub-surface interstitial titaniums [4] is still highly debated in the literature as well the actual (de)localisation of the associated excess electrons [4,5,6].

In our work, electron energy loss spectroscopy in low and high resolution modes was used to probe band gap state and phonon excitations in TiO_2(110) as a function of oxygen exposure at 100 and 300K. By comparing surfaces, from reduced to fully oxidized obtained by various means including electron bombardment, and by using EELS depth sensitivity in out-of-specular detection, a contribution from sub-surface defects is clearly evidenced. A method to prepare defect-free surfaces (as observed by EELS) is even proposed. Using dielectric modelling of spectra including phonons, carriers, gap state and interband transitions and multiple excitations, it was shown that “free-like” carriers characterized by their plasmon excitation coexists with band gap states. While the latter give rise to an obvious peak in the band gap, the former induce a temperature dependent broadening of the quasi-elastic peak and a sizeable screening and upward frequency shift of phonons compared to stoichiometric samples. Through data fitting, both surface and bulk carrier densities and dampings could be quantified as well their profile. A very different dynamics of the healing of the associated signals upon O_2 exposure was also observed. The implication of such findings in terms polaronic nature of excess electron will be discussed.

[1] U. Diebold, Surf. Sci. Rep. 48 (2003) 43; C. Pang *et al.*, Chem. Rev. 113 (2013) 3887

[2] C. Yim *et al.*, Phys. Rev. Lett. 104 (2010) 036806

[3] P. Kruger *et al.*, Phys. Rev. Lett 100 (2008) 055501

[4] S Wendt *et al.*, Science 320 (2008) 1755

[5] M. Setvin *et al.*, Phys. Rev. Lett. 113 (2014) 086402

[6] A. Janotti *et al.*, Phys. Stat. Solidi RRL 7 (2013) 199

6:00pm **SS+AS-TuA12 Vanadium on Anatase TiO_2***, **Stig Koust**, L. Arnarson,* iNANO, Aarhus University, Denmark*; P.G. Moses,* Haldor Topsøe Research Lab, Denmark*; I. Beinik, J.V. Lauritsen, S. Wendt,* iNANO, Aarhus University, Denmark

Tighter regulations concerning nitrogen oxides (NOx) and an increased public concern, highlighted recently by a study from ICCT [1], demonstrating that new diesel cars emit more than seven times the allowed NOx, has clearly shown the urgent need for the development of more effective catalysts for the removal of NOx. The Selective Catalytic Reduction (SCR) is widely used to reduce NOx into N_2 and H_2O in flue and exhaust gasses. This reaction is best catalyzed using a TiO_2-anatase supported sub-monolayer VOx-based catalyst.

Unfortunately, the detailed reaction mechanism(s) are still debated, and the nature of the active site is uncertain [2]. To tackle these issues, the preparation and characterization of good model catalyst model systems may provide new fundamental insights.

Here we present atomically resolved STM images of sub-monolayer vanadium (V) supported on anatase TiO_2 (101). Upon V deposition at liquid nitrogen temperature (LT), the surface is covered with small isolated V clusters, distributed homogeneously on the terraces. Further characterization with XPS revealed the oxidation state of V being 2+, indicating a preferred binding between V clusters and surface oxygen atoms. This conclusion is further supported by the observed reduction of the titanium surface atoms.

Surprisingly, our STM studies revealed an embedding of vanadium into the near-surface region already at room temperature (RT). A significant decrease in the density of V clusters is observed after annealing at RT and new features in the STM images appeared, which we assign to monomeric V atoms at regular titanium lattice sites, substituting the surface titanium. This change in the surface is accompanied by a shift of the V2p XPS feature to higher binding energy, revealing the oxidation of the vanadium to be 3+/4+ as compared to only 2+ upon LT deposition. The V2p area is unaltered after annealing at RT, suggesting no loss of V due to re-evaporation or migration into the bulk. Our DFT calculations confirm the substitution of vanadium with surface titanium atoms.

Additionally we present STM and XPS studies of vanadia (V_2O_5) depositedon a-TiO_2 (101) in comparison to metallic vanadium on the same surface. Vanadia displays weaker interaction with the surface compared to vanadium and we observe diffusion in to the sub-surface for vanadia after annealing at ~700K, however subsequent oxidation pulls vanadia back out to the surface.

1. Vicente, B., et al. *REAL-WORLD EXHAUST EMISSIONS FROM MODERN DIESEL CARS* . 2014.

2. Busca, G., et al., Applied Catalysis B: Environmental, 1998. (1–2): p. 1-36.

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