**ATOMIC BONDING AT CERAMIC INTERFACES USING SCANNING TUNNELLING
MICROSCOPY**

**Progress Report
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Atomic Bonding at Ceramic Interfaces Using Scanning Tunneling Microscopy

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Progress made during the first two years of the above listed grant can be considered in terms of three approaches which converge in the third year. Specifically, results in STM analyses of oxide grain boundaries, in design and construction of a new microscope, and in theoretical calculations of space charge are summarized here. For clarity, calculation methodology is detailed in Appendix I. Publications, presentations, supported students are also listed.

Experimental: STM Analyses

In order to interpret STM images and spectroscopy in terms of local bonding, considerable work was directed towards understanding the general tunneling behavior in oxides. The first year was occupied by identifying and surmounting experimental obstacles to measuring local electronic structure at individual grain boundaries. Investigations were carried out to determine the effect of chemical inhomogeneity and segregation on local properties of ZnO surfaces. Then, a procedure was developed to identify grain boundaries in the topographic images. The procedure is based upon simultaneous measurement of topographic structure and spatial variation in electronic properties. Measurements of local conductance could then be made at individual grain boundaries in silicon, ZnO, and SrTiO₃. It was found in all cases that the local conductance at grain boundaries is increased over that of the grain, presumably due to the increased density of states that results from atomic disorder characteristic at all but coherent interfaces. In the case of SrTiO₃, the sign of the interface charge was deduced and local electronic properties in regions adjacent to grain boundaries were indicative of depletion in a space charge region. This observation represents the *first direct measurement of grain boundary space charge* and demonstrates the potential to address the phenomenon at a fundamental level.

Experimental: New Microscope Design

One major obstacle to the characterization of a large number of grain boundaries is the limitation in STM scan range to 1 μm . With this limitation it is possible to analyze only one grain boundary in each image area on even the smallest grain size materials. We have solved this problem by designing and constructing a SEM/STM which operates in ultra high vacuum and has large scale positioning capability ($> 1 \text{ cm}$). This configuration allows visual observation of sample-tip approach and tip positioning. The system includes imaging with secondary electrons, STM imaging and spectroscopy, Auger and LEED capabilities, along with in situ sample and tip exchange and sputtering and gas dosing, as illustrated in the attached figures.

Although a few groups and companies have developed combination STM/SEM, they are either in such a low vacuum that surface analysis is precluded or do not allow positioning. To our knowledge this is the first instrument of its kind in the world.

Theoretical: Space Charge Calculations

By writing equations for defect concentration profiles in terms of defect formation energies and solving simultaneously with Poisson's equation, the charge density profiles can be calculated. Such calculations were carried out for pure SrTiO_3 . As this work is not yet published, details of the calculations are provided in Appendix I. The results are presented in the attached figures. Controversy exists over the validity of defect energies in the literature. The purpose of these calculations is to develop a program into which future experimentally determined defect energies can be input to yield more accurate defect energies.

Chamber, Top View

Publications

Probing Surface Chemistry of Polycrystalline ZnO with STM and Tunneling Spectroscopy
G. S. Rohrer, D. A. Bonnell *J. Vac. Sci. and Technol. B* 9 (1991) 783-788.

Electronic Properties of Individual Grain Boundaries Determined by Spatially Resolved Tunneling Spectroscopy
G. S. Rohrer, D. A. Bonnell, *J. Am. Ceram. Soc.* 73 (1990) 3326-3332.

Measurement of Space Charge Adjacent to Oxide Grain Boundaries with Tunneling Spectroscopy
D. A. Bonnell, I. Solomon accepted by *Ultra Microscopy*

Direct Measurement of Local Properties of Interfaces with STM
D. A. Bonnell, I. Solomon, G. S. Rohrer, C. Warner accepted by *Acta Metall.*

The reprints/preprints were attached to the previous progress report.

Presentations

The results of this project were further disseminated through presentations at scientific meetings, and seminars at academic and industrial labs. Aspects of this work were discussed in presentations at the following meetings.

American Ceramic Society Annual Meeting - Symposium on Defects
Cincinnati April 1991

Max Planck Institut für Werkstoffwissenschaft
Stuttgart, Germany July 1991

International Conference on Metal/Ceramic Interfaces
Irsee, Germany July 1991

Institute for Electron Microscopy and Physics
Halle, Germany July 1991

Eidgenössischen Technischen Hochschule, Department of Nonmetallic Materials
Zurich, Switzerland August 1991

International STM Conference
Interlaken, Switzerland August 1991

American Chemical Society Meeting - Symposium on High Spatial Resolution Imaging
New York, NY August 1991

Aluminum Company of America, Physics and Chemistry Seminar Series
Pittsburgh, PA September 1991

American Ceramic Society Basic Science Div. *Atomic Bonding and Properties of Ceramics*
Marco Island, FL October 1991

MIT, Materials Science Symposium
Boston, MA Nov. 1991

Abstracts for the following future presentations are attached.

American Ceramic Society Annual Meeting - Symposium Electronic Structure (invited talk)
Minneapolis, MN April 1992

NUMBER DENSITY OF VACANCIES VERSUS DISTANCE FROM BOUNDARY

for pure SrTiO_3

CHARGE DENSITY VERSUS DISTANCE FROM BOUNDARY

Appendix I: Calculation of Space Charge Adjacent to the Surface of Perovskite

To calculate the space charge for an ABO_3 structure, the crystal is assumed to be of infinite dimensions in both y and z , but semi-infinite in x . Thus, this is a one-dimensional problem.

Let $x = 0$ define the surface and $x = L$ define the center of the crystal

Let $\phi \equiv$ electric potentials $\nabla\phi$ and $\rho \equiv$ charge density

Let $N =$ number of A or B atom sites $\rightarrow 3N =$ number of O atom sites

Let $n =$ number of A or B atom sites/length

Let $N_A =$ number of A atom vacancies

$N_B =$ number of B " "

$N_O =$ number of O " "

Similarly,

$n_A =$ number of A atom vacancies/length

$n_B =$ number of B " " "

$n_O =$ number of O " " "

Furthermore, let $F_A =$ energy required to take an A atom from the bulk to the surface ($x = 0$). Same for F_B and F_O . Consistent with the typical perovskite structure

assume the	A atom carries a charge of	+2
	B " " " "	+4
	O " " " "	-2
	A vacancy carries a charge of	-2
	B " " " "	-4
	O " " " "	+2

The crystals total free energy is given by:

$$F = U - TS$$

$$F = \int_0^L dx \left[n_O F_O + n_A F_A + n_B F_B + \frac{1}{2} \rho \phi \right] - TS$$

$$S = k \ln(\Omega) \quad \Omega = \frac{(3N)!}{N_O! N_A! N_B!}$$

Minimize F with respect to n_O , n_A , and n_B , using Stirlings approximation for $\log(N!)$, yields the following number density distributions.

$$n_o(x) = 3n \frac{\exp \left[\frac{F_o + 2e\phi(x)}{-kT} \right]}{1 + \exp \left[\frac{F_o + 2e\phi(x)}{-kT} \right]}$$

$$n_A(x) = n \frac{\exp \left[\frac{F_A - 2e\phi(x)}{-kT} \right]}{1 + \exp \left[\frac{F_A - 4e\phi(x)}{-kT} \right]}$$

$$n_B(x) = n \frac{\exp \left[\frac{F_B - 4e\phi(x)}{-kT} \right]}{1 + \exp \left[\frac{F_B - 4e\phi(x)}{-kT} \right]}$$

Using the following assumptions about the defect concentration, we arrive at a simpler form:

$$n_o(x) = 3n \exp \left[\frac{F_o - 2e\phi(x)}{-kT} \right], \quad \frac{3n}{n_o} \gg 1$$

$$n_A(x) = n \exp \left[\frac{F_A - 2e\phi(x)}{-kT} \right], \quad \frac{n}{n_A} \gg 1$$

$$n_B(x) = n \exp \left[\frac{F_B - 4e\phi(x)}{-kT} \right], \quad \frac{n}{n_B} \gg 1$$

Knowing that the form of the charge density is:

$$\rho(x) = 2e [n_o(x) - n_A(x) - 2n_B(x)], \quad \rho(L) = 0$$

We must simultaneously satisfy Poisson's equation:

$$\phi''(x) = -\frac{4\pi \rho(x)}{\epsilon} \quad \text{where } \phi = 0 \text{ at } x = 0$$

$$\text{where } \phi' = 0 \text{ at } x = L$$

The above nonlinear differential equation must be solved numerically. Using $\rho(L) = 0$ one can show that

$$\phi(L) = -\frac{kT \ln(Z^0)}{2e} \quad \text{where } Z^0 \text{ is the only positive root of } Z^3 - aZ - b = 0$$

$$\text{when } a = \frac{1}{3} \exp \left[\frac{F_A - F_o}{-kT} \right] \quad \text{and} \quad b = \frac{2}{3} \exp \left[\frac{F_B - F_o}{-kT} \right]$$

Thus using published values for F_o , F_A , F_B and ϵ and knowing that

$$\phi(0) = 0, \quad \phi(L) = \frac{-kT \ln(Z^0)}{2e}, \quad \text{and} \quad \phi'(L) = 0,$$

$$\phi''_{(x)} = -\frac{4\pi}{\epsilon} \rho(x)$$

using a 4th order Runge-Kutta technique. This calculation was done on an IBM clone 386 machine, running at 33 MHz. The code was written in Turbo Pascal.

The depth of the space charge $\equiv \left[\frac{\epsilon k T}{16\pi e^2 [3n_o(L) - n_A(L)]} \right]^{1/2}$ This sets the length scale of the problem.

Solving for a Special Case:

If one can assume $-\frac{2e}{kT} \phi(L) \ll 1$ and one knows the following constants $F_o, F_A, F_B, n, \epsilon, T$ and one can find λ^{-1} (depth of space charge, ϕ, n_o, n_A, n_B , and $\rho(x)$).

1st Step

Find positive root for $Z^3 + aZ + b = 0$ $Z^0 \equiv$ positive root

$$a = -\frac{1}{3} \exp \left[\frac{F_A - F_o}{-kT} \right] \quad b = -\frac{2}{3} \exp \left[\frac{F_B - F_o}{-kT} \right]$$

$$\text{Then } \phi(L) = \frac{kT \ln(Z^0)}{2e}$$

2nd Step

$$n_o(L) = 3n \exp \left[\frac{F_o + 2e\phi(L)}{-kT} \right] \quad n_A(L) = n \exp \left[\frac{F_A - 2e\phi(L)}{-kT} \right]$$

$$\text{Then } \lambda^2 = (16\pi e^2, \epsilon k T) [3n_o(L) - n_A(L)]$$

3rd Step

$$\phi(x) = \phi(L) [1 - e^{-\lambda x}]$$

4th Step

$$n_o(x) = 3n \exp \left[\frac{F_o + 2e\phi(x)}{-kT} \right] \quad n_A(x) = n \exp \left[\frac{F_A - 2e\phi(x)}{-kT} \right]$$

$$n_B(x) = n \exp \left[(F_B - 4e\phi(x)) \right] \quad \rho(x) = 2e [n_o(x) - n_A(x) - 2n_B(x)]$$

END

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