DEFECT-GOVERNED LOW-TEMPERATURE REDOX TRANSFORMATIONS IN Ar^+-IRRADIATED TiO_2 SURFACES

F. Krok*[1], M. Rogala[2], D. Wrana[1], C. Rodenbücher[3], L. Bodek[1], P. Dabrowski[2], P.J. Kowalczyk[2], L. Mohrhusen[4], K. S. Szot[5]

[1]Marian Smoluchowski Institute of Physics, Jagiellonian University, Łojasiewicza 11, 30348 Krakow, Poland
[2]Department of Solid State Physics, Faculty of Physics and Applied Informatics, University of Lodz, 90-236 Lodz, Poland
[3]Forschungszentrum Jülich GmbH, Institute of Energy Technologies (IET-4), 52425 Jülich, Germany
[4]Institute of Chemistry, Carl von Ossietzky University of Oldenburg, Carl-von-Ossietzky-Straße 9-11, 26129 Oldenburg, Germany
[5]A. Chełkowski Institute of Physics, University of Silesia, 41-500 Chorzow, Poland

* corresponding author: *franciszek.krok@uj.edu.pl*

In this presentation, we report on the modification of rutile TiO_2 surfaces induced by low-energy Ar^+ ion irradiation. The 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 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 nanometers, accompanied by pronounced changes in local conductivity and surface ordering.

Particular attention is given to the thermal reoxidation of Ar-sputtered TiO_2(110). Using operando X-ray photoelectron spectroscopy and electron diffraction 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. Reoxidation 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.