GROWTH, SURFACE CHARACTERIZATION, AND REACTIVITY OF TiO_2 ANATASE FILMS – EPSCOR

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Ulrike Diebold,

Tulane University,
New Orleans, LA 70118

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Ulrike Diebold, Tulane University, New Orleans, LA 70118
in Collaboration with Gregory S. Herman, Michael A. Henderson, and Scott A. Chambers, Pacific Northwest National Laboratory

1. Objective:

TiO_2 is as promising photocatalyst for environmental degradation of organic compounds and solar energy conversion. Commercial titania is a mixture of rutile and anatase phases, and, for as of yet unknown reasons, anatase is the photocatalytically more active form. In contrast to rutile, atomic-scale information on well-characterized anatase surfaces and their chemical properties is virtually absent. The goal of this project was to perform surface science investigations of anatase with the goal to understand, and ultimately control, the surface chemistry underlying its diverse applications.

2. Achievements:

2.A. Surface Structure of Anatase

We have characterized, using Ultrahigh Vacuum (UHV) Scanning Tunneling Microscopy (STM) and related surface science techniques, all main crystallographic orientations of anatase surfaces.

We have published the first STM study of single-crystalline anatase (ref. 1). Atomically-resolved images of the (101) surface are consistent with a bulk-truncated (1x1) termination. Step edges run predominantly in [0 1 0], [-1 1 1], and[-1 -1 1] directions. The surface is stable with very few point defects. Four-fold coordinated Ti atoms at step edges are preferred adsorption sites and allow the identification of tunneling sites in STM.

An STM/LEED study of anatase (100) and (103) was completed (ref. 2). It was found that, contrary to theoretical predictions, this surface does not terminate in a (1x1) structure but forms a (1x3) reconstruction.

In addition to determine the surface crystallography of the systems, common defects such as point defects and step edges were investigated (ref. 3)

2.B. Surface Chemistry of Anatase

We have investigated the interaction of water and methanol with well-defined surfaces of anatase-TiO_2(101) with temperature programmed desorption (TPD) and x-ray photoelectron spectroscopy (XPS). These experiments were performed at Pacific Northwest National Laboratory (PNNL). The homoepitaxial anatase-TiO_2(101) thin films were found to be (1x1) terminated by low energy electron diffraction and fully

oxidized with only the presence of Ti^{4+} by XPS. For water two desorption states were observed in the TPD spectra for submonolayer exposures. The first saturated for a water exposure of ~4.6 x 10^{14} molecules/cm^2 with a desorption peak at 250 K and the second saturated at ~9.8 x10^{14} molecules/cm^2 with a desorption peak at 190 K. The number of 5-fold coordinated Ti and 2-fold coordinated O sites on the surface are equal with both having concentrations of 5.2 x10^{15} sites/cm^2. The XPS results indicated that the adsorbed water was bound to the surface in a molecular state, with no evidence for dissociation. Higher water exposures led to a desorption peak related to multilayer water which had a desorption temperature of 160 K. The TPD spectra for methanol are more complicated. For methanol two main desorption peaks are observed for submonolayer exposures. The first saturated for a methanol exposure of ~3.9 x 10^{14} molecules/cm^2 with a desorption peak at 265 K and the second saturated at ~5.9 x10^{14} molecules/cm^2 with a broad desorption peak between 155-190 K. Higher methanol exposures peak resulted in a desorption peak related to multilayer methanol with a desorption temperature of 135 K. Two other high temperature desorption peaks were also observed for all exposures investigated for methanol. These peaks were observed at 425 and 610 K and effectively saturated at sub-monolayer exposures. Furthermore, the O 1s core-level binding energy for water and methanol were found to shift to ~0.75 eV lower binding energy for sub-monolayer exposures (exposures before multilayer desorption is observed in the TPD spectra). The C 1s core-level binding energy for methanol was found to remain constant in the same exposure regime.

These results were published in Ref. 4.

2. C. Doped Anatase

We have used oxygen-plasma-assisted molecular-beam epitaxy (OPA-MBE) to grow $Co_xTi_{2-x}O_2$ anatase on $SrTiO_3$(001) for x = ~0.01–0.10, and have measured the structural, compositional, and magnetic properties of the resulting films. Whether epitaxial or polycrystalline, these $Co_xTi_{2-x}O_2$ films are ferromagnetic semiconductors at and above room temperature. However, the magnetic and structural properties depend critically on the Co distribution, which varies widely with growth conditions. Co is substitutional in the anatase lattice and in the formal oxidation state in ferromagnetic $Co_xTi_{2-x}O_2$. The magnetic properties of OPA-MBE grown material are significantly better than those of analogous pulsed laser deposition-grown material. The results were published in ref. 5.

We have also investigated the influence of dispersed V dopants on the local electronic structure with STM (ref. 6). We have found that the local adsorption properties are affected as well (ref. 7).

In addition, some results from these studies have been incorporated in invited review articles written by the P.I. (refs. 8-12)

3. Personnel:

One graduate student (Nancy Ruzycki) was fully supported from this project. She has spent the summer of 2001 at the Pacific Northwest National Laboratory, and has

performed several experiments at the Advanced Light Source at Lawrence Berkeley National Laboratory. She graduated in July 2003 and is now a post-doc at Colorado State University, Ford Collins, where she works with Bruce Parkinson on dye-sensitized anatase surfaces. In addition, one student (Nora Hebenstreit, graduated 2002, went on as a post-doc at Berkeley) as well as two part-time post-docs (Dr. Wilhelm Hebenstreit , now OCLI Industries, and Dr.Igor Kuyanov) have been partially supported by this project.

4. Publications and Activities:

4. A. Papers in peer-reviewed journals and books:

1. W. Hebenstreit. N. Ruzycki, G. S. Herman, and U. Diebold
"Scanning Tunneling Microscopy Investigation of the TiO_2 Anatase (101) Surface"
Physical Review B, rapid communications, 64 (24) (2000) R16334

2. N. Ruzycki, G.S. Herman, L.A Boatner, and *U. Diebold*
"Scanning Tunneling Microscopy Study of the TiO_2 Anatase (100) Surface"
Surface Science Letters, 529/1-2 (2003) L239 - L244

3. I. Kuyanov, D. Lacks, D. R. Jennison, and *U. Diebold*
"Dynamics of TiO_2(110) surface and step: Onset of defects in the ordered structure"
Physical Review B, 68 (2003) 233404.

4. G.S. Herman, Z. Dohnalek, N. Ruzycki, and *U. Diebold*
"Experimental Investigation on the Interaction of Water and Methanol with Anatase-TiO_2(101)"
Journal of Physical Chemistry B, 107 (2003) 2788 - 2795

5. S.A. Chambers, S. Thevuthasan, R.F.C. Farrow, R.F. Marcks, J. Ulrich-Thiele, L. Folks, M. Samant, N. Ruzycki, D.L. Ederer, and U. Diebold
"Epitaxial Growth and Properties of Ferromagnetic Co-doped TiO_2 Anatase"
Applied Physics Letters, 79 (2001) 3467

6. M. Batzill, B. Katsiev, D.J. Gaspar, and *U. Diebold*
"Variations of the Local Electronic Surface Properties of TiO_2(110) Induced by Intrinsic and Extrinsic Defects"
Physical Review B 66 (2002) 235401

7. Batzill, E.L.D. Hebenstreit, W. Hebenstreit, and *U. Diebold*
"Influence of Charged Subsurface Impurities on the Adsorption of Cl on TiO_2(110)"
Chemical Physics Letters, 367 (3-4) (2002) 319 - 323

8. U. Diebold
"Understanding Metal Oxide Surfaces at the Atomic Scale: STM Investigations of Bulk-defect Dependent Surface Processes"

Proceedings of the Materials Research Society Meeting, Fall 2001, "Structure-Property Relationships of Oxide Surfaces and Interfaces",vol. 654 (2001) AA.5.1.1 - AA.5.1.9

9. U. Diebold
"The surface structure of TiO_2(110)"
Chapter 11 in: "The Chemical Physics of Solid Surfaces, Vol. 9: Oxide Surfaces", edited by D.P. Woodruff, Elsevier (2001), p.443-480

10. U. Diebold
"Structure and Properties of TiO_2 Surfaces: A Brief Review"
Applied Physics A, 76 (2002) 1 – 7

11. U. Diebold, N. Ruzycki, G.S. Herman, and A. Selloni
"One Step Towards Bridging the Materials Gap: Surface Studies of TiO_2 Anatase" in
"Metallic Oxides Filling the Gap between Real Catalysis and Surface (eds. H. Idriss and M.A. Barteau), Special Issue in Catalysis Today, 85 (2003) 93-100.

12. (Invited) U. *Diebold*
"The Surface Science of Titanium Dioxide"
Surface Science Reports 48/5-8 (2003) 53 - 229.

4. B. Contributed Talks and Poster Presentations at Conferences:

1. American Vacuum Society Meeting of the Pacific Northwest Chapter, October 2000
"Measurement of the Surface Bandgaps of TiO_2 Polymorphs using Electron Energy Loss Spectroscopy,"
Presenter: Michael A. Henderson

2. International Workshop on Oxide Surfaces, IWOX-2, Taos, New Mexico, January 2001
"Soft X-ray Spectroscopy Study of Single Crystalline Rutile and Anatase Films"
Presenter: Nancy Ruzycki

3. American Physical Society Meeting, Indianapolis, March
"Axis Orientation Dependent Polarization of TiO_2 Polymorphs Anatase (001) and Rutile (001)"
(Presenter: Nancy Ruzycki)

4. American Physical Society Meeting, Indianapolis, March
" Surface Morphology Study of Co-doped Anatase Films
Grown on Various Substrates by OPE-MBE"

(Presenter: Nancy Ruzycki)

5. Tulane Engineering Forum, Sept. 21, 2001, New Orleans, LA
"Epitaxial Growth and Morphology of Ferromagnetic Co-doped TiO_2 Anatase"
Presenter: Nancy Ruzycki

6. IVC-15/ AVS-48/ ICSS-11, San Francisco, CA, USA, Oct. 28 - Nov. 2, 2001
"Surface Investigations of TiO_2 Anatase (101)"
Presenter: Nancy Ruzycki

7. American Physical Society Meeting, Indianapolis, March 2002
" Surface Morphology Study of Co-doped Anatase Films
Grown on Various Substrates by OPE-MBE"
(Presenter: Nancy Ruzycki)

8. American Physical Society Meeting, Indianapolis, March 2002
"Axis Orientation Dependent Polarization of TiO_2 Polymorphs Anatase (001) and Rutile (001)"
(Presenter: Nancy Ruzycki)

9.EURESCO Conference, Fundamentals on Surface Science, Mareata, Italy, June 2002
"The influence of subsurface vanadium dopants on the chemical and electronic surface properties of TiO_2"
(Speaker: Matthias Batzill)

10. American Vacuum Society Meeting, Denver, Co, Fall 2002
Measurement of the Dependence of Bulk Defects on the Reactivity of the TiO_2(110) Surface
(Presenter: S.N. Thornburg)

11. American Vacuum Society Meeting, Denver, Co, Fall 2002
"The Influence of Subsurface, Charged Defects on the Adsorption of Chlorine on TiO_2(110) "
(Presenter: Matthias Batzill)

12. 225 National Meeting of the American Chemical Society, New Orleans, March 23 - 28, 2003
"Scanning Tunneling Microscopy Study of the Anatase (100) Surface"
(Presenter: Nancy Ruzycki)

4. C. Invited Presentations:
(Partially based on results from this projects)

1. International Workshop on Oxide Surfaces, IWOX-2, Taos, New Mexico, January 2001

"Structural and Chemical Characterization of Epitaxial Anatase Thin Films"
Presenter: Gregory S. Herman

2. Seminar, Loyola University, New Orleans
"Looking at Atoms at Surfaces", October 8, 2001
Presenter: Ulrike Diebold

3. University of South Carolina, Columbia, South Carolina, Feburary 1, 2002
"Surface Investigations of Single Crystalline Oxide Materials"
Presenter: Ulrike Diebold

4. University of Louisiana at Lafayette, Feburary 27, 2002
"Surface Science Investigations of Metal Oxides"
Presenter: Ulrike Diebold

5. STM'01, Vancouver, July 16-20, 2001
"Defects and Adsorbates on Metal Oxide Surfaces"
Presenter: Ulrike Diebold

6. EURESCO Conference Computer Simulation of Complex Interfaces: Out of the Vacuum into the Real World", Giens, France, Sept 7 - 12, 2001
"The Interplay between Bulk Defect Structure and Surface Reactions on Reducible Metal Oxides"
Presenter: Ulrike Diebold

7. Frühjahrstagung der Deutschen Physikalischen Gesellschaft (Spring Meeting of the German Physical Society), Regensburg, Germany, March 11 - 15, 2002
"Struktur und Eigenschaften von TiO_2 Oberflächen" ("Structure and Properties of TiO_2 Surfaces")
Presenter: Ulrike Diebold

8. Chemical Physics of Nanostructured Surfaces, Workshop Schloß Ringberg/Tegernsee, Germany, Sept. 29 - Oct. 05, 2002
"Nanostructures and Surface Reactvities of TiO_2"

9. Gordon Conference on Chemical Reactions at Surfaces, Ventura, California, February 16 - 21, 2003
"Scanning Tunneling Microscopy Studies of Semiconducting Metal Oxides"

10. 7th International Conference on Atomically Controlled Surfaces, Interfaces and Nanostructurres (ACSIN-7), Nara, Japan, 16-20 November, 2003
"Atomic-scale properties of oxide surfaces"

11. XI Latin American Congress of Surface Science and its Applications (XI CLACSA), Pucón, Chile, December 7 - 12, 2003
"Atomic-scale Studies of Metal Oxide Surfaces"

12. Loyola University, New Orleans

"Looking at Atoms at Surfaces"
October 8, 2001

13. Technische Universität München, October 22, 2001
"Oberflächenphysik an oxidischen Materialien"

14. Universite Fribourg, Fribourg, Switzerland, November 21, 2001
"Struktur und Reaktivität von Oxidischen Oberflächen"

15. University of South Carolina, Columbia, South Carolina, Feburary 1, 2002
"Surface Investigations of Single Crystalline Oxide Materials"

16. University of Louisiana at Lafayette, Feburary 27, 2002
"Surface Science Investigations of Metal Oxides"

17. Universität Konstanz, Germany, May 2, 2002
"Oberflächen und Grenzflächen oxidischer Materialien"

18. Universität Osnabrück, April 29, 2002
"Rastertunnelmikroskopie an oxidischen Oberflächen"

19. University of Ulm, Germany, July 23, 2002
"Titanium Dioxide -- Surface Structure, Chemistry, and Modifications"

20. Institute of Ion Beam Physics and Materials Research, Forschungszentrum Rossendorf, Germany, Nov.13, 2002
"Oberflächen von oxidischen Materialien"

21. Insitut für Physikalische Chemie, Universität Bochum, Germany, Nov. 18, 2002
"TiO_2 -- Struktur(en) und Reaktivität"

22. Colloquium, Karl-Franzens Universität and Technische Universität Graz, December 10, 2002
"Nanostrukturen und Oberflächen auf Titandioxid"

23. University of California, Santa Barbara, February 21, 2003
"Nanostructures and Surfaces of TiO_2"

24. Technische Universität Wien, Institut für Festkörperphysik, Vienna, Austria, May 27, 2003
"Charakterisierung und Wachstum von neuen elektronischen Materialien"

25. Technische Universität Wien, Institut für Materialchemie, Vienna, Austria, June 13, 2003
"Rastertunnelmikroskopie an halbleitenden oxidischen Oberflächen"

26. Technische Universität München, Fakultät für Chemie, Garching, Germany, June 30, 2003
"Oberflächenuntersuchungen an Oxiden und geträgerten Clustern"

27. Iowa State University, Physical Chemistry Seminar Series, September 26, 2003
"Metal Oxide Surfaces Studied at the Atomic Scale"

28. Xavier University of Louisiana, October 16, 2003
"How About Seeing Atoms? Scanning Tunneling Microscopy on Metal Oxide Surfaces"

29. University of Tokyo, Tokyo, Japan, November 21, 2003
"Atomic-Scale Investigations of Semiconducting Metal Oxides"

30. Florida International University, Miami, FL, February 13, 2004
"Scanning Tunneling Microscopy on Metal Oxide Surfaces"

4. D. Proposals Funded:

The following projects have been funded since the inception of this grant.

1. NASA EPSCoR
"Toward Improving the Pulsed Laser Deposition (PLD) of Hard Materials Such as SiC"
(Co-P.I. Ulrike Diebold, $1,035,000, Aug 1, 2001 - July 31, 2006)

2. National Science Foundation
"Nanoscale Surface Investigations of Semiconducting Metal Oxides"
(P.I. Ulrike Diebold, August 1, 2001 - July 31, 2004, $363,500, CHE-0109804)

3. Department of Energy
"Establishment of the Livingston Digital Millenium Center for Computational Sciences at Tulane and Xavier Universities"
(Co-P.I. Ulrike Diebold,, May 15, 2001 - May 14, 2003, $1,922,000)

4. Louisiana Board of Regents Support Fund, Traditional Enhancement Program
"A Sample Growth/Preparation Apparatus to Enhance Research and Instruction in Nanoscale and Materials Physics"
(Lead P.I. Ulrike Diebold, $200,000, June 1, 2002 - May 31, 2003)

5. National Science Foundation, Major Research Instrumentation (MRI) Program
"Acquisition of a Sample Growth/Preparation Apparatus for Nanoscale and Materials Physics at Tulane and Xavier Universities"
(Lead P.I. Ulrike Diebold, requesting $325,000, pending)

6. National Science Foundation, Extension for Special Creativity Award
(Single PI, $310,000, Aug 1, 2004 - July 31, 2006, CHE-010908)

7. Petroleum Research Fund, AC sub-program
"Towards a better fundamental understanding of metal-oxide gas sensing materials -- Atomic scale surface science investigations"
(Single PI, $80,000, 6/1/2004 - 8/31/2006, PRF #40919-AC5)

4. D. Honors, Promotions, Awards:

1. Ulrike Diebold was promoted to Full Professor (as of July 1, 2002)

2. Nancy Ruzycki, a graduate student supported by this grant, was selected by the DoE to attend the 51st meeting of Nobel Laureates in Lindau, Germany, June 25 - 29, 2001. The Lindau meeting has been a tradition since 1951 to help promising young scientists connect with the best in their fields.

3. Ulrike Diebold will be listed in "2000 Outstanding Scientists of the 21st Century", First Edition, International Biographical Centre of Cambridge, England.

4. In 2002, Ulrike Diebold received the "Friedrich Wilhelm Bessel Research Award" from the Alexander von Humboldt Foundation, Germany. This newly-established award is given to 20 young scientists from any discipline world-wide. The prize consists of a cash award ($75,000) and an invitation to perform research at the Fritz-Haber Institute in Berlin, Germany.

5. In 2004, Ulrike Diebold received Tulane University's Liberal Arts and Sciences Faculty Research Award (one award/year)