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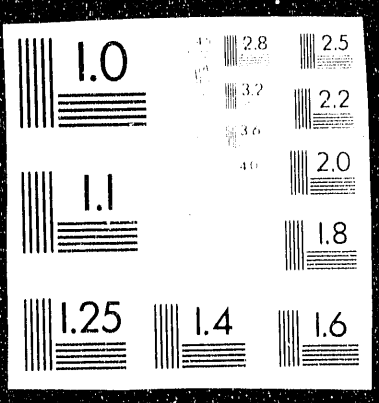

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# ENERGETICS, BONDING MECHANISM AND ELECTRONIC STRUCTURE OF METAL/CERAMIC INTERFACES



Annual Progress Report

to the

## U.S. DEPARTMENT OF ENERGY

by

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# I. Overview

Good progress has been achieved during the last 10 months on several projects proposed last year. Our work is proceeding along several lines proposed last year. Collaboration with the group of Dan Lam has become close and effective (see below). Indeed, most of our effort during the last 9 months has been devoted to this collaboration on $TiO_2$ and $VO_2$ thin films and multilayers (see II.B below).

The $Pd/Al_2O_3$ results have been finalized and are being written up for publication. The structural properties results obtained for $PbZrO_3$ are also being written up. We are hoping to parallelize our codes for a CM-5 ("Connection Machine") so that we can treat the full 40 atoms/cell of the antiferromagnetic structure of $PbZrO_3$. This is a massive undertaking for which we are collaborating with Dale D. Koelling of ANL.

Experimental confirmation of our earlier predictions on the structural, electronic and magnetic properties of metal overlayers on MgO are now appearing. Sam Bader of ANL and his group have confirmed, after 18 months of effort, that a monolayer of Fe on MgO is indeed ferromagnetic. This was made possible only by cleaving the MgO surface in high vacuum before depositing the Fe. Felcher of ANL was the first to detect magnetism in a bilayer Fe sample using neutrons at IPNS. Very recently, Jang and Seidman (of Northwestern) and Merkle (of ANL) - supported by DOE (grant No. DE-FG02-89ER45403, J.B. Darby, Jr., Grant Officer) - submitted a paper in which they presented a combined transmission electron microscopy, HREM and atom-probe field-ion microscopy (APFIM) study of a Cu/MgO heterophase interface produced by internal oxidation of a Cu(Mg) alloy. This heterophase interface is an interesting one as it consists of joining a noble free-electron metal (Cu) to a strongly heteropolar metal oxide (MgO). They demonstrated, for the first time, that by combining these three microscopies it is possible to determine the chemical identity of the terminating plane on the oxide side of a Cu/MgO {111}-type interface directly without any deconvolution of the experimental data. In particular, they demonstrated that the bonding across a Cu/MgO {111}-type interface, in a common <111> direction, has the sequence Cu|O|Mg|... and not Cu|Mg|O|... via APFIM measurements of this high localized chemistry. We are pleased to report that these measurements constitute excellent direct confirmation of our predictions made for Ag/MgO(001) and Fe/MgO(001), namely that the preferred site for the metal iron is directly above the oxygen. They are also the first results of what is a close experimental/theoretical collaboration on DOE sponsored research.

## II. Progress

Among the tremendous variety of oxide materials currently used for technological applications, those based on titanium and vanadium oxides are not only among the most important, but are also the most intriging. Relatively small changes in crystallographic modifications and valencies of metal atoms, as the wide class of Magnelli phases and related compounds, may result in abrupt metal-insulator transitions and sharp changes of magnetic ordering with critical temperatures that may vary in the hundreds of degrees range. When doped by other transition, or s and p metals, these oxides exibit a vast variety of complicated cooperative phenomena, starting from unusual ferroelectricity up to superconductivity at moderately high temperatures.

Most of these unusual materials have been extensively studied and used in the bulk or polycrystalline thin film form. For the fabrication of novel devices of micron or submicron sizes, however, single crystal films and superlattices are preferred or required. Moreover, one may expect that such "man-made" artificial structures will reveal new and unusual physical properties. These are the reasons for the Renaissance in experimental and theoretical investigations of these oxides that is now occurring.

### A. Structural and Electronic Properties of the Clean and Hydroxylated $TiO_2$ Surface

We have successfully treated the clean and hydroxylated $TiO_2$ surface (in collaboration with R. Podloucky and S.G. Steinemann. As per the preprint attached of the paper presented at the December 1991 meeting of the MRS, we carried out an ab initio FLAPW study of the electronic structure and energetics of the clean and hydroxylated $TiO_2(110)$ rutile surface. In this study, the most important relaxation and reconstruction effects of surface geometries were derived from total energy minimization. Some results are given in the preprint. A full paper is being prepared for Phys. Rev.

### B. Electronic Structure of $VO_2$ and $TiO_2$ Thin Films and Multilayers

A process for the fabrication of such single crystal epitaxial ceramic films and multilayers has been developed recently by Dan Lam, et al. by making use of an elaborate MOCVD technique. These authors succeeded in growing $VO_2$ and $TiO_2$ single crystal films of variable thickness on a number of substrates, of which sapphire appears to be the most appropriate for the growth of films of different crystallographic orientations. The unique system which has been grown and

characterised is the $TiO_2/VO_2$ multilayer structure, which can be looked at as the first artificial oxide ceramic modulated system composed of alternating layers of materials that have highly different physical properties: insulating and nonmagnetic titanium oxide and magnetically ordered semiconducting (or metallic at higher temperatures) vanadium oxide. Since not much is known yet about the peculiarities of electromagnetic or other physical properties of this unusual material, it is a challenge for contemporary computational physics to model the electronic structure and to determine the nature of interatomic interactions in such complicated systems.

To this end, electronic structure calculations for $VO_2$ and $TiO_2$ bulk crystals, their surfaces and $VO_2/TiO_2$ superlattices have been carried out by the full-potential LMTO method and compared with the results obtained recently by Lam et al. on epitaxial prepared films. Although the nature of surface states for $TiO_2$ and $VO_2$ appear to be very different, in the multilayered structures a common $VO_2$-$TiO_2$ conduction band is readily formed and the distinction between "insulating" $TiO_2$ and "metallic" $VO_2$ layers is almost lost in very thin multilayered structures. Vanadium electrons are essentially delocalized in the $TiO_2$ layers and the electronic charge distributions in the $VO_2/TiO_2$ superlattice are similar to those in the usual $VO_2$ rutile lattice. The results obtained give some insight into the experimental data obtained by MOCVD for epitaxially grown $TiO_2/VO_2$ multilayers.

As a result, we are writing up the first results ever obtained of the electronic structure of $VO_2/TiO_2$ multilayered films. The full potential LMTO method provided a sufficiently accurate decription of the electronic states and bonding in the bulk titanium and vanadium dioxides, used as reference points, and allowed a detailed analysis to be made of the band structure and chemical bonding peculiarities for some surfaces and interfaces relevant to the multilayered $TiO_2/VO_2$ systems obtained recently by the MOCVD process. We found that when the crystallographic structure of both types of layers in $TiO_2/VO_2$ multilayers is not different enough, vanadium d-electrons easily delocalize into the "insulating" titanium-dioxide layers, common metallic band of the superlattice is formed and the difference between the $TiO_2$ insulating and $VO_2$ metallic layers is mostly lost. In order to keep this separation, which might be needed in microelectronics, rather different crystal lattice structures should be maintained for those layers when grown in the MOCVD experiments.

# A.J. Freeman

## Publications Supported by the

## U.S. DEPARTMENT OF ENERGY (DE-FG02-88ER45372)

1990-present

### Publications

"Structural, Electronic, and Magnetic Properties of Thin Films and Superlattices", (with A. Continenza and Chun Li), MRS Bull. Vol. XV.9, (1990) p. 27.

"Energetics, Bonding Mechanism and Electronic Structure of Metal/Ceramic Interfaces", (with Chun Li and C.L. Fu), Acta/Scripta Conf., Santa Barbara, CA, Jan. 16-18, 1989, in *Metal-Ceramic Interfaces*, eds. M. Rühle, A.G. Evans, M.F. Ashby and J.P. Hirth, Pergamon Press (1990) p. 2.

"Structural, Electronic, and Magnetic Properties of Interfaces", (with A. Continenza and Chun Li), to appear in *Atomic-Level Properties of Interface Materials*, ed. by D. Wolf and S. Yip, Chapman and Hall, Press, London, lst ed. 1991).

"Giant Monolayer Magnetization of Fe on MgO: A Nearly Ideal 2D Magnetic System", (with Chun Li), Phys. Rev. B 43, 780 (1991).

"Computational/Theoretical Approach to the Design of New Materials", (with S.P. Tang, A. Continenza, and C. Li), in *Computer Aided Innovation of New Materials*, M. Doyama, T. Suzuki, J. Kihara and R. Yamamoto, eds., (Elsevier Sci. publ. B.V., North-Holland, 1991), p. 143-153.

"Atomistic Study of the Clean and Hydroxylated $TiO_2$ Surface", (with R. Podloucky and S.G. Steinemann), Proc. Fall Matls. Res. Soc. Mtg., Boston, MA, (proceedings to appear).

"Energetics, Bonding Mechanism and Electronic Structure of Metal/Ceramic Interfaces: Ag/MgO(001)", (with Chun Li and C.L. Fu), Phys. Rev. B (submitted).

"Electronic Structure of $VO_2$ and $TiO_2$ Thin Films and Multilayers", (with V.A. Gubanov, D.L. Novikov and D.J. Lam), (in final preparation).

"Electronic Structure of $Pd.Al_2O_3$ Interface", (with K.T. Park) (to be published).

"Electronic Structure and Magnetic Properties of Metal/Ceramic Interface: Co/MgO(001)", (with Chun Li), (in process).

### Presentations

"Structural, Electronic and Magnetic Properties of Metal/Ceramic Interfaces: Fe/MgO(001)" (with Chun), paper presented at the March 1990 APS Mtg., Anaheim, CA.

"Computational/Theoretical Approach to the Design of New Materials", (with S.P. Tang, A. Continenza, and C. Li), invited paper for Proc. Intl. Conf. on Computer Applications to Matls. Sci. & Engr., Tokyo, Japan, Aug. 28-31, 1990.

"Atomistic Study of the Clean and Hydroxylated $TiO_2$ Surface", (with R. Podloucky and S.G. Steinemann), Paper presented at the Fall Matls. Res. Soc. Mtg., Boston, MA, Dec. 2-6, 1991 .

"Electronic Structure, Frozen Phonons and Origin of the Ferroelectricity Instability in $PbTiO_3$", (with Guangwei Li and Key Taeck Park), paper to be presented at the March 1992 APS Mtg., Indianapolis, IN, March 16-22, 1992.

"Electronic Structure of Thin Films and Multilayers of $TiO_2$ and $VO_2$" (with D.L. Novikov and V.A. Gubanov), paper to be presented at the March 1992 APS Mtg., Indianapolis, IN, March 16-22, 1992.

# END

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