

Reducing and oxidizing a non-reducible oxide: Crystallographic and electronic structure of ZrO₂ films

Peter Lackner, Zhiyu Zou, Sabrina Mayr, Ulrike Diebold, and Michael Schmid

Institute of Applied Physics, TU Wien, Vienna, Austria

lackner@iap.tuwien.ac.at

The applications of zirconia (ZrO₂) are manifold, e.g. as catalyst support or solid electrolyte in solid oxide fuel cells. ZrO₂ is usually considered a non-reducible oxide: There are no stable sub-stoichiometric phases, and the formation of oxygen vacancies costs more energy than disintegration into metal Zr plus O₂ [1]. Despite the technological importance of the material, ZrO₂ surfaces have not yet been thoroughly studied on an atomic scale. This has a simple reason: ZrO₂ has a band gap of more than 5 eV and is therefore non-conductive, which makes the study of bulk zirconia with surface sensitive methods like x-ray photoelectron spectroscopy (XPS) impracticable, and scanning tunneling microscopy (STM) close to impossible. To circumvent this issue, we prepared five-monolayer-thick films of ZrO₂(111) [2] on Rh(111) using a home-built UHV-compatible sputter source [3]. We show that it is possible to control the crystallographic phase of the films: By annealing in $p_{\text{O}_2} = 10^{-6}$ mbar at $T < 700$ °C, we can prepare tetragonal ZrO₂, while above 700 °C a phase transformation to monoclinic ZrO₂ – the stable bulk structure – was observed. We have achieved atomic resolution by STM on tetragonal ZrO₂, showing the expected (2 × 1) structure (w.r.t. cubic ZrO₂). The domain size increases with annealing temperature; at 650 °C, domains of 40 × 40 nm² are common. For monoclinic ZrO₂, a (2 × 2) structure was resolved. In XPS, the two phases have distinct binding energies in the Zr 3d region, with an unexpectedly high difference in binding energy of ca 1.4 eV. We demonstrate that this difference is not an intrinsic property of the phases, but due to differences in the stoichiometry (reduced vs. stoichiometric) of these phases. The influence of oxygen vacancies stabilizing the tetragonal phase is known for ZrO₂ powder, which gets reduced at very high temperatures only [4].

Beyond this fundamental characterization of the two phases, we will present the mechanisms of creation of a substoichiometric phase, oxidation and reduction; the latter transforming a previously monoclinic film back to its tetragonal state. We show that oxidation is limited by negligible oxygen dissociation on ZrO₂, probably related to the vacancy formation energy being higher at the surface than in the bulk [5]. This requires oxygen spillover from a metal catalyst for full oxidation.

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References:

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