

Technical report to  
The Department of Energy, Office of Basic Energy Sciences

## SCANNING TUNNELING MICROSCOPY AND SPECTROSCOPY OF CERAMIC INTERFACES

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### SUMMARY

This document reports advances made on the Penn DoE project focused on using Scanning Probe Measurements at individual interfaces to relate nanometer scale property variation to behavior in ceramic systems. All interface studies involved a multitude of experimental tools including Auger electron spectroscopy, low energy diffraction, scanning electron microscopy with electron backscattering, transmission electron microscopy, etc.; however, the results presented here emphasize high spatial resolution measurements of electric and magnetic fields. Most studies utilized *in situ* observations in which lateral applied fields, current flow, or temperature variations are imposed during measurement. Single crystals,  $\Sigma 3$  and  $\Sigma 5$  bi crystal grain boundaries, tri crystal junctions, and polycrystalline materials were examined. In many cases these results represent the first such measurements and in all cases they are first application to oxides.

Since this approach to interface structure/property measurement is new, it was necessary to establish protocols for quantification and to consider potential influences of artifacts. Consequently, modeling was a significant part of the program. Quantum mechanical calculations of tunneling were modified to include space charge and segregation so that they could be applied to ceramic materials. Finite element modeling was used to explore resolution limits of electric and magnetic field imaging and potential artifacts contributing to *in situ* experiments. Analytical electrostatic models of simple geometries were used to test numerical models.

The report body summarizes annual technical accomplishments; the details are provided in papers in the Appendix. Related collaborative interactions are described after which the project productivity is reported in terms of human resource development and publications.

Aspects of this work are highlighted on the covers of Advanced Materials and the Journal of the American Ceramic Society, both of which appeared in December 1998. Student awards associated with this project include the silver and gold medals of the MRS, finalist in the AVS competition in Nanoscale Science and Technology, and winner in the American Ceramic Society Ceramographic Contest.

DOE Patent Clearance Granted

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Date  
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## ACCOMPLISHMENTS IN YEAR 1

Scanning electrostatic force measurement of tri crystal boundaries of  $\text{TiO}_2$  with applied bias.

Quantification of tunneling spectra acquired *in situ* on MOS-FET type devices to develop dynamic tunneling calculations including band bending.

Development of models that allow surface charge to be a boundary condition for STS tunneling calculations.

## ACCOMPLISHMENTS IN YEAR 2

Scanning Surface Potential measurement of polycrystalline ZnO varistor type boundaries and ZnO-NiO PTCR composites. Comparison of local variations in grain boundary properties with macroscopic behavior.

Magnetic Force Microscopy measurements imaging current through oriented microstructures of semiconductors and superconductors. Finite element calculations of local magnetic fields in the vicinity of sample-tip interactions.

The computer code developed under the previous program to calculate electrostatically induced diffusion was expanded to a broader set of ceramic materials (thus in increasing mathematical difficulty we now have solutions for ZnO,  $\text{TiO}_2$ ,  $\text{SrTiO}_3$  and  $\text{Y}_2\text{Al}_5\text{O}_{12}$ , with and without aliovalent dopants).

Redesign of a UHV Photo-STM to obtain wavelength dependent measurements of tunneling current on  $\text{SrTiO}_3$ .

STM/S was used to determine size dependent interface properties of metal-ceramic interfaces produced from metal cluster-single crystal interactions. We found that in a size range larger than that of quantum effect, contact potential at Cu- $\text{TiO}_2$  and Cu- $\text{SrTiO}_3$  interfaces is size dependent. Continuum electrostatic models and thermodynamic models were developed that generalize the phenomena.

## ACCOMPLISHMENTS IN YEAR 3

Scanning Surface Potential measurement of  $\Sigma 3$  and  $\Sigma 5$  bicrystal grain boundaries in  $\text{SrTiO}_3$ . The bias dependence and positional variations of nm scale electric fields in the vicinity of the boundary were correlated to macroscopic electrical properties.

Finite element calculations of tip geometry effects, surface space charge effects, distance dependence, and grain boundary orientation of local electric fields and consequent manifestation on a Kelvin probe type image.

Comparison of analytical solutions and numerical simulations of magnetic fields in the limit of point/plane geometry were used for image interpretation of fields in the presence of current flow.

Temperature dependence of local potential variations at grain boundaries were explored.

## COLLABORATIONS

Within the scope of the DoE project we have developed 4 international collaborations. The interaction with the thin film group of Prof. Pompe at the University of Dresden involved exchange of students for 6 month visits and yielded the publications on nanofabrication of titania features on metal films.

The cooperative research program with the ceramic processing group of Prof. Gauckler at ETH Zürich has involved student and faculty exchange visits. Two master's theses have been produced on this project, a new low temperature MFM was designed and built, and first measurements of supercurrent flow were made.

In an ongoing collaboration with the electron microscopy group of Prof. Ruhle in the Materials Science Division at MPI, Stuttgart, we have focused on interface properties. Interfaces of various size scales that are of interest to electronic ceramic systems were correlated in terms of atomic structure and bonding at the interface by combining quantitative tunneling spectroscopy with analytical TEM (for example EELS). This interaction included exchange of post docs.

The most recent collaboration is with the defect chemistry/transport group of Prof. Maier at the Physics Division of MPI. High temperature transport properties across SrTiO<sub>3</sub> bicrystal grain boundaries were measured at MPI and local electric fields were measured by SPM at Penn.

We have results at all 5 sites and joint publications with 3 out of 4 the collaborators, to date.

## PERSONNEL AND PRODUCTIVITY

In addition to the PI, the following personnel were supported on the current DoE project.

The previous student on this project, P. Thibado, is now on the faculty at Univ. of Arkansas in the Physics Department.

Bryan Huey	PhD in Materials Science March 1999
	<i>Local Electronic Structure of Individual Grain Boundaries in Oxides</i>
	1994 finalist in MRS student paper competition
	1996 William Yerger Memorial Prize
	1998 silver medal winner in MRS student competition
	1998 gold medal winner in MRS student competition
	1998 finalist in AVS competition in Nanoscale Science and Technology
	1998 American Ceramic Society Ceramographic Contest

Bryan will begin a post doc position at Oxford University in March.

Asa Frye	PhD in Materials Science expected 1999
	<i>Optical-STs Study of Grain Boundaries in SrTiO<sub>3</sub></i>

Publications emanating from this project from 1994.

In Situ Measurements of Electric Fields at individual Grain Boundaries

D. A. Bonnell, B. Huey, D. Carroll *Solid State Ionics* **74** (1994) 35-42.

SEM combined with STM for the Study of Grain Boundaries

P. Thibado, Y. Liang, D. Bonnell *Rev. Sci. Instr.* **65** (1994) 3199- 3203.

Experimental and Simulation of Tunneling Spectra of Polar ZnO Surfaces

P. Thibado, G. Rohrer, D. Bonnell *Surface Science* **318** (1994) 379-394.

In Situ Measurement of Electric Fields at TiO<sub>2</sub> Grain Boundaries

B. Huey, D. Bonnell *Proc. of the Materials Research Society Symposium* **357** (1995).

Laser Induced Nanofabrication on Titanium Thin Films

B. Huey, . D. A Bonnell, A. D Akhsakhalian, A. A Gorbunov, A Sewing, W Pompe *Proc. of the Materials Research Society Symposium*, (1996)

Minimale Strukturbreite Bei Lokalen Laserinduzierten Thermochemischen Reaktionen In Ultradünnen Schichten

A. Gorbunov, B.Huey, A. Akhsakhalian, W. Pompe und W.Sewing *Verhandlungen der Deutschen Physikalischen Gesellschaft* **6**, 31, (1996) 1217.

Lateral Self-Limitation In The Laser-Induced Oxidation Of Ultrathin Metal Films

A. Gorbunov, H.Eichler, W.Pompe, and B.Huey, *Applied Physics Letters* **69** (1996) 2816-2818.

Quantification of Band Bending in MOS Devices Using Dynamic Band Bending Calculations and Tunneling Spectroscopy

P. Thibado, T. Mercer, S. Fu, J. Dinardo, T. Egami, D. Bonnell *J. Vac. Sci. and Tech.* (1996).

Morphology and Electrical Properties of Cu Segregated and Deposited TiO<sub>2</sub> Surfaces

P. Thibado, D. Bonnell *J. Am. Ceramic Soc.* **80** (1997) 1267.

Schottky Barrier Formation at Nano Scale Metal-Oxide Interfaces

D. Carroll, M. Wagner, M. Ruhle, D.Bonnell *Phys. Rev. B* **55** (1997) 9792-99.

Effect of Size Dependent Interface Properties on Stability of Metal Clusters on Ceramic Substrates

D. A. Bonnell, Y. Liang, M. Wagner, D. Carroll, M. Rühle, *Acta Met* **46** (1998) 2263-2270.

Atomic Structure of Transition Metal Oxide Surfaces from Scanning Tunneling Microscopy

D. A. Bonnell *Progress in Surface Science* **57** (1998) 187-252.

Local Structure and Properties of Oxide Surfaces: Scanning Probe Analyses of Ceramics

D. A. Bonnell *J. Am. Ceramic Soc.* "feature article" **81** (1998) 3049-70.

Self-Limitation Of The Laser-Induced Thermochemical Reactions In Ultrathin Films

A. Gorbunov, H. Eichler, W. Pompe, B. Huey, D. A. Bonnell, and  
A. Akhsakhalyan, submitted to *Proceedings of SPIE*, 1997.

Nanostructuring of Laser-Deposited Ti Films by Self-Limited Oxidation

A. Gorbunov, W. Pompe, H. Eichler, B. Huey, D. A. Bonnell *J. Am. Cer. Soc.*, **80** (1997) 1663-7.

Imaging Current Flow In Single and Polycrystalline  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$  Superconductors By MFM  
F. Král, D. Perednis, D. A. Bonnell, B. Huey, G. Kostorz, L. Gauckler, *Nature* under review.

Nanoscale Variations in Potential at Ceramics Surfaces and Interfaces  
B. Huey, D. Lisjak, D. A. Bonnell *J. Am. Cer. Soc.* In press.

Local Potential Variation at Bi Crystal and Polycrystal Grain Boundaries  
B. Huey, D. A. Bonnell *Solid State Ionics* under review.

Invited Presentations of this work

International Conference on Electrically Active Interfaces, Ringberg, Germany (March 1998)  
University of Arkansas Physics Department (September 1998)  
Annual Meeting of the Mexican Vacuum Society, Puerto Valarta, Mexico (Sept 1998)  
Annual Meeting -American Ceramic Society "Centennial Symposium" (April 1998)  
Gordon Conference on the Science of Ceramics NH (August (1997)  
ETH Department of Solid State Physics Zürich (July 1997)  
Max Planck Institute for Solid State Physics Busneau, Germany (April 1997)  
Oxford University, Materials Science Department, Oxford UK (Feb 1997)  
Queens University, Materials Theory Department, Belfast Ireland (Feb 1997)  
Ceramics Composites Group, Wright Patterson Air Force Base Dayton OH (Oct 1996)  
ETH Materials Science Department, Zürich (Oct 1996)  
Fudan University Department of Physics Shanghai, China (Sept 1996)  
International Meeting on Interfaces in Ceramics Santiago, Spain (Sept (1996)  
Annual Meeting of the American Ceramic Society (April 1996)  
Rutgers University Ceramics Department NJ (March 1996)  
Annual Meeting of the American Vacuum Society Minn (Oct 1995)  
Univ. of Minn. Department of Physics (Oct 1995)

Also students presented contributed talks or posters at the Annual Meetings of the American Ceramic Society, the American Vacuum Society, the Materials Research, and several Gordon Conferences.

## APPENDIX

Journal covers highlighting recent work:

Advanced Materials

Journal of the American Ceramic Society

Papers outlining some of the recent accomplishments:

Nanoscale Variations in Potential at Ceramics Surfaces and Interfaces  
B. Huey, D. Lisjak, D. A. Bonnell *J. Am. Ceramic Soc.* 82 (1999) 1941.

10/13/03 Papers  
not received by  
OSTI

Nanoscale Variations in Electrical Potential at Oxide Bicrystal and Polycrystal Interfaces  
B. Huey, D. A. Bonnell, *Solid State Ionics* 131 (2000) 51.

Schottky Barrier Formation at Nano Scale Metal-Oxide Interfaces  
D. Carroll, M. Wagner, M. Ruhle, D. Bonnell *Phys. Rev. B* 55 (1997) 9792-99.

Spatially Localized Dynamic Properties of Individual Interfaces in Semiconducting  
Oxides  
B. Huey, D. Bonnell. *Applied Physics Letters* 76 (2000) 1012

Review papers summarizing our progress in the field:

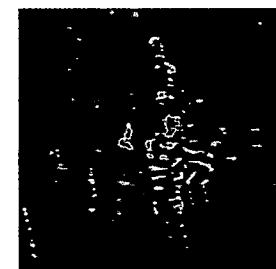
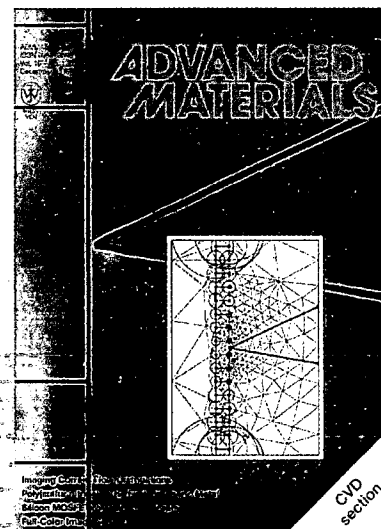
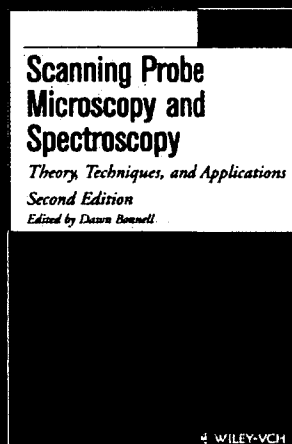
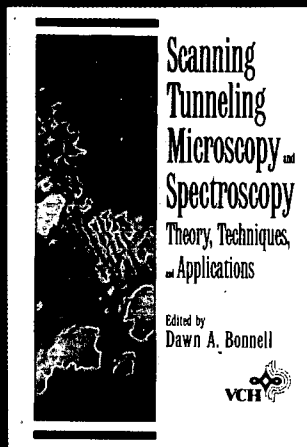
Atomic Structure of Transition Metal Oxide Surfaces from Scanning Tunneling Microscopy  
D. A. Bonnell *Progress in Surface Science* 57 (1998) 187-252.

Local Structure and Properties of Oxide Surfaces: Scanning Probe Analyses of Ceramics  
D. A. Bonnell *J. Am. Ceramic Soc.* 81 (1998) 3049-70.



# Nano Scale Phenomena from Penn Make the Covers !

## Books

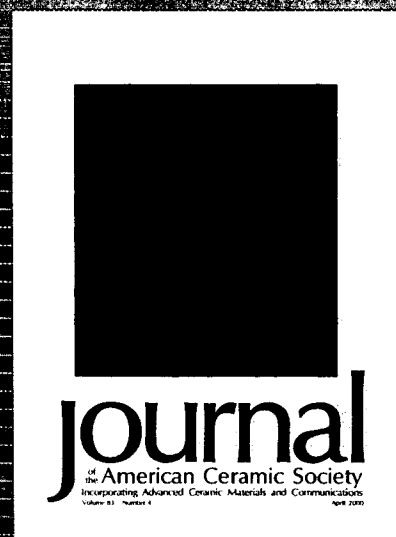
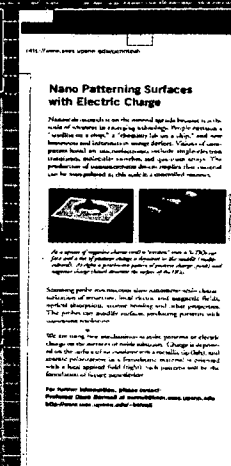
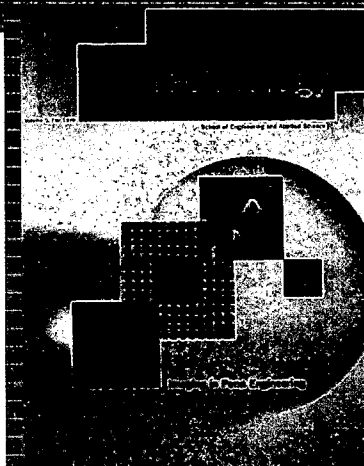
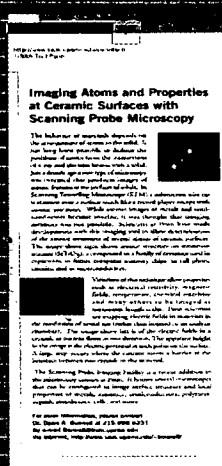


**Journal**  
of the American Ceramic Society  
Incorporating Advanced Ceramic Materials and Communications  
Volume 81 Number 1  
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**Calculations of Magnetic Forces  
due to Current Flow- MFM**

**Magnetic Fields Near a  
Defect in Magnetite**

## Penn Publications



**Calculations of STM  
Images of TiO<sub>2</sub>**



**Superconductive Current Flow**