

COST CM1104 WG1/WG2 meeting

Universität Osnabrück 6.5. to 8.5.2015

Meeting program

Wednesday, 6.5.2015

Registration starting at 09:00. Discussions in small groups of cooperating scientists.

Thursday, 7.5.2015

Oral presentations of Working Group members in **room 93/E07**.

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|-------|----------------|--|
| 09:00 | Geoff Thornton | Interpreting atomically resolved STM images of CeO ₂ (111) ultrathin films. |
| 10:00 | Jolla Kullgren | Fluorine – an agent in disguise? |
| 11:00 | Mathew Wolf | Superoxide formation at fluorine doped ceria surface facets. |
| 12:00 | LUNCH BREAK | |
| 13:00 | Niklas Nilus | Preparation and optical properties of ZnO thin films: an STM luminescence study. |
| 14:00 | Paola Luches | Reversible reduction of cerium oxide ultrathin epitaxial films on Pt(111). |
| 15:00 | Jan-Ingo Flege | Low-energy electron microscopy and micro-diffraction analysis of nanoscale transient cerium oxide phases during reduction by molecular hydrogen. |
| 16:00 | plenum | concluding discussion. |

Friday, 8.5.2015

Rooms are available from 09:00. Discussions in small groups of cooperating scientists.

Interpreting atomically resolved STM images of CeO₂(111) ultrathin films

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Due to the pivotal role they play in many catalyst systems, ceria surfaces have been the focus of much research over the last few years, particularly with regards to forming a deeper understanding of their structure and behaviour at the atomic scale. One of the key experimental techniques employed to study these surfaces is scanning tunnelling microscopy (STM), however the interpretation of atomically resolved images and point defects is not always an easy task. In this work we prepare well-ordered ultrathin films (3-4 trilayers) of CeO₂(111) on a Pt(111) substrate and probe them with high resolution STM imaging combined with density functional theory (DFT) simulations. We examine the appearance of surface oxygen vacancies, which are expected to play an important role in the oxygen storage and release characteristics of ceria, vital for its catalytic behaviour. We also discuss the presence of minor fluorine contamination, an important factor in future studies of this and similar systems. To identify and categorise the different defect species observed, we employ simultaneous filled and empty states STM imaging. Additionally, we demonstrate the origin of the atomic-scale contrast for some of the commonly observed STM imaging modes of the CeO₂(111) surface.

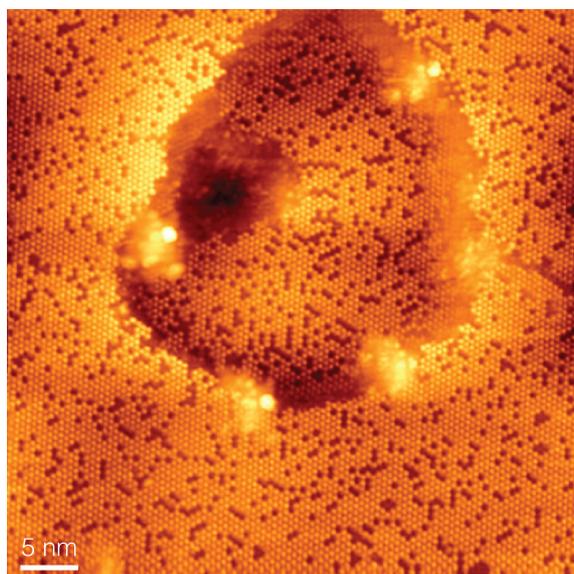


Figure 1. Filled-states STM image (50 x 50 nm²) of ultrathin CeO₂(111) on Pt(111). The oxygen atoms which terminate the ceria surface have a distinct hexagonal lattice, with dark spots attributed to surface oxygen vacancies which form a number of cluster structures.

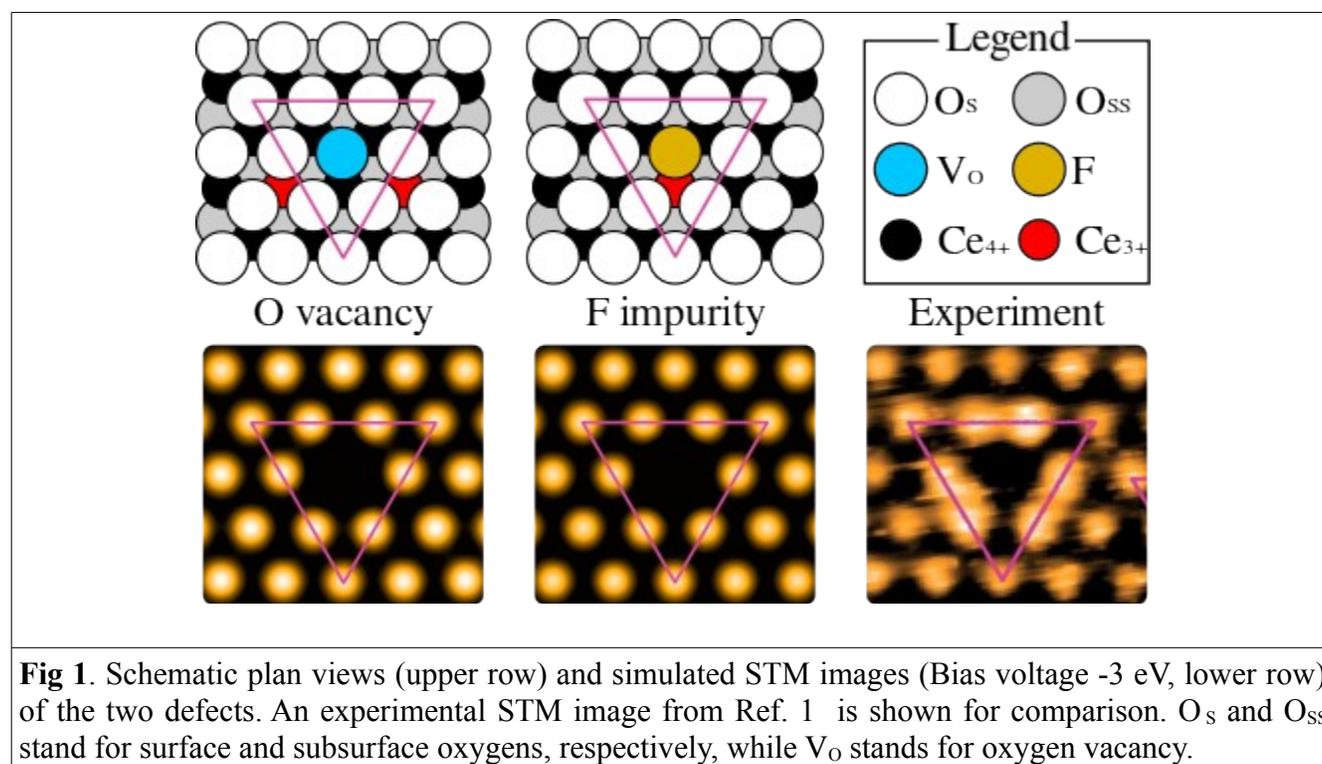
(V_s = -3.2 V, I_t = 0.05 nA)

Flourine – an agent in disguise?

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Experimental techniques such as scanning tunneling microscopy (STM) can provide images with atomic resolution have been obtained for a large number of catalytically interesting surfaces. However, the interpretation of the images are not always straightforward and are sometimes even misleading. For example, as illustrated below, STM features assigned to vacancies on a surface may in fact originate from both impurities and adsorbates. Here we propose a reinterpretation of defects observed with STM at the $\text{CeO}_2(111)$ surface. They were identified with oxygen vacancies in the seminal paper of Esch *et al.* [1]. We find that the simulated filled-state STM images of surface-layer oxygen vacancies and fluorine impurities are essentially identical (see Fig. 1), the latter having recently been shown to exist in high concentrations in single crystals from a widely used commercial source of CeO_2 crystals. Furthermore, we find that our theoretical results for the most stable location, mobility, and tendency to cluster, of fluorine impurities are consistent with experimental observations, in contrast to those for oxygen vacancies.



1. F. Esch, S. Fabris, L. Zhou, T. Montini, C. Africh, P. Fornasiero, G. Comelli, and R. Rosei, *Science* 309, 752 (2005).

Superoxide formation at fluorine doped ceria surface facets

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Recently, it has been found that ceria crystals from a widely used commercial source contain a large concentration of fluorine impurities (FIs) [1], and compelling theoretical evidence [2] has been presented that such defects could have been mistaken for oxygen vacancies in seminal STM experiments [3] on CeO₂(111). In this study, we investigate whether FIs could have a beneficial effect on the redox chemistry of the material, rather than simply being unwanted contaminants, by considering their interaction with adsorbed oxygen molecules.

We find that an oxygen molecule is weakly physisorbed both at the stoichiometric (111) and (110) terraces, in agreement with previous studies [4]. This is also the case close to a FI on the (111) terrace, with the excess electron associated with the defect remaining in the surface on a Ce ion. However, close to a FI at the (110) terrace, the oxygen molecule is reduced to form a superoxide molecule. Furthermore, we show that further reduction of the molecule to form a peroxide molecule does not take place close to a FI dimer, despite the presence of a second excess electron. Finally, we find that superoxide formation can also take place close to a FI at a "type I" step on the (111) facet, the edge of which exhibits a similar structure to the ridges of the (110) facet and the edges of ceria nano-particles [5], and to which both oxygen molecules and FIs should segregate.

[1] H. H. Pieper *et al.*, Phys. Chem. Chem. Phys. **14** (2012) pp 15361–15368

[2] J. Kullgren *et al.*, Phys. Rev. Lett. **112** (2014) 156102

[3] F. Esch *et al.*, **309** (2005) pp 752–755

[4] M. Huang and S. Fabris, Phys. Rev. B **75** (2007) 081404(R)

[5] J. Kullgren *et al.*, J. Phys. Chem. Lett. **4** (2013) 604–608

PREPARATION AND OPTICAL PROPERTIES OF ZNO THIN FILMS: AN STM LUMINESCENCE STUDY

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ZnO is a promising material for the next generation of optoelectronic elements, solar cells and all-oxide electronic devices, and therefore in the focus of current research. The functionality of this oxide is tightly connected with its geometric manifestation, being a single crystal, thin film or nanomaterial either in wurtzite, zinc-blende and graphitic configuration. Moreover, its electronic and optical behavior is governed by defects in the oxide lattice. Atomic-scale data that connect the presence of ZnO defects with distinct electronic states or luminescence maxima are nonetheless scarce.

In this study, we have tackled this situation by preparing well-defined and atomically flat O-terminated ZnO films on crystalline Au(111) supports. By exploiting the imaging and spectroscopic capabilities of our scanning tunneling microscope, we have characterized the morphological and optical properties of the oxide films down to the atomic scale. In particular, we have detected a number of maxima in the spatially resolved luminescence of the oxide. The associated lattice defects have been identified by a systematic variation of the ZnO preparation conditions and the insertion of single-ion impurities, such as nitrogen. By monitoring the corresponding changes in the luminescence behavior, we have tried to correlate the optical fingerprints with certain irregularities in the lattice, e.g. Zn or O vacancies and N interstitials. On this basis, we have developed a tentative energy diagram for defect levels in the ZnO band gap, to be compared with theoretical predictions.

Reversible reduction of cerium oxide ultrathin epitaxial films on Pt(111)

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We have studied the modifications of morphology and structure of ultrathin epitaxial cerium oxide films supported on Pt(111) during reduction and re-oxidation induced by thermal cycles in vacuum and oxygen atmosphere. The oxidation state is evaluated by XPS, while the evolution in surface structure and morphology are investigated by LEED and STM, respectively [1]. Different surface reconstructions appear in the LEED at increasing degrees of reduction, and they are accompanied by non negligible modifications in morphology. [1]

To have more information on the structure of the different reduced phases we performed a LEEM/ μ -LEED experiment on the cerium oxide/Pt(111) system, prepared with similar procedures. The experimental setup allowed to observe in real time the evolution of the surface structure and morphology during reduction, induced not only by thermal treatments, but also by metallic cerium deposition.

We have also studied the modifications of the electronic structure of the films during reduction/oxidation by high-resolution XANES measurements at the Ce L₃ edge. The evolution of the empty state structure close to the Fermi level and of the 4f electronic configuration during reduction was found to be much more significant on an ultrathin film than on a thicker one.

[1] P. Luches, F. Pagliuca, S. Valeri, *Phys. Chem. Chem. Phys.* **16**, 18848 (2014).

Low-energy electron microscopy and micro-diffraction analysis of nanoscale transient cerium oxide phases during reduction by molecular hydrogen

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Employing the combination of electron spectro-microscopy with synchrotron radiation, low-energy electron microscopy, and micro-illumination diffraction analysis, we follow *in situ* the complex structural transformations of few-nanometer thin ceria islands on a Ru(0001) surface when exposed to a reactive H₂ environment. While X-ray photoemission electron microscopy (XPEEM) following resonant photoemission of the Ce4d levels shows the reduction of the surface, the oxidation state of the whole island is probed by local X-ray absorption spectroscopy (μ XAS) performed on a single ceria island, which proves substantial reduction of the deeper layers.

Insight into concomitant structural transformations is gained by micro-illumination low-energy electron diffraction (μ LEED). Specifically, by modeling the time-dependent, experimental diffraction profiles acquired during the reduction process we demonstrate that the transition from CeO₂ to crystalline Ce₂O₃ occurs through a mixture of transient, ordered cerium oxide phases whose average size is on the order of just a few nanometers. Furthermore, these crystalline surface phases are shown to exhibit characteristic intensity-voltage curves, which allow their spatial distribution directly to be imaged in real space. From the analysis of the oxidation state resolved images we find that the reduction of the ceria islands does not proceed from the boundaries to the adjacent Ru surface, but rather randomly as corroborated by the LEED simulations.

In-situ reduction of CeO₂/Ru(0001)

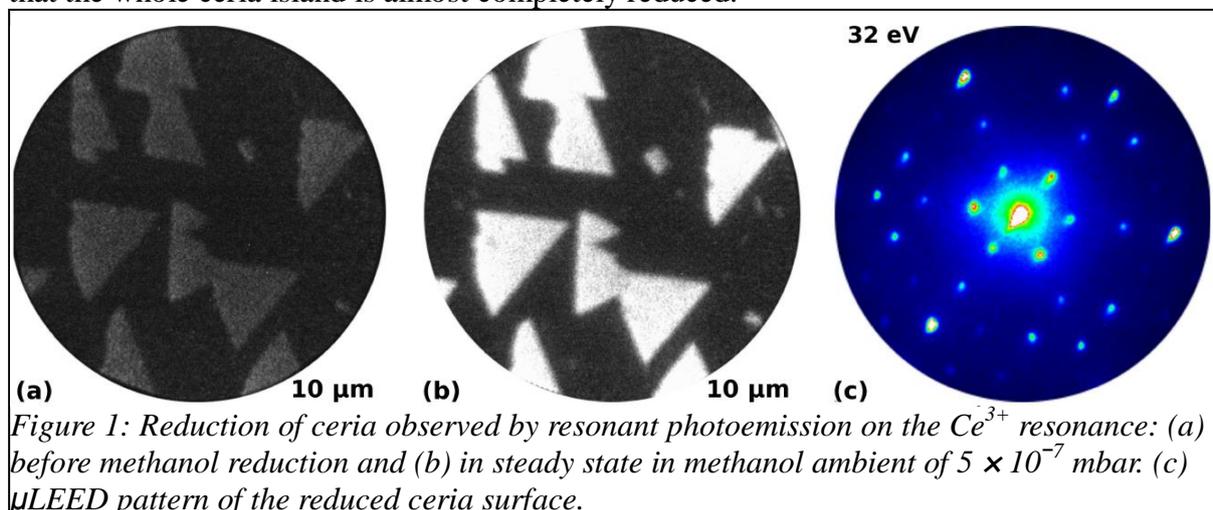
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Cerium oxide is an important component in various today's catalysts. Due to its remarkable ability to change its oxidation state completely and reversibly between CeO₂ (Ce⁴⁺) and Ce₂O₃ (Ce³⁺), ceria can serve as oxygen storage or reducing agent. When combined with transition metals, ceria catalyzes hydrogen production via partial oxidation, decomposition or steam reforming of methanol, which makes it a promising candidate for hydrogen production in future applications. For a deeper understanding of the reversible transformation between CeO₂ and Ce₂O₃ we studied the reduction and reoxidation of the CeO_x/Ru(0001) inverse model catalyst by applying spectroscopic photoemission and low-energy electron microscopy. After growth, the ceria islands exhibit the known triangular shape [1], and are fully oxidized. Using methanol as reducing agent we monitored the reduction by resonant photoemission spectroscopy (RPES) employing the enhanced sensitivity to the Ce³⁺ species. Initial and final state of the reduction are displayed in fig. 1(a,b). After reduction, μ LEED patterns recorded from single ceria islands exhibit a (3 × 3)-like reconstruction. Comparing RPES and micro x-ray absorption spectroscopy (μ XAS) we find that both the surface and "bulk" of the islands are reduced. I(V) curves obtained from the ceria islands are very similar to those measured from ceria treated by cyclic methanol exposure and thermal annealing [2]. During reduction with molecular hydrogen, μ LEED shows a gradual transition from a 2.5-fold periodicity to 3-fold and finally 4-fold periodicity, proving ordered vacancy formation. μ XAS demonstrates that the whole ceria island is almost completely reduced.



[1] B. Kaemena et al., J. Phys. Chem. C 117, 221-232, (2013)

[2] J.I. Flege et al., Phys. Rev. B 88, 235428, (2013)

A MODEL CATALYST SYSTEM FOR THE WATER-GAS-SHIFT REACTION

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In this work, we study the model catalyst system of CeO₂(111). In order to circumvent some of the difficulties of working with an insulating oxide, we prepare ultrathin epitaxial films of CeO_{2-x}(111) on the conducting substrates Pt(111) and Rh(111). The films are prepared via evaporation of cerium metal onto the substrates followed by oxidation by annealing in a partial pressure of O₂ to form discrete islands of CeO₂(111) that have heights of ~2 nm and widths up to ~100 nm. To characterise these films we have employed a combination of techniques including scanning tunnelling microscopy (STM) and low energy electron diffraction (LEED).

Filled-states atomically resolved STM has been used to characterise the CeO_{2-x}(111) surface. A host of defects are observed including surface and subsurface oxygen vacancies, which play a key role in the surface chemical properties. STM has also been employed to investigate the interaction of gold atoms and with the CeO_{2-x}(111) films on both Pt(111) and Rh(111), at room temperature.