LEEM/μLEED Study of Defect-Governed Low-Temperature Redox Transformations in Ar^+-Irradiated TiO_2 Surfaces

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In this presentation, we report on the modification of rutile TiO_2 surfaces induced by low-energy Ar^+ ion irradiation. TiO_2 surfaces were irradiated with 2 keV Ar^+ ions at moderate fluences of up to 10^{17} ions/cm². The resulting structural and electronic changes were investigated using local-conductivity atomic force microscopy, in situ electron diffraction and microscopy techniques, including μLEED/LEEM, and X-ray photoelectron spectroscopy. The results show that ion irradiation produces a strongly reduced near-surface region extending over several tens of nanometres, accompanied by pronounced changes in local conductivity and surface ordering.
Particular attention is given to the thermal self-oxidation of Ar-sputtered TiO_2(110). Using operando X-ray photoelectron spectroscopy together with LEEM/μLEED analysis under UHV conditions, we demonstrate that redox processes in irradiated TiO_2 begin already well below 400 °C, significantly lower than commonly assumed for this material. Self-oxidation does not proceed through simple restoration of an ideal stoichiometric lattice but is instead governed by extended structural defects that are inherently present in real crystals and further activated by ion irradiation. These defects act as highly efficient pathways for oxygen migration, coupling ionic transport with electronic conduction and enabling a global insulator-metal transition under relatively mild annealing conditions.
The presented results show that LEEM/μLEED-based surface analysis, combined with local conductivity mapping and chemical spectroscopy, provides a powerful approach for following defect-mediated redox transformations in transition metal oxides. This makes Ar^+-irradiated TiO_2 a useful model system for understanding how extended defects control surface structure, oxygen exchange and electronic transport in functional oxide materials.